UTILIZATION OF WASTE EXPANDED POLYSTYRENE IN THE PROCESSING OF RUBBERS AND UNSATURATED POLYESTER

Thesis submitted to

Cochin University of Science and Technology

in partial fulfilment of the requirements

for the award of the degree of

Doctor of Philosophy

under the

Faculty of Technology

by

Renju V. S.

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi- 682 022, Kerala, India

February 2016

Utilization of waste expanded polystyrene in the processing of rubbers and unsaturated polyester

Ph. D Thesis

Author

Renju V. S.
Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India
E-mail:renjusnath@gmail.com

Supervising guide

Dr. Eby Thomas Thachil
Professor (Retd.)
Department of Polymer Science and Rubber Technology,
Cochin University of Science and Technology
E-mail: ethachil@gmail.com

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India

February 2016

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India

Dr. Eby Thomas Thachil
Professor (Retd.)
E-mail: ethachil@gmail.com

15/02/2016

Certificate

This is to certify that the thesis entitled "**Utilization of waste expanded polystyrene in the processing of rubbers and unsaturated polyester**" is an authentic report of the original work carried out by Ms. Renju V. S., under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi – 682 022. No part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Dr. Eby Thomas Thachil
(Supervising Guide)

Declaration

I hereby declare that the thesis entitled "**Utilization of waste expanded polystyrene in the processing of rubbers and unsaturated polyester"** is the original work carried out by me under the guidance of Dr. Eby Thomas Thachil, Professor (Retd.), Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682 022, and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Kochi – 22
15/02/2016

Renju V. S.

Dedicated to

My Loving Husband & Sweet Kids

Acknowledgements

At this moment I whole heartedly thank the almighty for venturing me into the field of research and for enabling me to complete this phase of endeavour. I cherish and admit my profound gratitude to the veterans in the field of research who paved me the right path and made to enlightened me 'determination' 'perfection' and 'destiny' as rather words and who showered and extended me whole hearted support with stern, specific and innovative ideas during the entire phase, the first among them being my mentor and Guide Dr. Eby Thomas Thachil. Words are inadequate to express my mind in full on my Guide Dr. Eby Thomas Thachil who always consented me to equally weigh my family with that of research. I have only this work and my future research ambitions to present him as my 'Gurudakshina'.

I wholeheartedly thank Dr. Thomas Kurian, the Head of the Department of PS & RT for his profound support and for providing necessary infrastructure and resources to accomplish my research. I owe Dr. Sunil K. Narayanankutty, the former head of the Dept of PS & RT for his invaluable advice and his willingness for sharing his expertise as and when required. The lessons of punctuality and discipline I had learned from the said veterans will always be an asset.

I am extremely indebted to Dr. Rani Joseph for her motherly affection showered on me by clarifying my doubts on all topics of research. I am also thankful to Dr. Jayalatha Gopalakrishnan for being supporting me with valuable suggestions and tips.

At this point I sincerely thank Dr. K.E. George, Dr.Philip Kurian for their support bestowed on me.

I am extending a special word of thanks to Dr. Honey John, Dr. Sailaja G.S., Dr. Prasanth R Krishna, Dr. Jinu George, Ms. Abitha and Dr. Jyothish Kumar, Inspire Faculty for their valuable suggestions and inputs extended to me.

I remember with thanks Dr. Beena T. Abraham, Dr. Laliamma Jose and Dr. Shiny Palatty for their motivation.

I am thankful to ad-hoc teachers and non teaching staff for their co-operation and support.

I express my gratitude to the scientists and staff members of STIC, CUSAT especially Dr. Shibu Eapen, for their support in instrumental analysis, Govt. Engineering College, Thrissur and Rubber Park, Irapuram for characterization and I am grateful to University Grants Commission and CUSAT for providing fellowship to carrying out my research work.

It is pertinent to cherish the peerless way of extending and sharing of their effort, experience and intelligence unconditionally among their fellow researchers of the Department of PS& RT. I sincerely thank Dr. Bipin Pal P.K. for his effort and immense support during my entire research. Dr. Saisy K. Esthappan, Dr. Sona Narayanan, Dr. Nisha Nandakumar, Dr. Prameela Devi, and Ms. Jebin are all individually instrumental in fulfilling my research assignment with their friendly support and motivation. Dr. Sinto, Mr. Abilash, Mr. Sreejesh, Dr. Ajalesh, Mr. Jolly, Ms. Dennymol, Dr. Preetha K Nair, Dr. Suma, Ms. Teena and Mr. Manoj are names to be remembered only with thanks for their unconditional support in my research. Remembering with thanks Dr. Jenish, Dr. Anna Dilfi, Dr. Vidya Francis, Dr. Vidya G., Dr. Nimmy K.P., Ms. Ayswarya, Ms. Shadiya, Dr.Asha Krishnan and Ms. Bindhu, Dr. Zeena and Dr. Newly for their love and support extended to me. I cherish the friendly support, fruitful discussion and valuable inputs shared by Dr.Resmi V.C., Ms.Julie Chandra and Ms.Neena George (FIP). I am extremely thankful to Ms. Neena, Mr. Jayesh, Ms. Sobha, Ms. Sreedevi, Ms. Sunitha, Mr. Muralidharan, Ms. Dhanya, Dr. Anjana, Dr. Praseetha, Mr. Bhagyesh, Ms. Neethu, Ms. Remya, Ms. Shinu, Ms. Anju, Ms. Jisha, Ms. Soumya, Ms. Nishad, Ms.Rehana, Ms.Bhavya, Ms. Divya Jose, Ms. Asha

Paul, Mr.Kingsly, Ms. Molice, Mr. Venugopal, Mr. Gean Mr. Dileep and Dr. Raju Parameswaran for their friendship and support.

I express my sincere gratitude to Mr. Rohith, Mr. Ali, Mr. Vishnu and Mr. Binoop for their timely help and technical support.

I cherish the prayers and support of Adv. Binny Thomas and Mrs. Rani Binny and motivation, inspiration and support extended by Dr. Arul George Scaria, Mr. Arun John Cherian and George Davis Thattil. I am always indebted to all my teachers.

At this moment of their dream coming true, I remember my Achan, Amma and Chettan for their prayers and support in fulfilling my research. I admit my thanks to my in-laws who were always encouraging and motivating in my endeavour.

Thank you Mamma for the mental support showered on me though you are not with me to share the happiness.

Words cannot express the feelings I have for my husband and Children. My husband has been always there with constant encouragement and motivation throughout the research period. With immense patience he managed the inconveniences of my family. My kids, Chinmayi and Chandrakanth missed many of their childhood enjoyments during this period. I thank them for all their sacrifices.

Renju V.S.

Preface

Waste generated by polymers is a major environmental issue today. These polymer wastes remain practically without any degradation in the natural environment even after a long period of exposure and pose a grave threat to the ecology of the planet. Management of polymer waste involves options such as reduction of use, re-use, recycling, incineration and landfill. There are six main thermoplastics which contribute to municipal solid waste- high density polyethylene, low density polyethylene, polyethylene terephthalate, polystyrene, polypropylene and polyvinyl alcohol. Among these the expanded form of polystyrene (expanded polystyrene/EPS) is a major problem for the environment. Due to its versatile nature there is an increasing trend in the production and consumption of EPS products. The world wide consumption of EPS was 5.833 million t/annum in 2011. After use, EPS usually ends up in landfills or is incinerated, both of which are not environment-friendly solutions. Hence any attempt to reduce the amount of waste EPS littering the environment can be considered an ecologically significant step.

Its nuisance value in the environment is high because of the low bulk density (15–50 kg/m3) and voluminous nature. A large space is consumed by EPS. Still the recycling of EPS has not attained the same status as the recycling of other polymers because of the high transportation cost as well as small price difference between the virgin and recycled products. Therefore, a cost effective method for the reuse of this waste material is indispensable in the present scenario. This work aims to investigate economically significant techniques for the utilization of this material in various polymers without compromising the polymer properties.

The thesis consists of eight chapters. A brief introduction on the relevance of recycling of waste expanded polystyrene, blending techniques and compatibilisation, is presented in Chapter 1. A review of elastomer/thermoplastic blends and thermoset/thermoplastics blends is provided. The scope and objectives of the present work are also included.

Chapter 2 of the thesis gives a detailed description of the materials used and the methods employed for the present study.

Part A of Chapter 3 focuses on comparative studies of the effect of EPS on the mechanical, thermal and morphological properties of gum, black filled and silica filled NR. Silica is the best filler for NR/EPS blends. Part B describes the effect of maleic anhydride compatibilization on the cure characteristics, physico-mechanical properties, dynamic-mechanical studies, solvent sorption, thermal analysis and phase morphology of silica filled NR/EPS blends. The overall data suggest that the incorporation of 5% waste EPS in NR is promising step for both waste management and the economy of NR processing.

Chapter 4 of the thesis reports studies on the effect of EPS in SBR compounding. Cure characteristics, physico-mechanical properties, dynamic-mechanical, solvent sorption, thermal analysis and phase morphology of the blends were studied. Between carbon black and silica, better performance is observed in the case of silica. That a significant proportion of EPS (15%) can be incorporated in SBR with advantageous results is very significant.

Chapter 5 investigates the utilization of EPS in commercial unsaturated polyester resin (UPR). The results prove that modification of EPS by MA and subsequent blending with UPR is a useful step which improves many properties of UPR.

Chapter 6 deals with synthesis of UPR and the incorporation of EPS at the final stages of synthesis to make UPR/EPS blends. Blends were prepared for neat UPR, UPR/5EPS(unmodified) blend and UPR/5EPS(modified) blend for two styrene concentrations. Here also modified blend showed better properties than unmodified blend. UPR/40% styrene showed better properties compared to UPR/35% styrene.

Chapter 7 describes the effect of EPS/modified EPS on the volume shrinkage and transparency of both commercial as well as synthesised UPR samples. The volume shrinkage of UPR is reduced in the presence of EPS. Hence EPS acts as an effective LPA. The loss of transparency due to LPA is reduced by modified EPS. This is yet another advantage when EPS is incorporated into UPR as a pollution control method.

Chapter 8 summarizes the major findings of the study and presents the conclusions reached.

Abstract

Expanded polystyrene (EPS) is a persistent nuisance to the environment compared to other thermoplastic waste. The recycling of EPS is uneconomical and therefore after use it ends up in landfill or is incinerated. However, these methods are becoming less practical due to increasing land cost and public opposition. Therefore utilization of waste EPS in other polymers will be more economical as it uses less energy and fewer resources.

The strategy adopted here is the incorporation of waste EPS in other polymers by blending techniques. In this study, an attempt has been made to utilize waste EPS by blending it in elastomeric and thermosetting polymers without compromising the polymer properties. Natural rubber, styrene butadiene rubber and unsaturated polyester resin were used for the purpose. In order to retain the inherent properties of the polymers, modification was also done using grafting technique. The study establishes a potential method for utilizing waste EPS.

Mechanical, thermal and morphological properties of unfilled and filled (carbon black and silica) NR/EPS blends were studied and compared with the corresponding unfilled and filled NR without EPS for selecting the best filler for the blend. The properties suggest that silica is the best suited filler for NR/EPS blend. The effect of compatibilization on the properties of silica filled NR/EPS blends using maleic anhydride was investigated. Grafted blends were prepared for compatibility enhancement at varying MA content, iniator (DCP) content and blend ratios. The final cured blends were obtained after adding required quantity of NR and compounding ingredients. Cure characteristics, physico-mechanical properties, dynamic-mechanical properties, solvent sorption, thermal stability, phase morphology etc. of the final cured blends were analysed

and compared with that of NR. On compatibilization, most properties of the silica filled 95/5 NR/EPS blends are either at par or better than that of silica filled NR at an optimum MA (1%), DCP (15% of MA). The overall data suggest that the incorporation of 5% waste EPS in NR is promising step for both waste management and the economy of NR processing.

A study on the effect of EPS in SBR compounding has also been carried out. Blends of SBR and EPS were first prepared initially in a Brabender Plasticorder. These were subsequently blended with required quantity of SBR and compounding and curing done. Different blend ratios of unfilled compounds were prepared and the properties were compared with the corresponding samples without EPS. A remarkable improvement in properties was found with unfilled compounds. Between carbon black and silica, better performance is observed in the case of silica. A significant proportion of EPS (15%) can be incorporated in SBR with some advantageous results.

The other important part of the study was the investigation on the utilization of EPS in commercial unsaturated polyester resin (UPR). Blends of UPR/EPS were prepared by dissolving EPS at varying concentrations in styrene and this was mixed with UPR by mechanical stirring, designated as unmodified blends. Maleic anhydride grafting was done on EPS and the modified blends were also prepared. Curing was done using methyl ethyl ketone peroxide (catalyst) and cobalt naphthenate (accelerator) combination for 24 h, followed by post curing at 80 °C for 3 h. Neat resin samples without EPS were also prepared for comparison. Better adhesion between the UPR and EPS as evidenced in the SEM, supports the mechanical property improvement of modified blends. The results prove that modification of EPS by MA and subsequent blending with UPR is a useful step to utilize waste EPS and to improve many properties of UPR.

Synthesis of UPR at two different styrene concentrations with incorporation of EPS in the final stage of synthesis is also done. UPR/5EPS (unmodified/modified EPS) blends with two different styrene ratios (35 and 40 wt %) were prepared and the results were compared with their pure forms. Here also modified blend showed better properties than unmodified blend. UPR/40% styrene showed better properties compared to UPR/35% styrene. The results provide an ample scope for the utilization of waste EPS in UPR synthesis.

A significant aspect of this work is the study on the effect of EPS and modified EPS as low profile additives (LPA) on the volume shrinkage and transparency of both commercial as well as synthesised UPR samples. The volume shrinkage of UPR is reduced in the presence of EPS. The loss of transparency due to EPS is reduced by modification. Utilization of 5phr EPS in UPR results the best compromise between volume shrinkage, transparency and desirable properties.

The study establishes the potential of utilizing waste EPS in commercial polymers. Any reduction in the amount of waste EPS will have a salutary impact on the environment considering the voluminous nature of EPS. While addressing the environmental problems arising from waste EPS, this technique also holds promise for rubber as well as resin processing as a cost reduction/property modification method.

Contents

Chapter 1

Chapter 2

EXPERIMENTAL TECHNIQUES..67 - 97

Part A

MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF UNFILLED AND FILLED NR/EPS BLENDS

Part B

COMPATIBILIZATION OF SILICA FILLED NR/EPS BLENDS USING MALEIC ANHYDRIDE

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

……

Chapter 1

INTRODUCTION

1.1 Polymer recycling: A general introduction

Polymer, one of the most important materials in the modern society has become the substantial part in all aspects of daily life, that, without which survival would be practically impossible. Over the past 50 years, there has been a very steep rise in plastic production. The worldwide production of plastics was estimated to be around 230 million tonnes in 2009 [1], rose to 299 million tonnes in 2013 (3.9%

increase compared to 2012) [2] and continues to grow at approximately 9% per annum. More than 4% of the annual petroleum production is used as the feedstock for plastics [3]. The industrial production of thermoplastics has zoomed to approximately 300 million tonnes per year due to the unparalleled versatility of applications over a wide range of temperatures. Plastics have considerably spread their application potentials in diverging areas because of the diversity in properties such as a high strength-to-weight ratio, stiffness and toughness, ductility, corrosion resistance, bio-inertness, high thermal/electrical insulation and outstanding durability at a relatively low cost in a lifetime compared with competing materials. Approximately 50% of plastics manufactured are used for single-use disposable applications such as packaging, films and disposable consumer items. Other durable applications include pipes, cable coatings, furniture, vehicles, structural materials, electronic goods etc. A considerable potential of plastics is the new generation applications which are to bring benefits in the future. These include novel applications in the field of medicine, generation of renewable energy and reducing energy use in transport [4]. The application of plastics in various fields and production of plastics worldwide from 1950 to 2013 (in million tonnes) is shown in Fig. 1.1 and Fig. 1.2 respectively.

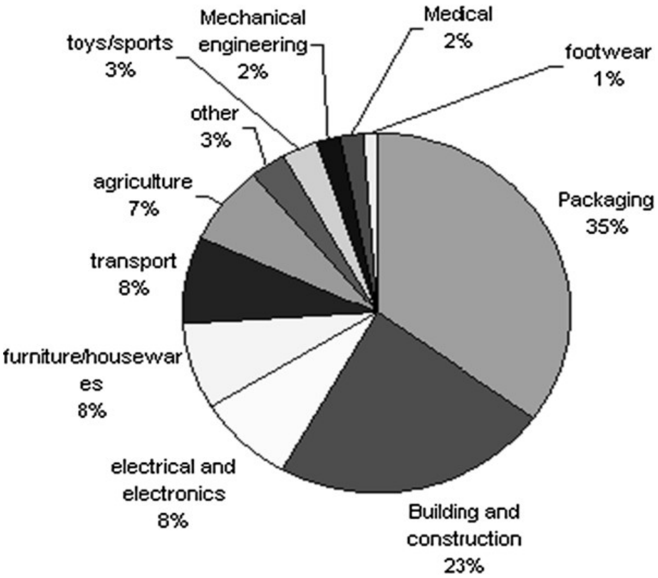


Fig. 1.1. The application of plastics in various fields

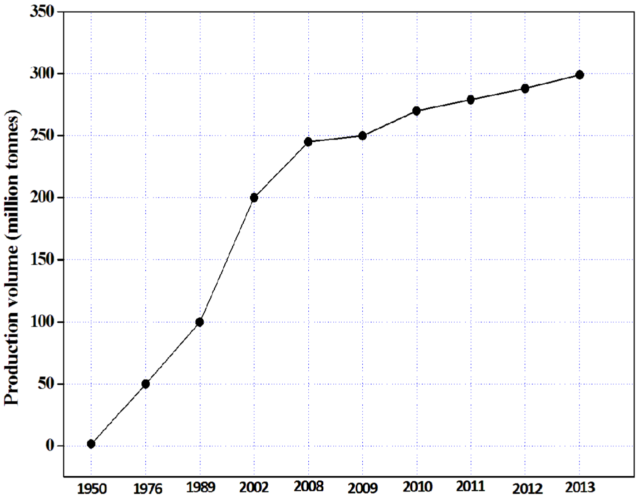


Fig. 1.2. Worldwide production of plastics

An analysis of plastic consumption among different countries in 2000 has revealed that the highest consumption of plastics was found in USA and India had a plastic consumption of 3.2 MT. Hindu Business line, January 21, 2006 revealed that India will be the third largest plastics consumer by 2010 after USA and China. The highest growth rate of plastic consumption worldwide is mainly concentrated on the middle class people because their rising needs can be satisfied by the application of plastics at a cheaper rate compared to other materials [5]. The increasing usage and rapid production of plastics has led to a large amount of waste generation. This is a major threat to the environment because of the non-biodegradability of plastic materials. Considerable accumulation of plastic wastes contaminates the environment [6]. The buoyant nature makes waste plastics floating on the sea surface. In addition to the visual disturbance, it also causes threat to marine life [7, 8] Other issues associated with the plastic waste is that its disposal by landfill requires large area of land and the leaching out of hazardous chemicals cause soil as well as water contamination [9]. Hence the lack of efficient waste management of plastics poses a serious problem.

1.2 Sources of plastic wastes

Plastic wastes can be classified as municipal and industrial plastic wastes according to their origin.

The municipal plastic waste is a part of municipal solid waste (MSW). This includes domestic items (disposable cups, packaging foam, parts of electronic equipments, food containers, bottles, pipes, thermal insulations, kitchen utensils, surface coatings, etc.), agricultural items, wire and cable, automotive parts etc. The percentage of plastic waste in MSW is found to increase significantly year by year [10]. According to estimates, plastic wastes represent 15– 25% of municipal waste in Europe [11]. In USA, waste plastics amounted to 1% of the weight of all MSW during 1960, 8% in 2000 and increased to 11.7% in 2006 (Environmental Protection Agency (EPA) report 2000 and 2006). Plastic wastes constituted 7% in Japan (2001) and 13% in China (2000) of the total MSW [12]. A dramatic increase in percentage of plastic wastes, 0.7% in 1971 to 4% in 1995 and 9% in 2003 was also noticed in India [13-14].

Industrial plastic wastes are those generated from plastic industries (manufacturing, processing and packaging), construction and demolition companies, electrical and electronics industries and the automotive industries. Normally the industrial plastic wastes have relatively good physical characteristics because they are free of contamination. They are available in fairly large quantities. Some of them may have poor characteristics due to exposure to high temperatures during the manufacturing process, but have not been used in any product applications. Unlike municipal plastic waste, industrial plastic wastes are heterogeneous in nature. Hence repelletization and remolding are found to be simple and effective means of recycling. But for heterogeneous plastic wastes chemical recycling is the most suitable method [15].

1.3 Waste management of plastics

The steady increase in production and consumption of plastics, the increased demand due to population growth, the versatile nature and wide range of applications give emphasis to the importance of waste management. There are several methods for disposal of municipal and industrial plastic waste. The ‘three Rs’ (reduce, reuse and recycle) [16] together with ‘fourth and fifth Rs’ (‘energy recovery’ and ‘molecular redesign') [6, 17] have been extensively advocated as solutions to the plastic waste management. Landfill is the least desirable management strategy. An efficient waste management treatment is the foremost factor regarding the energetic, environmental, economical and social aspects.

1.3.1 Landfill

A conventional and easy approach to plastic waste management is landfill and a large amount of waste is disposed off by land filling. But this method has many disadvantages. One is the insufficient space for landfills, along with the impacts of collection and transport. A crucial problem is the long-term risks associated with the life of the non biodegradable plastic materials (persistent organic pollutant), hazardous additives used in plastics and byproducts of plastics production causing contamination of natural terrestrial, freshwater and marine habitats [16].

1.3.2 Incineration and energy recovery

Incineration reduces the cost of landfill. The benefit of this approach lies in the fact that it can be used for the recovery of energy content in the plastic. The recovered energy can vary according to the application (electricity generation, combined heat and power, or as solid refuse fuel for co-fuelling of blast furnaces or cement kilns). Production of monomers (BTM-back to monomer), liquid fuels or gases (BTF-back to feedstock) through pyrolysis [18-19] is also possible and interest in this approach is increasing owing to the rise in fuel price [20]. This process can be considered as one of the most suitable means for dealing with mixed plastics. Yet this technique is considered as less energy efficient compared to recycling and it cannot fulfill the demand of raw materials for plastic production. In addition, the release of hazardous substances into the atmosphere during the process cannot be circumvented. Therefore in many countries incineration of plastics is not a common waste-management strategy as landfill/mechanical recycling whereas in countries such as Japan, Denmark, Sweden etc., which have good incinerator infrastructure, the method is promising.

1.3.3 Reducing (Down gauging)

Reducing the usage of plastics is important in the waste management. Down gauging the amount of packaging used per item can reduce waste volumes. Optimizing the required amount of plastics, especially in the packaging field can avoid the unnecessary liberal use. Economics dictate that the use of minimum required material necessary for a given application has been initiated by many manufactures [6]. But this is against the aesthetics, convenience and benefits of marketing. Traditional way of usage leads to over-use of packaging [17]. The breakthrough in mechanization and production process also results in escalation of packaging of products.

1.3.4 Re-use of plastic packaging

There are scopes to 'reuse' plastics, for example, in the transport of goods on an industrial and a domestic scale, in high value consumer goods such as vehicles and electronic equipment. However wide scale reuse is not practically logical when distribution and collection points are distant from centralized product-filling factories .Then take-back and refilling of empty containers by the suppliers are not feasible [6]. Several European countries have such large-scale strategy schemes to reduce packaging waste but still these are rather less realistic. Voluntary behaviour change programmes [21] (Australia), plastic bag levy [22] (Ireland) or banning of lightweight carrier bags (India, Bangladesh and China) are some of the programmes commenced for the 'resuse' of plastics.

1.3.5 Plastics recycling

Plastics recycling involve a wide range of recycling strategies, viz. primary recycling, secondary recycling, tertiary recycling and quaternary recycling. A detailed classification is described in Table 1.1[17].

Table 1.1. Classification of Plastics recycling

ASTM D5033 definitions	Equivalent ISO 15270 definitions	Other equivalent terms
Primary recycling	Mechanical recycling	Closed-loop recycling
Secondary recycling	Mechanical recycling	Downgrading
Tertiary recycling	Chemical recycling	Feedstock recycling
Quaternary recycling	Energy recovery	Valorisation

The primary recycling refers to mechanical reprocessing into products and the new products have properties equivalent with the former ones [17]. This method is applicable to uncontaminated plastic wastes of similar grades. Moreover, the material should be stable against degradation on mechanical reprocessing. Therefore, only a part of the post-consumer plastic waste stream can have routinely recycled by this method. For example, PET bottles are of similar grades and are suitable for reprocessing to both polyester fibres and bottle manufacturing process, whereas HDPE used for blow moulding is least applicable to injection moulding.

Primary recycling is more suited for pre-consumer plastic wastes than post-consumer wastes because of their purity and availability.

Under certain circumstances, recovered plastics may undergo some degradation resulting in downgrading of properties and have to be put into some other applications. This is secondary recycling which also belongs to mechanical recycling. Downgrading refers to the recycling when the recovered plastic is put into an application that would not typically use virgin polymer, e.g. ‘plastic lumber’ as an alternative to higher cost/shorter lifetime timber [17]. Mechanical recycling carried out by physical means ie grinding, shredding or melting does not affect the material’s chemical structure [23].

Tertiary recycling is either described as chemical or feedstock recycling during which the polymer gets depolymerised. This method aims to convert waste polymer into original monomers which can be used for the re-manufacture of the polymer or other valuable chemicals. There are three main approaches: depolymerisation, partial oxidation and cracking (thermal, catalytic and hydrocracking). The main advantage of chemical recycling is that a low quality input of plastic waste ie., heterogeneous and contaminated polymers can be used and can expect a higher quality of output [24]. However, plastic recycling has been dominated by mechanical recycling so far. The inadequacy of chemical recycling mainly arises from economic concerns because of the low price of petrochemical feedstock compared with the plant and process costs incurred to produce monomers from waste plastic [25].

Quaternary recycling is the recovery of energy, energy from waste or valorization. This is not generally considered recycling in the EU context [9].

1.3.6 Alternative materials

Alternative materials such as biodegradable plastics are a means to solve waste-management issues and their production has increased considerably in recent decades. But this needs appropriate technical features, handling systems and consumer education. Another concern is that there should be sufficient resources to replace the ever growing consumption of polymers. Biopolymers are derived from renewable biomass and are more expensive than the oil based conventional polymers [6].

Molecular redesign (the 5th R) is incorporated by the green chemists within the design and life cycle analysis of plastics. Fully effective chemical products designed with little or no toxicity, break down into harmless substances after use and may be based upon renewable feedstocks, such as agricultural wastes [6]. One of the main drawbacks from all the other Rs is that the monomers are designed to form products with limitations in reusability, recyclability or recovery of plastic. Typically, problems involving waste and/or adverse health effects have begun to appear only after the marketing of such products. Designing monomers to produce risk free products remains largely in the laboratory.

1.4 Various steps involving plastic recycling

One of the challenging factors associated with plastics waste is that it consists of a wide variety of plastics that are not compatible with each other due to the immiscibility at molecular level and the differences in processing requirements [17]. Another problem related with waste plastics is the heterogeneous nature and contamination by other materials. Therefore it is not possible to use the waste polymer along with virgin polymer without compromising the quality of virgin polymer such as colour, clarity or properties. Even 1% of an incompatible polymer is sufficient to degrade the properties of the entire recycled material [26]. But the plastics waste is used for certain non-critical applications. The recycled plastic can substitute virgin plastic based on the purity of the recovered plastic feed and the required property of the plastic product meant for the specific application. In the case of sorted plastic wastes more accepted properties can be expected. Recycling therefore comprises of several steps, collection, sorting, cleaning, size reduction and separation.

1.4.1 Collection

Collection of plastic wastes can be done by two ways, ‘bring-schemes’ and ‘kerbside, collection [17]. A low collection rate is the disadvantage of Bring-schemes. Hence, the general trend of collecting recyclable materials is achieved through kerbside collection. But since most of the kerbside collections are mixed recyclables (paper/board, glass, aluminium, steel and plastic containers) the cost efficiency of such collection programmes has increased. Though the recovery of plastic bottles from homes (only 30–40% of postconsumer) by this method of collection is appreciable, most of the packaging waste comes from food and beverage consumed away from home. Therefore ‘on-the-go’ and ‘office recycling’ collection schemes are required for the overall collection of plastic packaging waste.

1.4.2 Sorting

Sorting of waste plastics is a major part of polymer recycling. The importance of sorting and separation has already been discussed in section 1.4. The sorting and separation are based on the difference in physical properties of various plastics, properties like chemical, optical and electrical If a method is fast, reliable and economical, then it can be treated as commercially successful.

1.4.2.1 Manual sorting

Visually distinguishing features other than the recycle code on plastic containers can be identified by trained persons. For example, features such as slight blue tint, horizontal crescent and presence of whitish areas (stress whitening) are some of the distinguishing features of PVC bottles from PET bottles. Ultraviolet light can also be used for separation as different plastics exhibit different colours. Manual sorting is economically unfavorable due to reasons like intensive labour and low value products as a result of human error.

1.4.2.2 Density based methods

Density based method has been widely used for many years till date for sorting waste plastic flakes. The method includes wet separation (float sink method), dry separation, centrifugal sorting, sorting with near critical and super critical fluids, float-sink methods (preferential solvent absorption, hydrophobicity) and froth floatation.

1.4.2.3 Optical sorting

Optical sorting method is based on colour or transparency. Examples are separation of coloured PET from clear PET, coloured PP caps from natural HDPE milk bottle flakes etc. Optical sorting is effective in obtaining recycled products with almost same colour purity and consistency as virgin resins. However this method lacks the chemical identification of polymers.

1.4.2.4 Spectroscopic methods

Spectroscopic method is one of the most proven and established technologies. It includes MID-IR , NEAR-IR, laser acoustic sensing, Raman spectroscopy, sorting by laser induced emission spectral analysis, plasma emission spectroscopy, and other techniques such as polarized light, UV light and fluorescent tagging etc.

1.4.2.5 X-ray fluorescence (XRF)

. X-ray fluorescence is used for removing PVC contamination of PET, which is a common problem encountered in the recycling of PET. The chlorine atoms in PVC emit low- level X-rays whereas other plastics without chlorine atoms give different response on exposure to light. The sensitivity of XRF lies in the fact that this can even identify PET bottles possessing PVC labels.

1.4.2.7 Electrostatic sorting techniques

Exchange of charges across the interface of materials occurs (some become negative, other positive) when two materials come into contact with each other, is the principle behind electrostatic sorting techniques. A triboelectric separator can sort materials based on surface charge transfer.

1.4.2.8 Sorting by difference in melting temperature

Sorting by difference in melting temperature can be adopted for polymers with significant difference in their melting points. For example a hot belt separator is used for separating PVC flakes from PET. Softening of PVC occurs first and it adheres to the heated belt before the melting of PET and the later can be separated [27]. Though this method is economical, its requirement that plastic materials must form a monolayer is a main drawback.

1.4.2.9 Sorting by selective dissolution

Because of thermodynamic differences, polymers dissolve at different temperatures in solvents like xylene. This is the basic concept behind the selective dissolution. Careful solvent selection and control of temperature are the key factors associated with this method. Benefits of this method are separation of individual plastic from complex mixtures, absence of disturbance from contaminants (dirt, soil etc.), separation of closely related polymers such as PS and ABS, similarity between recycled product and the virgin counterpart, minimum labor requirements etc.

1.4.3 Size reduction

Size reduction is the main part of plastic recycling, that converts the waste plastics plastics into more convenient form for transportation and feeding. Size reduction is important for most of the recycling methods such as mechanical, feedstock or even incineration to convert waste into a consistent manageable form. This method is widely applied to expanded polystyrene to reduce the bulk density of the material. Shredding, granulation, densification, compaction, agglomeration and pulverization are the techniques involved in this method.

1.4.4 Removal of contamination

Waste plastics are associated with many contaminants like dirt, soil, glass, metal fragments, incompatible polymers etc. Hence removal of such contaminants is necessary to produce a high quality recycled product. Melt filtration is an effective tool in this contest, resulting in a less contaminated product but with a higher price than unfiltered ones. Therefore a specified percentage of recycled material can be used with the virgin counterpart. In addition to upgrading the quality of recycled material, this method improves the productivity as well as prevents the damaging of die.

1.5 Expanded polystyrene [28]: An overview

Although hundreds of plastic materials are commercially available, only a few of these qualify as commodity thermoplastics in terms of their high volume and relatively low price. These include low-density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) that account for approximately 90 per cent of the total demand. Among these the expanded form of polystyrene (expanded polystyrene/EPS) is a major constituent in terms of its applications.

Expanded polystyrene is a rigid cellular plastic and is the foam product of expandable polystyrene. Expandable polystyrene is manufactured in the form of very small polystyrene beads (diameter 0.2 mm - 3.0 mm) with a weight-average molecular weight between 160,000 and 260,000 and contains blowing agent, usually pentanes or butane. There are two methods involved in the manufacturing of expandable polystyrene. One is a two step process of polymerization of styrene monomer followed by impregnation of the polymerized polystyrene bead with a blowing agent. A common method employed is a single step process in which reactions occur in a single reactor designed to control the temperature and pressure of the reaction.

1.5.1 Manufacturing of expandable polystyrene

Manufacturing of expanded polystyrene (EPS) involves three stages, viz., pre-expansion, stabilization of pre puff and molding.

1.5.1.1 Pre-expansion

Pre-expansion is achieved by steam heating the expandable polystyrene beads. This results in increasing pressure of the blowing agent as well as softening of polystyrene and thereby causes the expansion of beads. The extent of expansion can be controlled by temperature and heating duration. By this process the density is lowered from 673 g/l to 12 g/l. To achieve the correct bulk density during pre expansion is important.

1.5.1.2 Stabilization of pre stuff (maturation)

After the pre-expansion, the residual blowing agent condenses on cooling causing a partial vacuum. Stabilization process is required for the diffusion of air inside the beads to reach equilibrium with atmosphere. This results the beads to become resilient, which do not collapse when squeezed. In this condition the beads are ready for molding and ensure good fusion. During maturation, the elimination of excess water contained in and on the surface of the pre puff that is harmful to the molding process is also possible.

1.5.1.3 Molding

When maturation is completed the pre expanded beads are then fed into the mold. It is then closed and steam heated again. The residual blowing agent and the air which entered the beads get expanded and the polystyrene is again softened. Since the beads are closed in the mould, the expansion of air and blowing agent within the bead causes them to distort and the beads get merged giving a non-communicating microcellular structure.

1.5.2 Properties and applications of expanded polystyrene (EPS)

Expanded polystyrene exhibits a number of outstanding properties that fulfill a number of applications. Among the outstanding properties, most noted are light weight as a result of low density, thermal insulation capacity, excellent mechanical properties (resistance in compression, capacity for dampening shocks), insensitivity to water (buoyancy), chemical resistance, electrical properties, hygienic appearance, dimensional stability,

ability to be molded or cut into nearly unlimited shapes, ability to be recycled etc.

The common applications include,

Thermal insulation: Expanded polystyrene is used as thermal insulators in cold stores, refrigerated transport, chill rooms, freezer display cabinets, factory roofs, farm buildings, broiler houses and other buildings where fuel costs are expensive.

The insulation value ‘K’ (for EPS 0.24 and for cork 0.28-0.32) suggests that 6inches of EPS is equivalent to 7 & 8 inches of cork.

Packaging: Because EPS can be molded to close tolerance, it is used as packaging with maximum protection against vibration and impact. The clean and nonabrasive surface eliminates the overwrapping. Metal articles can also be packed by EPS because of its neutral p^H. It is also used for industrial and consumer products packaging. Another advantage lies in the shock absorbance, appearance, customer acceptance, costs etc in the packaging and safe transportation of electronic goods. It offers convenient storage space because of the contour molding. Most efficient cushioning is provided in EPS packaging because of the low density.

Marine applications: In the construction of marinas and many other marine applications the buoyancy of EPS can support more weight than the alternative materials.

Horticulture: EPS trays or boxes are used for horticultural products and for wet fish due to its thermal insulation property.

1.6 Relevance of Waste Management of EPS

Owing to the versatile properties and wide range of applications mentioned above, expanded polystyrene is undoubtedly a unique and important polymer. It is user friendly in terms of financial viability and convenience. Therefore the production and consumption of EPS have increased significantly and EPS packaging is a multi-billion dollar industry. The world wide consumption of EPS was 5.833million t/annum in 2011 [29] and the year wise consumption of EPS is graphically shown in Fig 1.3.

Fig. 1.3. Year wise consumption of EPS

Expanded polystyrene is a major constituent among the plastic waste stream. Most of its applications are those with single use only (single-life or cycle) or for a short time e.g. food packaging. The recycling of expanded polystyrene (EPS) involves various technological challenges stemming mainly from its low bulk density (15-50 kg/m^3)[26]. Due to its light weight, buoyancy, thermal insulation, dimensional stability, chemical resistance, electrical properties, hygienic appearance, low cost etc., EPS is widely used in applications as shape-moulded packaging foam, building insulation, vegetable and fish crates, catering and fast-food restaurant trays and boxes, soil filler etc. After use, EPS usually ends up in landfills or is incinerated. The major source of waste EPS is the manufacture of industrial and commercial goods where large quantities of foam are scrapped at a single location and recycling is both practical and economic. But its light weight, though a valuable attribute to many applications, also means that the mass of material obtained for recycling from any given location is rather limited. Its nuisance value in the environment is so high because of its large volume. Added to this are the high transportation costs associated with shipping the low bulk density waste EPS. The high cost of land filling has been an important driving force in EPS recycling. Though EPS does not leech or pose toxic dangers like many other materials, the volume of EPS consumed as landfill has earned it a bad reputation as a major pollutant of the environment. The landfilling of waste EPS is not practicable due to the high land cost and it has been reported that the cost of land filling amounts to between $500 and $2500 per tone [26]. EPS is also one of the least economical polymer to be recycled and has not attained the same status as that of recycling of other polymers. One of the main reasons is the small price difference between the already cheap virgin and recycled EPS. Recycling of a low cost polymer is least preferable since the recycling results in a product with inferior properties. Besides the available quantity of polymer at a given location for recycling is limited and the transport of the bulk volumes to distant recycling units is impractical as well as uneconomical [30].

1.7 Reuse of waste EPS in other polymers as a waste management measure

The major drawbacks in the waste management of EPS emerge from its low cost and bulky nature associated with low density. Since the recycling of EPS is not cost effective, the common methods of waste management of EPS are landfill and incineration. But in response of growing public opposition and land cost these two methods are not practical. Therefore reusing of waste EPS as a blend in other polymers by cost effective method is more attractive and preferable to recycling in the present scenario as it uses less energy and fewer resources. If the waste EPS can be used in other polymers by cost effective methods then the economical impact of recycling may be more favorably averted. Thus utilization of waste EPS can be done by blending with other polymers and this method will be a favorable route for the waste management of EPS. Any reduction in the amount of waste EPS will have a salutary impact on the environment in terms of reduction in volume of waste.

1.8 Polymer blends

The importance of polymer blends has achieved a promising status in the field of polymer science. The mixture of two or more polymers or copolymers comprising more than 2 wt% of each component is referred to as polymer blend [31]. The blending technique is fairly an attractive tool for obtaining new materials with synergistic and tailored properties not observed in the constituent polymers. The advantage of blending is that it can be used for developing ‘new materials’ with desired properties by cost effective method and thus the expensive production of of new polymers by synthesis can be avoided. The time required for developing a new blend commercially is very low compared to new polymers. The use of blends is significant with respect to the performance of a specific article, improvement in the technical properties compared to the original polymers, control of processing characteristics together with economic viability [32-35]. Blending technology also provides attractive opportunities for reuse and recycling of polymer wastes [36-38].

Polymer blends are either homogeneous or heterogeneous. In the case of homogeneous blends, the final properties usually are the arithmetical average of those of individual components whereas heterogeneous blends, show the properties of all the blend components present. Limitations of one polymer can be compensated by the other to a certain extent. In a few exceptional cases, some properties of either the homogeneous or heterogeneous blend can be better than those of the individual components. This synergism is unfortunately hard to predict.

1.8.1 Classification of polymer blends based on miscibility

Depending on the miscibility, there are three different types of polymer blends [39]. They are completely miscible, partially miscible and immiscible blends. For completely miscible blends $\Delta Hm < 0$, molecular level of mixing is observed and are characterized by a single phase morphology and single glass transition temperature (T_g) in between the T_gs of the components. An example is PS/PPO. Partially miscible blend exhibits a fine phase morphology (either single or two phase) with satisfactory properties. A wider interface and good interfacial adhesion are characteristics of partially miscible blends. Here the blend components have their own T_gs and are shifted towards each other. PC/ABS is an example of partially miscible blends. Fully immiscible blends show coarse morphology with sharp interface and poor adhesion between the phases. Different T_gs corresponding to the components are observed for immiscible blends and are not usable without compatibilization. Examples are PA/PP, PA/ABS, etc.

1.8.2 Thermodynamics of miscibility

According to thermodynamics a completely miscible blend requires a negative free energy of mixing,

$$\Delta G_m = \Delta H_m - T\,\Delta S_m \qquad (1.1)$$

ΔG_m is the Gibb's free energy of mixing, ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing and T is the absolute temperature. Because of high molecular weight of polymers, ΔS_m is small in the case of polymer blends. Hence the value of free energy change of mixing depends on ΔH_m. Since many of the polymers (non-polar) shows a positive ΔH_m the required negative free energy change for the thermodynamic miscibility is difficult to realize and therefore the number of miscible blends is limited [40]. A miscible blend is homogenous down to the molecular level, the following conditions should be satisfied: (i) The free energy of mixing should be negative or zero and (ii) the second derivative free energy function with respect to volume fraction of the dispersed phase (φ) should be a positive value.

$$\Delta G_m \approx \Delta H_m \leq 0 \quad \text{.......} \quad (1.2)$$

$$\partial^2 \Delta G_m/\partial\varphi^2 > 0 \quad \text{.......} \quad (1.3)$$

Immiscible blends do not satisfy the conditions proposed in equations (1.2) and (1.3), and show a two-phase morphology. In the case of partially miscible blends, the second criterion is not satisfied and shows either two phases or single-phase morphology.

1.8.3 Concept of compatibility

Complete miscibility is not required for many applications of polymer blends. Commercial applications can be achieved even with immiscible blends that are technologically compatibilized. Therefore polymers that are compatibilized in the technological point of view, may or may not be miscible in a thermodynamic sense. Since the material performance of a blend depends on morphology, the control of morphology through compatibilization is the key factor in making a successful blend. The shape, size, and spatial distribution of the phases is the consequence of viscosity of the phases, interfacial characteristics, blend composition and processing parameters [39]. Therefore compatibilized blends are characterized by synergistic properties and a stable morphology with a finer and homogenous dispersion of the minor phase in the matrix. Compatibilization is a process of modification of the interfacial properties in immiscible polymer blend and can be achieved by the addition of suitable compatibilisers or interfacial agents. It reduces interfacial tension, facilitate dispersion, stabilize the morphology against abusive stress/strain (arising out of processing), enhance adhesion between phases and improve the overall mechanical properties of the products [31, 41]. Interfacial agents, including both reactive (chemical blending) and non-reactive types (physical blending) are used for the compatibilization.

1.8.3.1 Addition of Block and Graft Copolymers

In this method an already prepared compatibilising agent (either a block or graft copolymer) is added in the blending process as a non-reactive component. It is not necessary for the copolymer to have identical chain segments as those of the main polymers, but it is only adequate that the copolymer has segments miscible with the main polymeric components.

Due to the chemical and molecular characteristics, the added agent is able to locate at the interface. Each segment will penetrate into the phase with which it has specific affinity. This reduces the interfacial tension between the blend components and increases the adhesion between the phases. The interfacial addition, blend morphology and blend properties depend on molecular weight of the copolymer segments, blend compositions, blending conditions etc.; which have been the keen interest in several recent reviews [42-44]. Tendency of the added copolymers to form micelles is one of the disadvantages of this addition method [45].

1.8.3.2 Utilization of Non-Bonding Specific Interactions

The compatibility of polymer blends can also be achieved by some non-bonding specific interactions such as hydrogen bonding, ion-dipole, dipole-dipole, donor- acceptor, and π-electron interactions. Typical examples are polyvinyl acetate (PVA)/polyvinyl chloride (PVC), polyesters/PVC (hydrogen bonding), poly (vinylidene fluoride) /polyacrylates (dipole-dipole). Role of specific interactions in the miscibility of polymer blends has been reported earlier [46-49]. However these interactions are weak and high concentration of polymer is required for effective compatibilization.

1.8.3.3 Addition of Low Molecular Weight Coupling Agents

Low molecular weight reactive compounds are effective in compatibilization of polymer blends. Copolymer is formed during this type of blending. Many studies have been carried out in this area by using peroxide and coagents in PE/PP [50], PS/PE [51,52], PS/EPDM [53] etc, organosilanes in PPE/PS [54], bismaleimide in PBT/PE [55] etc.

1.8.3.4 Reactive Compatibilization

Reactive compatibilization [43], is the dominant method in which the copolymers are formed in-situ through covalent or ionic bonding during melt blending process. In this kind of reactive compatibilization, generally one phase contains reactive groups inherent in the polymer, while the other has no such functionality. Reactive groups can be incorporated into the second phase by adding a functionalized polymer, which is miscible. In some cases, both polymers have to be functionalised. In contrast to physical compatibilization, a high molecular weight copolymer is formed at the interface immediately. Therefore in concern with the economics as well as performance, the technique is more applicable than the previously discussed one. This method engenders a thick interface in between the components leading to a stable morphology. Many studies were carried out based on reactive compatibilization for different polymer blend systems

[56-61]. R. Zacur et al. have studied the effect of MA-g-PP in polypropylene and polyhydroxyaminoethers (PHAE) blend [62]. Melt free radical grafting of glycidyl methacrylate monomer (GMA) on to high density polyethylene, followed by reactive blending with PET was done by F. Pazzagli and M. Pracella [39]. Another study has been reported in using a terpolymer based on maleic anhydride (MA), acrylic ester and ethylene in PE/polyamide (PA) blend system [63]. The compatibilizing action of liquid polybutadiene (PB) and diallyl peroxides in the case of low density polyethylene LDPE/PS blends was reported by D. Hlavata et al. [64]. J. K. Kim et al. have studied the effect of blend compositions on the morphology of two different blend systems using poly (styrene-ran-glycidyl methacrylate) (PS-GMA) as the in situ compatibilizer [61]. An improvement in the mechanical properties of PVC/styrene butadiene rubber (SBR) blend compatibilized by acrylonitrile-butadiene rubber was observed [65]. In situ compatibilization during extrusion processing of the PP/PA6 blend by using a PP solid-phase graft copolymer has been reported by L. Duxin et al. [66]. The compatibilization effect of S-MA on thermoplastic polyurethane (TPU) and poly(styrene-co-acrylonitrile) SAN, was studied by S. N. Jaisankar and G. Radhakrishnan [67] Reactive compatibilization of the poly(butylene terephthalate) – EVA blend by maleic anhydride has been reported by Kim S. J. et al. [68]

Reactive compatibilization through maleic anhydride functionality

Reactive compatibilization is achieved when one of the polymers is reactive or containing a functional group and should be miscible with the other component. Since many of the polymers do not have functional groups, functionalization of the blend components is very often required [69-71]. Normally functionalization reactions are of great importance in reactive blending. Though various functional monomers are effective for reactive compatibilization, maleic anhydride is the extensively used one because of the relative ease with which it can be grafted onto many polymers at normal melt processing temperature without homopoly merization. The incorporation of MA has been used to improve the compatibility of waste poly(vinylchloride) PVCw/acrylonitrile butadiene-rubber (NBR) blends [72]. G. B. Patel et al. has studied the effect of acrylic acid and maleic anhydride on the properties of natural rubber (NR)/LLDPE and NBR/LLDPE blends [73]. The effect of different monomers including maleic anhydride (MA) in the melt mixed acrylonitrile butadiene rubber/poly(vinyl chloride) (NBR/PVC) in different proportions were investigated by Shokri, A. A et al. [74] The role of maleic anhydride to effect the reactive blending of immiscible polymers in situ, has been studied by many researchers [75-80]. The in situ reactive blending of three immiscible polymers, polyolefins, styrene polymers, and engineering plastics, achieved by using a multi-phase compatibilizer (PP-g-(MAH-co-St) prepared by MA and styrene (St) dual monomers melt grafting into PP has been successfully carried out by Dong Wang et al. [81]. A study based on the in situ reactive compatibilization of the blend of poly(butylene terephthalate) (PBT) and ethylene/vinyl acetate copolymer (EVA) by MA has been reported [82]. Some recent studies have also been done by many researchers based on the in situ reactive blending of polymers via maleic anhydride functionality [83-86].

1.9 Blending techniques

Different techniques employed for preparing the polymer blends are melt mixing, solution casting and in situ polymerisation.

Among these solution casting is the simplest method, in which dissolution of the blend components in a common solvent takes place. The resulting homogenous solution is then fed into the mould or Petri dish and dried. In this method choice of a common solvent is important for making a homogenous solution. The main disadvantage of this method is the cost and toxicity of organic solvents. A slow evaporation of the solvent is required to produce smooth film without bubbles. Hence this method is limited in the laboratory. However the method has some industrial application for the preparation of thin membranes, surface layers, paints, etc. [87].

Melt mixing is the widely used method of preparation of blends in both laboratory scale as well as industrial scale. Here blending of polymers is done in the molten stage using a batch mixer or an extruder. Using this technique a large quantity of sample can be processed. The main advantage of melt mixing over solution casting is that solvent is not required in the former case. Also it reduces material and energy costs and needs a less production time. Moreover, melt mixing avoids evaporation of toxic solvents. The drawbacks are less shear strength, deterioration of some properties due to high temperature mixing and the non-uniformity in properties of the final product even when the blend ratios are same.

In situ polymerisation and crosslinking of the constituent polymers leads to the formation of a chemical blend. The resultant polymer blend is an interpenetrating polymer network (IPN). These blends are characterized by improved mechanical strength, thermal stability, chemical resistance etc. when compared to conventional blends.

1.10 Elastomer- thermoplastic blends

Most of the elastomer -thermoplastic blends are immiscible and incompatible. Sometimes immiscible blends seem to be preferable over miscible blends since properties of both the components are exhibited by immiscible blends while in miscible blends only an average of the individual properties is obtained [88]. However, in most, the miscibility of individual components in the blend is necessary to get the desired properties. Studies on the properties of elastomer/thermoplastic blends have been done by many researchers and these blends are commercialized as thermoplastic elastomers (TPEs). The TPEs are increasingly replacing conventional rubbers and thermoplastics. Easy processability of thermoplastics at high temperatures and rubber-like character at low temperatures are the major advantages of this group. The drawbacks associated with TPEs are high creep, and compression set on extended use and the high temperatures for melting. Although there is limited information in the literature about high rubber content elastomer/ thermoplastic blends based purely on conventional rubber processing methods [89], there are some detailed references concerning the studies of TPEs based on simple blending or reactive blending by the addition of a suitable compatibiliser . In order to solve the problem of low thermal and chemical stability, dynamic vulcanization technique has also been used. Several reviews on thermoplastic elastomer blends have been reported earlier [90, 91]. Several blends have been prepared and studied using low and high crystalline thermoplastics like polyvinyl chloride, polystyrene, polyethylene, polypropylene etc. as the plastic phase and nitrile rubber, polybutadiene rubber, natural rubber, butyl rubber, etc. as the elastomer phase [92, 93].

1.10.1 Natural rubber-polystyrene blend

Though synthetic rubber has proved its potential in the rubber industry, NR still exists as the supreme candidate for rubber processers. NR is cis- 1,4- poly isoprene with molecular weight in the range of 1,00,000 to 10,00,000. The structure is given below in Fig. 1.4.

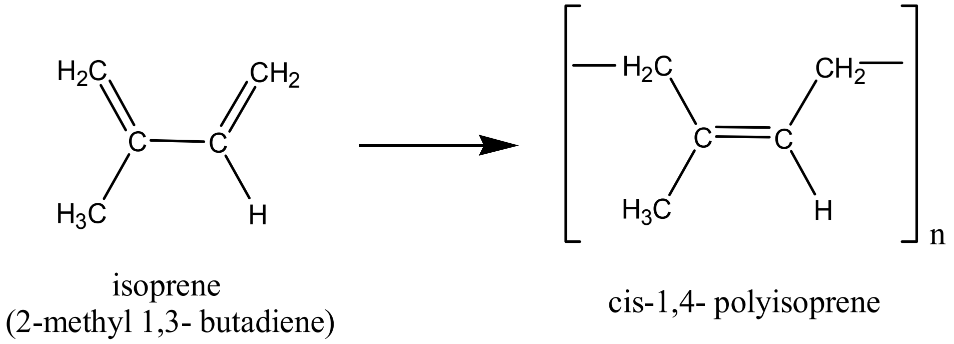


Fig.1.4. The structure of Natural rubber

This versatile renewable material is distinct from other rubbers because of the green strength associated with strain induced crystallisation due to high structural regularity. Its applications extend into industry as well as the domestic field. Good elastic properties, high resilience, superior building tack, low damping behavior, excellent dynamic properties, processability, high green strength, resistance to tear, fatigue and abrasion and good low temperature properties of NR make it a popular rubber for several major engineering applications. It can be directly used without vulcanization for making adhesive tapes, rubber solutions or art gum. It is preferred in large tyres such as truck tyres thanks to poor heat conduction and heat build-up. The excellent flexibility of natural rubber is suitable for sidewall compounds and its low heat build-up results in cooler running tyres. Due to its strain crystallization and self-reinforcing properties NR is widely used in the production of thin walled articles such as balloons, surgical gloves, sanitary rubber products etc. The main drawbacks are poor oil and solvent resistance due to non polar nature, and high sensitivity to heat, oxygen, and ozone due to its reactive double bonds [94].

Morphology and mechanical properties of NR/PS blends based on different blend ratios, processing conditions and vulcanising systems were studied by Asaletha and co-workers [95]. The effects of blend composition and compatibilizer loading on the thermal behaviour of NR/PS blends were reported in another study and an improvement in thermal stability was found [96]. Physical properties of NR glove waste/PS foam waste/cellulose fibre composites were analysed and reported by P. Phummor [97]. Asaletha et al. have studied the melt rheology and morphology of physically compatibilized NR/PS blends by the addition of NR-g-PS [98]. It was found that melt mixed blends showed lower viscosity compared to solution cast blends. Full interpenetrated polymer networks of natural rubber/polystyrene reinforced by carbon black was synthesized and the properties were studied by Seyed Hamid Heidary and co-workers [99]. A correlation between static and dynamic properties as well as better thermal stability was observed for the blend. Solution-casting technique was used by S. Chuayjuljit et al. [100] for the preparation of thermoplastic elastomer films from natural rubber and polystyrene using NR-g-PS as compatibiliser. The effects of blend ratio, crosslinker level and initiating system on the thermal degradation behaviour of NR/PS semi- and full-IPNs were studied using thermogravimetry by A. P. Mathew et al. [101] and they have reported that the thermal stability is in the order, full-IPNs> semi-IPNs >pure components due to higher entanglement density. The effects of strain level, composition, compatibilizer loading, and aging on the stress-relaxation behavior of natural rubber (NR)/polystyrene (PS) blends were investigated by R. Asaletha and co-workers [102]. Several studies have been reported on natural rubber/polystyrene blends with special reference to Izod impact behavior [103], mechanical and morphological properties of IPN [104], viscoelastic properties of nano structured IPN [105], reinforcing and compatibilizing effect of bentonite [106], effect of blend ratio on the solution cast NR latex/PS blends [107] and effect of initiating system and crosslink density on the mechanical properties and failure topography of nano-structured full IPN [108].

1.10.2 Styrene butadiene rubber-polystyrene blend

Among the synthetic rubbers, styrene-butadiene rubber (SBR) produced by both emulsion and solution polymerisation covers the largest volume and is one of the most widely used elastomers worldwide. This is a general purpose non polar synthetic rubber, a copolymer formed by the polymerization of monomers, butadiene and styrene (about 20-23% of styrene) in random sequences [109]. This provides the rubber like behavior, but at the same time lacking the crystallization on stretching. The structure is given below in Fig. 1.5.

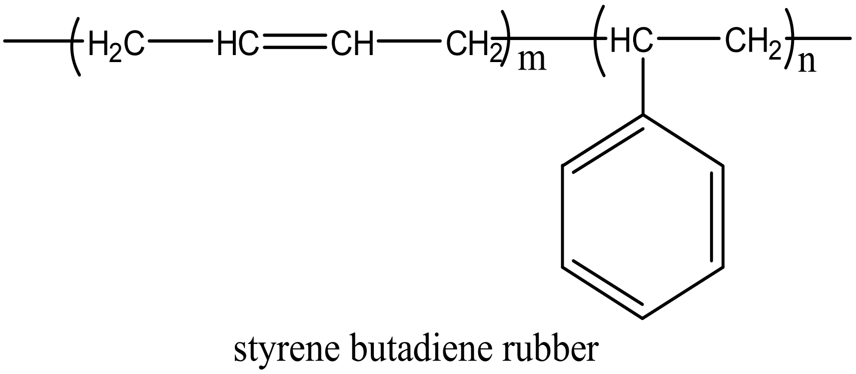


Fig.1.5. Structure of styrene butadiene rubber

It behaves similar to NR when compounded with carbon black. Unlike NR, styrene butadiene rubber needs reinforcing fillers to provide high tensile strength. It has better abrasion resistance, thermal aging properties, high filler-loading, good flex resistance and crack-initiation resistance. However, its ageing resistance is poor, due to the unsaturation in the butadiene component [110]. The major application of solid SBR is in the automotive industry. Due to superior traction and tread wear, the largest application is concentrated in tread compounds. Approximately 70 percent of SBR is used in tyres and the rest has got applications in foot wears, mechanical goods, sponge, foamed products, water proof articles, adhesives, hoses, belting, wire and cable jacketing [111].

Though several studies have been devoted to the properties of SBR/PS blends, most of them focus on impact modification in which SBR is used as an impact modifier for PS [112-116]. Some research in literature concentrate on dynamically vulcanized TPEs based on SBR/PS blends [117-119]. Two methods viz. twin screw extruder and solution method for improving the compatibility and mechanical properties of recycled PS/SBR blends have been studied by Justine Veilleux and Denis Rodrigue [120] and solution method was found to be more effective. The effect of molecular weight of PS on the compatibility and phase behaviour of SBR/PS blends was studied by Dai Y. and Feng Z [121]. They have inferred that PS with low molecular weight shows better compatibility with SBR from knowledge of glass transition temperature and transition region. Ultrasonic pulse echo technique has been used by A.A. Higazy et al. [122] to study the compatibility of blends such as PS/SBR filled with glass fiber and PS/SBR filled with talc. Munir Tasdemir and Ebru Ulug [123] investigated the mechanical, morphological and thermal properties of polystyrene toughened by SBR. The influence of morphology as well as the chemical structure of the rubber phase on the mechanical and rheological properties of PS/SBR copolymer prepared for impact modification has been studied by G. Martínez and co-workers [124]. The effect of fillers such as rice husk powder (RHP) and silica on the different properties of polystyrene/styrene butadiene rubber blends have been investigated by H. Ismail et al. [125]. Another study was done by D. Ciesielska et al. [126] to investigate the mechanical, rheological and morphological properties of recycled expanded polystyrene/ styrene-butadiene rubber (rPS/SBR) blends. Properties of brittle rPS could be changed by SBR with significant increases in elongation at break and impact strength, whereas properties such as tensile strength, hardness were decreased and an increase in viscosity was found. The mechanical and the thermomechanical properties of PS/SBR blend were investigated in comparison with those of SBS copolymer [127] and it was observed that Tg of the SBR phase changes with composition of PS/SBR blend according to changes in dynamics of SBR inclusions .

1.11 Rubber processing

Compounding and vulcanization are the two steps involved in rubber processing.

Compounding is the process of incorporation of compounding ingredients including vulcanization agents in the raw polymer. The various ingredients generally added to the rubber are plasticisers, processing aids, activators, accelerators, vulcanizing agents, fillers, antidegradents, etc. The compounding balances the properties, ensures durability and reduces the cost [128]. The compounding method depends on whether the rubber is saturated or unsaturated, natural or synthetic, polar or non- polar etc. For dry rubber, the compounding methods used are mill mixing or internal mixing and latex stage compounding is done by ball milling. Mastication is the initial step of compounding, which is important for reducing the viscosity of the elastomer for easy processing.

Vulcanization or curing is the process of converting the linear raw rubber to a crosslinked network, so that it becomes useful with improved properties. The moulding of the product is achieved during this process, except in extrusion and calendaring techniques where the vulcanization is not completed inside a mould. As more crosslinks are formed a tight network develops and a greater force is required for deformation.

Sulphur vulcanization is applicable only to unsaturated rubbers or other rubbers with unsaturated side groups and the process depends on the vulcanizing system. Curing agents other than sulphur are organic peroxides, quinones, metal oxides, bifunctional oligomers, resins, amine derivatives etc. Vulcanization can also be achieved by using high energy radiation without any vulcanization chemicals. Higher flexibility during compounding, easier adjustment of the balance between vulcanizing stages, possibility to control the length of crosslinks, better mechanical properties of the vulcanizates and favourable economics are the advantages of the sulphur system. But other systems like peroxide curing become significant when properties such as heat and reversion resistance, compression set and possibility of corrosion in cable metal cores are considered.

1.12 Blends of unsaturated polyester resin and polystyrene

1.12.1 Unsaturated polyester resin [29,129-131]

In recent years, a widespread increase in the use of thermosetting resins is noticeable in the industry. Thermosetting resins are usually of low molecular weight and are brittle due to their high crosslink density. Thermosetting resins change irreversibly under heat because of the presence of covalently cross linked stable networks. This makes them suitable for applications that require high resistance to heat. Thermosetting resins include polyester resins, epoxies, phenolics, aminoplasts, polyurethanes, silicones, furans and a few others. Of these polyester resins are one of the most important of the lot and a large number of thermoset polyester resins are commercially available. They are classified as unsaturated polyester resin, alkyd resins, vinyl esters and allyl resins.

Unsaturated polyester resins (UPR) were first commercially developed in the 1940s spurred by the wartime shortage of acrylics and has grown to be one of the most versatile, globally used, thermoset polymer systems. Though polyester does not constitute the largest group among commercial synthetic polymers, the range of applications makes it the major choice among thermosets. This is because of their good range of mechanical properties, relatively low cost, ease of processing, excellent wetting properties with reinforcement, corrosion resistance, and low molecular weight. Because of the brittle nature, UPRs are generally reinforced using glass and other fibres. The important features of polyester-glass laminates are good strength, rigidity, toughness, low density, translucence, fire retardency, superior heat resistance etc. Because of the low price polyesters are preferred to epoxies and furans. A small amount of UPRs are used as such in embedding decorative objects, in furniture lacquers, adhesives, paints and casting resins for insulating electrical equipment. About one third of the resin goes into applications such as sheeting for roofing and building insulation. The second major application area includes the building of sports car bodies, paneling for lorries and public transport vehicles. Other applications are the manufacturing of boat hulls, decorative laminates, high strength-weight ratio aircraft radomes, ducting, etc. However, unsaturated polyester resins products have poorer chemical resistance compared to expensive epoxy resins. One of the major problems with these resins is their high shrinkage during curing.

1.12.1.1 Structure

Unsaturated polyester resins are linear condensation products with low molecular weight (1200-3000 $gmol^{-1}$) prepared by reacting a mixture of unsaturated and saturated acids/anhydrides with diols or oxides followed by dissolution in co-reactant diluent (styrene/methyl methacrylate/diallyl phthalate) to get the resin formulation. The unsaturation provides the site for crosslinking with the diluents to form a three dimensional network structure as shown in Fig.1.6 [132].

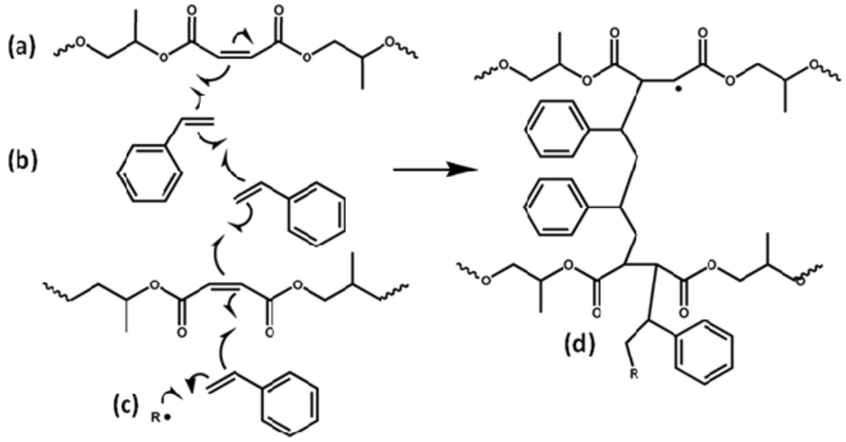


Fig. 1.6. Crosslinking of unsaturated polyester resin. (a) unsaturated polyester chain (b) co-reactant diluents (styrene) (c) free radical initiator (d) structure of cured polyester resin

1.12.1.2 Classification of UP Resins

Based on the structure polyester resins are classified as general purpose ortho phthalic resins (UPR), isophthalic resins (IUPR), bisphenol resins, chlorendics, vinyl ester resins etc. Type and proportion of raw materials, degree of condensation, acid and hydroxyl numbers, crosslinking monomers, etc. are the determining factors of the structure of polyester resins.

(a) Orthophthalic resins (UPR)

General purpose orthophthalic resins are based on phthalic anhydride (PA), maleic anhydride/fumaric acid (FA) and glycols. This is the cheapest (the presence of low priced phthalic anhydride, provides inflexibility) and widely used resin. Limited chemical resistance and processibility are the main drawbacks. They are used for indoor applications such as laminates, statues etc. Among the glycols propylene glycol is the most important and because of the pendant methyl group, more compatible with styrene.

(b) Isophthalic polyester resins (IUPR)

Isophthalic resins are prepared by the condensation of isophthalic acid, MA/FA and glycol. The cost and viscosities are higher than that of ortho resins. The high viscosity requires more quantities of diluents and because of enhanced styrene content, they possess greater water and alkali resistance. Better thermal resistance and improved mechanical properties are the other features of iso resins. They are used in the manufacture of land transport vehicle parts, boat hulls, aircraft radomes, swimming pools, water tanks, high pressure pipes of chemical plants etc.

(c) Bisphenol-A fumarates

Bisphenol resins are synthesized from bisphenol A and fumaric acid. They are characterized by a higher degree of hardness, rigidity and enhanced thermal performance. Therefore these are used for making tough FRP products for specialized applications. The acid and alkali resistance of these resins are good and have comparatively higher heat deflection temperature.

(d) Chlorendics

Chlorendics are flame retardant UP resins in which chlorine/ bromine containing anhydrides or phenols are used. Flammability can be adjusted by using other additives such as antimony trioxide and phosphours compounds or partial replacement of styrene by dichlorostyrene. The use of hydrated alumina imparts low smoke generation along with fire retardancy.

(e) Vinyl ester resins

Vinyl ester resins are prepared by the reaction of acrylic acid or methacrylic acid with epoxy resin. They have unsaturated sites only in the terminal position. Notable advantages of these resins are low styrene emission, high tensile strength and heat deflection with automotive grades, balanced performance, low cost and corrosion resistance with hybrid grade.

1.12.1.3 Curing of UP Resins

The curing of UP resins is based on free radical polymerization between the reactive diluents and unsaturated polyester in which the reactive diluent acts as the bridge between adjacent polyester molecules to form the crosslinked network. The reaction kinetics include usual steps like initiation, propagation, and/or retardation and termination. The physical changes involved in this process are gelation and vitrification [133].

In the initiation step, initiator decomposes to produce free radicals. Some of the free radicals get neutralized by the inhibitor present in the polyester/styrene solution. Commonly used initiators are peroxides, azo, amine compounds etc. based on the curing temperature. Curing is initiated by methyl ethyl ketone peroxide (MEKP) at room temperature, benzoyl peroxide (60-90 °C), di-t-butyl peroxide, t-butyl perbenzoate (130-150 °C) etc. The decomposition of initiator is achieved by certain metal compounds, tertiary amines, mercaptants etc. These are termed as accelerators and cobalt naphthenate (CoNp) and cobalt octoate (CoOc) are the most commonly used ones. Excess accelerator results in darkening of colour and bubble formation in the cured products.

In the propagation step, the polymer chain grows and crosslinks are formed. This involves reactions such as styrene-polyester copolymerization, styrene homopolymerisation and polyester homopolymerisation depending on curing conditions. Gelation occurs at the early stage of curing at which the liquid resin transforms to a soft rubbery gel and vitrification involves the transformation of resin from rubbery state to a glassy state containing a cross-linked three-dimensional network with the liberation of heat as a result of an increase in molecular weight. This exothermic effect accelerates the cross-linking. The rate of reaction is expected to decrease in the final stage of curing.

During curing the viscosity increases and a substantial volumetric shrinkage is observed. There are several approaches to study the curing behaviour of UPRs. Differential scanning calorimetry (DSC) is one of the most commonly employed procedures in the literature to study the curing reaction of unsaturated polyester resins [134-137]. Other methods are infrared spectroscopy (IR) [138-140], gel time studies [141], dynamic mechanical and thermal studies and electron spin resonace (ESR) spectroscopy.

1.12.1.4 Volume shrinkage in UPR

In spite of the many significant advantages of UPR, their applications in certain areas are limited due to a number of problems. The free radical copolymerisation of UPR and styrene ends up in a diffusion controlled process. During curing the degrees of freedom of molecules get restricted due to polymerization. This implies that the free monomers become constrained to a tight network of polymer units so that the weak Van der Waals bonds get converted in to a strong but shorter covalent bonds. This results in a significant increase in the stiffness (chemical hardening) and reduction in specific volume (chemical shrinkage) of the system. Furthermore, if the system is cured at some elevated temperature an extra shrinkage (thermal shrinkage) may also be observed on cooling to ambient conditions [142, 143]. Thus the curing leads to negative volume change due to the density difference. The overall effect leads to a high degree of polymerization shrinkage of about 7-10%. This creates problems such as low quality surface, less dimensional stability for the material, warpage of moulded parts, internal cracks and voids [144-146].

To overcome the problems associated with volume shrinkage many researchers have attempted to modify UPR. There are different techniques to address the shrinkage related problems. They are inclusion of low profile additives (LPA) in formulation, in-mold coating (IMC), tuning of secondary and finishing operations, alterations in parts and tool design and modification of the molding process, such as vacuum molding and multiple pressurization. Except the first one, other methods are expensive being equipment /labour intensive. Therefore, using a low profile additive is the most desired method for minimising volume shrinkage in UPR [147]. For the past 25 years, low-profile additives (LPA), have been widely used in SMC (sheet moulding compound) and BMC (bulk moulding compound) formulations, resulting in a low shrinkage or even a zero-shrinkage moulding compound.

The function of LPA is to efficiently compensate the uneconomic methods: thermal and chemical (polymerisation) shrinkage of UPR [148,149]. The LPA acts as a non reactive component in the system so that its effect may be considered as merely "diluting" the resin shrinkage. However, it is known to have an effect on compound viscosity and thickening. The type of LPA, its molecular weight and concentration, UP resin structure, processing conditions etc. have a significant effect on resin shrinkage, surface quality and dimensional control of moulded polymer composites as reported by many researchers [149-152]. Several thermoplastics such as polyethylene, polystyrene, polyvinyl acetate, polymethyl methacrylate (PMMA), polyurethane (PU), etc. have been used as LPAs. Among these, PVAc, PMMA and PU are widely used. The effectiveness of controlling volume shrinkage is ranked as PU>PVAc>PMMA>PS.

1.12.1.4.1 *Role of LPA in offsetting volume shrinkage*

The mechanism of volume shrinkage control by LPA has not been fully understood yet. The necessary criterion for the LPA action is that the

UPR and LPA should be phase separated at the very beginning of the curing. This phase separation during curing depends on the chemical structure, molecular weight and dipole moment of LPAs [149]. Subsequent microvoid and/or microcrack formation at the interface between the LPA and crosslinked UP phases as well as inside the LPA phase due to the microstress cracking can lead to volume shrinkage compensation. Thus phase separation, void formation, and thermal expansion due to the low profile additives are three predominant mechanisms controlling the shrinkage of polyester matrices.The more the microvoids are formed, the better is the shrinkage compensation achieved. Also, higher the loading of LPA, higher is the micro void volume fraction. But this affects the mechanical properties similar to polymeric foams with negative shrinkage. Therefore, shrinkage reduction should be balanced against loss of mechanical properties of UPR when LPA is used.

There are two types of distinguished phase separations: nucleation and growth (NG) and spinodal decomposition (SD). Nucleation and growth results in dispersed domain size increasing with time, and the shape of the domains is spheroidal in nature. SD mechanism occurs with phase separation by interconnected cylinder-like structure. This tends to grow, coalesce and form larger spheroidal structure eventually. Initially miscible polymer blends follow the SD mechanism with high interconnectivity. Co-continuity is also observed with initially immiscible blends, but without SD mechanism. Here nucleation, growth, and droplet coalescence are the determining factors for co-continuity [153]. The LPAs form a homogenous solution with UPR irrespective of whether they are compatible or incompatible. This is because LPAs can be dissolved in styrene, so that LPAs are at least partly soluble in the uncured poly- ester/styrene solution. The compatible LPAs like PVAc in UPR is stable before polymerization, whereas PMMA, PS etc. form metastable/unstable mixture and phase separation occurs before the reaction [154].

1.12.2 Blending with polystyrene

Several articles have been published on blends of unsaturated polyester resin with different thermoplastics in the context of volume shrinkage as discussed in the previous section. The effect of chemical structure, molecular weight, concentration and glass transition temperature of thermoplastics on the shrinkage of UPR has been extensively studied [149,150, 155]. However there are only a limited number of papers concerning the miscibility & mechanical properties of polymer blends where one component is crystalline or amorphous and the other is highly crosslinkable UPR [156-159]. Techniques based on viscosity, ultrasonic velocity, density, and refractive index have been used to study the miscibility of the polymer blends of UPR with PS and polycarbonate (PC) as reported by Sun-Kuk Kim et al. [158]. N. Taheri Qazvini and N. Mohammadi investigated the segmental dynamics of UPR/HIPS (high impact polystyrene) blends [160]. Polymer composite material based on UPR/HIPS with waste dust from power production as filler has been studied by Milena Koleva and co workers [161]. Studies on the flammability of UPR/EPS have been done by S. A. B. Syed Mustafa et al. [162].

1.13 Scope and objectives of the work

Expanded polystyrene (EPS) constitutes a considerable part of thermoplastic waste in the environment. It is a persistent nuisance to the environment in terms of volume. Its light weight, a valuable attribute for many applications, makes the cost of transportation of the waste material high and limits recycling only to nearby localities. The low cost of EPS offers only a small price difference between the virgin and recycled products. So EPS has become the least economical polymer to recycle and its recycling has not attained the same status as that of other polymers. Due to economic reasons the waste EPS accumulated in the environment is usually incinerated. However, this method is becoming less practical due to increasing land cost and public opposition. Therefore waste EPS, if utilized in the processing of other polymers will be more economic as it uses less energy and fewer resources. If done effectively, this can favorably tilt the economics of the process.

The strategy adopted here is the utilization of waste EPS in other polymers by blending techniques. The use of this material in rubber compounding and unsaturated polyester resin formulations are investigated in this study. Elastomers such as natural rubber and styrene butadiene rubber were used for blending with EPS, followed by conventional sulphur vulcanization. The blending of EPS was also done with an unsaturated polyester resin, a thermosetting plastic. Blends of both commercial as well as synthesized resins were prepared. Since EPS is a thermoplastic, it may act as a low shrink additive and the volume shrinkage of UPR may be reduced. The properties of the above blends were evaluated. In order to improve the compatibility, modification was also done using a grafting technique.

The study establishes the potential of these methods for utilizing waste EPS. Any reduction in the amount of waste EPS will have a salutary impact on the environment considering the voluminous nature of EPS. While addressing the environmental problems arising from waste EPS, this technique also holds promise for rubber as well as resin processing as a cost reduction/property modification method.

The main objectives of the study are,

- To develop different techniques for utilization of expanded polystyrene (EPS) in compounding both natural & synthetic rubbers.
- To utilize EPS in unsaturated polyester resin formulations.
- Tailoring of polymer blends with EPS so that the attractive properties of the virgin polymers are not sacrificed.
- Evaluating the properties of thermoset and elastomeric blends containing EPS so as to find the optimum EPS content.

Reference

[1] Mudgal S, Lyons L, Bain J, Débora D, Thibault F, Linda J. *Plastic waste in the environment: revised final report*. European Commission DG Environment. France: Bio Intelligence Service. (2011). http://bookshop.europa.eu/en/plastic-waste-in-the-environment-pbKH3113768

[2] PlasticsEurope, *Plastics – the Facts 2014/2015 An analysis of European plastics production, demand and waste data*, p. 11. Brussels, Belgium: (2015). http://www.plasticseurope.org/documents/document/20150227150049-final_plastics_the_facts_2014_2015_260215.pdf

[3] British Plastics Federation. *Oil consumption.* (2015). http://www.bpf.co.uk/Press/Oil_Consumption.aspx

[4] Andrady, A. L. & Neal, M. A. Applications and societal benefits of plastics. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* **364,** 1977–84 (2009).

[5] Panda, A. K. Studies on process optimization for production of liquid fuels from waste plastics. PhD Thesis. National Institute of Technology, Rourkela. (2011).

[6] Thompson, R. C., Moore, C. J., vom Saal, F. S. & Swan, S. H. Plastics, the environment and human health: current consensus and future trends. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* **364,** 2153–66 (2009).

[7] Cole, M., Lindeque, P., Halsband, C. & Galloway, T. S. Microplastics as contaminants in the marine environment: a review. *Mar. Pollut. Bull.* **62,** 2588–97 (2011).

[8] Holmes, L. A., Turner, A. & Thompson, R. C. Adsorption of trace metals to plastic resin pellets in the marine environment. *Environ. Pollut.* **160,** 42–8 (2012).

[9] Mudgal, S. *et al. Plastic waste in the environment –Revised Final Report*. European Commission DG ENV. (2011). http://ec.europa.eu/environment/waste/studies/pdf/plastics.pdf

[10] Scott, D.S., Czernik, S.R., Piskorz, J., Radlein, D.S.A.G. Fast Pyrolysis of Plastic Wastes. *Energ. Fuel.* **4,** 407-411(1990).

[11] Narayan, P., Lindhqvist, T. & Tojo, N. Analysing plastic waste management in India. M.Sc. (Environmental Management and Policy) Thesis. *Lund University, Sweden* (2001).

[12] Dan, H., Philip, L., Chaudhry & Manisha. *Waste management in China : issues and recommendations*. (2005). http://www-wds.worldbank.org/external/default/WDSContentServer/WDSP/IB/2006/03/23/000160016_20060323131109/Rendered/PDF/332100CHA0Waste1Management01PUBLC1.pdf

[13] Mutha, N. H., Patel, M. & Premnath, V. Plastics materials flow analysis for India. *Resour. Conserv. Recycl.* **47**, 222–244 (2006).

[14] Gupta, S., Mohan, K., Prasad, R., Gupta, S. & Kansal, A. Solid waste management in India: options and opportunities. *Resour. Conserv. Recycl.* **24**, 137–154 (1998).

[15] Buekens, A. G. & Huang, H. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resour. Conserv. Recycl.* **23**, 163–181 (1998).

[16] Thompson, R. C., Swan, S. H., Moore, C. J. & vom Saal, F. S. Our plastic age. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* **364**, 1973–6 (2009).

[17] Hopewell, J., Dvorak, R. & Kosior, E. Plastics recycling: challenges and opportunities. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* **364**, 2115–26 (2009).

[18] Miskolczi, N., Bartha, L., Deák, G. & Jóver, B. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. *Polym. Degrad. Stab.* **86**, 357–366 (2004).

[19] Broek, van den. Chemometrics in spectroscopic near infrared imaging for plastic material recognition. Doctorate thesis, Netherland: *Katholieke Universiteit Nijmegen*, (1997).

[20] Scott, G. *Polymers and the Environment*. (Royal Society of Chemistry, 1999). doi:10.1039/9781847551726

[21] Cain, R. & Oke, M. *Plastic Retail Carry Bag Use*. Report to Environment Protection and Heritage Council, Australia (2008). http://www.scew.gov.au/system/files/resources/0c513e54-d968-ac04-758b-3b7613af0d07/files/ps-pbags-hyder-consulting-bag-use-2006-07-consumption-200805.pdf

[22] *Plastic bags*. Department of the Environment, Community and Local Government, Ireland (2008). http://www.environ.ie/en/Environment/Waste/PlasticBags/

[23] Villanueva, A. & Eder, P. *End-of-Waste Criteria for Waste Plastic for Conversion: Technical Proposals*. European Commission Joint Research Centre, Institute for Prospective Technological Studies (2014).

[24] Al-Salem, S. M., Lettieri, P. & Baeyens, J. Recycling and recovery routes of plastic solid waste (PSW): a review. *Waste Manag.* **29**, 2625–2643 (2009).

[25] Patel, M., von Thienen, N., Jochem, E. & Worrell, E. Recycling of plastics in Germany. *Resour. Conserv. Recycl.* **29**, 65–90 (2000).

[26] John Scheirs. Polymer Recycling. John Wiley & Sons Ltd. (1998).

[27] Toesmaier, P. A., *Modern Plastics*, June p.15 (1990).

[28] Brydson, J. A. *Plastic materials*. (Butterworth-Heinemann, 1999).

[29] Winterling, H. & Sonntag, N. Rigid polystyrene foam (EPS, XPS). *Kunststoffe International* **10**, 18–21 (2011).

[30] Shin, C., Chase, G. G. & Reneker, D. H. Recycled expanded polystyrene nanofibers applied in filter media. *Colloids Surfaces A Physicochem. Eng. Asp.* **262**, 211–215 (2005).

[31] Utracki L. A. *Polymer Blends*. Rapra Review Reports Vol. 11 No. 3, Smithers Rapra Publishing, (2000).

[32] Utracki L. A. *Polymer Alloys and Blends - Thermodynamics and Rheology*. (Carl Hanser Verlag GmbH & Co, 1989).

[33] Paul, D. R. In *Polymer Blends*, *Vol. 1*. Eds. Paul, D. R. & Newman, S. (Academic Press, New York, 1978).

[34] Robeson, L. M. Applications of polymer blends: Emphasis on recent advances. *Polym. Eng. Sci.* **24**, 587–597 (1984).

[35] Barlow, J. W. & Paul, D. R. Polymer blends and alloys: a review of selected considerations. *Polym. Eng. Sci.* **21**, 985–996 (1981).

[36] Di Lorenzo, M. L. & Frigione, M. Compatibilization criteria and procedures for binary blends: A review. *J. Polym. Eng.* **17**, 429– 459. (1997).

[37] Vyas, N. Polyolefin elastomer blends as an alternative to poly(vinyl chloride) flooring. Masters Thesis, *Concordia University, Canada* (2002). http://spectrum.library.concordia.ca/1907/1/MQ72901.pdf

[38] Pazzagli, F. & Pracella, M. Reactive compatibilization of polyolefin/PET blends by melt grafting with glycidyl methacrylate. *Macromol. Symp.* **149,** 225–230 (2000).

[39] Koning, C. Strategies for compatibilization of polymer blends. *Prog. Polym. Sci.* **23,** 707–757 (1998).

[40] Legge, N. R., Holden, G. & Schroeder, H. F. *Thermoplastic elastomers: A comprehensive review*. (Carl Hanser Verlag, Munich, 1987).

[41] Ajji, A. & Utracki, L. A. Interphase and compatibilization of polymer blends. *Polym. Eng. Sci.* **36,** 1574–1585 (1996).

[42] Fayt, R., Jérôme, R. & Teyssié, P. Interface Modification in Polymer Blends. In *Multiphase Polymers: Blends and Ionomers* (Utracki, L. A. & Weiss, R. A.) *ACS Symp. Ser.* **395,** 38–66 (American Chemical Society, Washington DC, 1989).

[43] Barlow, J. W. & Paul, D. R. Mechanical compatibilization of immiscible blends. *Polym. Eng. Sci.* **24,** 525–534 (1984).

[44] Bywater, S. Block polymers. Characterization and use in polymer blends. *Polym. Eng. Sci.* **24,** 104–111 (1984).

[45] Utracki, L. A. Compatibilization of Polymer Blends. *Can. J. Chem. Eng.* **80,** 1008–1016 (2002).

[46] Cangelosi, F. & Shaw, M. T. A review of hydrogen bonding in solid polymers: structural relationships, analysis, and importance. *Polym. Plast. Technol. Eng.* **21,** 13–98 (2006).

[47] Walsh, D. J. & Rostami, S. The miscibility of high polymers: The role of specific interactions. In *Key Polymers Properties and Performance. Adv. Polym. Sci.* **70,** 119–169 (Springer Berlin Heidelberg, 1985).

[48] Bouslah, N. & Amrani, F. Miscibility and specific interactions in blends of poly [(styrene) -co- (cinnamic acid)] with poly (methyl methacrylate) and modified poly (methyl methacrylate). *eXPRESS Polym. Lett.* **1,** 44–50 (2007).

[49] Kuo, S.-W., Shih, C.-C., Shieh, J.-S. & Chang, F.-C. Specific interactions in miscible polymer blends of poly(2-hydroxypropyl methacrylate) with polyvinylpyrrolidone. *Polym. Int.* **53,** 218–224 (2004).

[50] Yu, D. W., Xanthos, M. & Gogos, C. G. LDPE/PP blends modified by peroxide and radiation induced reactions. *J. Appl. Polym. Sci.* **52,** 99–105 (1994).

[51] Sun, Y.-J., Flars, V. & Baker, W. E. Evaluation and characterization of vector fluids and peroxides in a process of in situ compatibilization of polyethylene and polystyrene. *Can. J. Chem. Eng.* **75,** 1153–1158 (1997).

[52] Zhang, X. & Baker, W. E. Grafting styrene onto a polyethylene surface: A model study of an interfacial reaction. *J. Appl. Polym. Sci.* **67,** 427–440 (1998).

[53] Al-Malaika, S. & Artus, K. Chemical modification of polymer blends by reactive processing:In situ reactions of interlinking agents in PS/EPDM blends. *J. Appl. Polym. Sci.* **69,** 1933–1951 (1998).

[54] Gallucci, M., Robert, R., Avakian, R.W., Eur. Patent 182 163 (1984)

[55] Zhang, H. X. & Hourston, D. J. Reactive compatibilization of poly(butylene terephthalate)/low-density polyethylene and poly(butylene terephthalate)/ethylene propylene diene rubber blends with a bismaleimide. *J. Appl. Polym. Sci.* **71,** 2049–2057 (1999).

[56] Qiao, F., Migler, K. B., Hunston, D. L. & Han, C. C. Reactive compatibilization and in-line morphological analysis of blends of PET and a thermotropic liquid crystalline polymer. *Polym. Eng. Sci.* **41,** 77–85 (2001).

[57] Filippi, S., Yordanov, H., Minkova, L., Polacco, G. & Talarico, M. Reactive Compatibilizer Precursors for LDPE/PA6 Blends, 4. *Macromol. Mater. Eng.* **289,** 512–523 (2004).

[58] Kim, J. K., Kim, S. & Park, C. E. Compatibilization mechanism of polymer blends with an in-situ compatibilizer. *Polymer.* **38,** 2155–2164 (1997).

[59] Wang, R., Wang, W., Shi, Z. & Xia, Y. Reactive Compatibilization of Nylon 6/ABS Blends. *Polym. Prepr.* **45,** 754–755 ((Division of Polymer Chemistry, American Chemical Society), 2004).

[60] Hu, G.-H., Cartier, H., Feng, L.-F. & Li, B.-G. Kinetics of thein situ polymerization andin situ compatibilization of poly(propylene) and polyamide 6 blends. *J. Appl. Polym. Sci.* **91,** 1498–1504 (2004).

[61] Kroeze, E., ten Brinke, G. & Hadziioannou, G. Compatibilization of blends of low density polyethylene and poly(vinyl chloride) by segmented EB(SAN-block-EB)n block copolymers. *Polymer.* **38,** 379–389 (1997).

[62] Zacur, R., Goizueta, G. & Capiati, N. Compatibilized PP/PHAE Blends by Reactive Blending. in *Annual Technical Conference - ANTEC 2001, Society of Plastic Engineers Annual Technical Papers,* 3573–3577 (Dallas, Texas, 2001).

[63] Moan, M., Huitric, J., Médéric, P. & Jarrin, J. Rheological properties and reactive compatibilization of immiscible polymer blends. *J. Rheol. (N. Y. N. Y).* **44,** 1227 (2000).

[64] Hlavatá, D., Kruliš, Z., Horák, Z., Lednický, F. & Hromádková, J. The role of lubricants in reactive compatibilization of polyolefin blends. *Macromol. Symp.* **176,** 93–106 (2001).

[65] Zhu, S.-H., Chan, C.-M., Wong, S. C. & Mai, Y.-W. Mechanical properties of PVC/SBR blends compatibilized by acrylonitrile-butadiene rubber and covulcanization. *Polym. Eng. Sci.* **39,** 1998–2006 (1999).

[66] Li, D., Jia, D. & Zhou, P. Compatibilization of polypropylene/nylon 6 blends with a polypropylene solid-phase graft. *J. Appl. Polym. Sci.* **93,** 420–427 (2004).

[67] Jaisankar, S. N. & Radhakrishnan, G. Effect of compatibilizer on morphology and mechanical properties of TPU/SAN blends. *Polym. Eng. Sci.* **40,** 621–626 (2000).

[68] Kim, S.-J., Kang, C.-J., Chowdhury, S. R., Cho, W.-J. & Ha, C.-S. Reactive compatibilization of the poly(butylene terephthalate)-EVA blend by maleic anhydride. II. Correlations among gel contents, grafting yields, and mechanical properties. *J. Appl. Polym. Sci.* **89,** 1305–1310 (2003).

[69] Liu, N. C. & Baker, W. E. Reactive polymers for blend compatibilization. *Adv. Polym. Technol.* **11,** 249–262 (1992).

[70] Xanthos, M. Interfacial agents for multiphase polymer systems: Recent advances. *Polym. Eng. Sci.* **28,** 1392–1400 (1988).

[71] Dedecker, K. & Groeninckx, G. Interfacial Graft Copolymer Formation during Reactive Melt Blending of Polyamide 6 and Styrene−Maleic Anhydride Copolymers. *Macromolecules* **32,** 2472–2479 (1999).

[72] Ismail, H. & Yusof, A. M. M. Blend of waste poly(vinylchloride) (PVCw)/ acrylonitrile butadiene-rubber (NBR): the effect of maleic anhydride (MAH). *Polym. Test.* **23,** 675–683 (2004).

[73] Patel, G. V., Patel, H. B., Sharma, P., Patel, H. A. & John, N. A Study on Grafting of Natural Rubber and Nitrile Rubber on Thermoplastic Low Density Polyethylene Using Maleic Anhydride and Acrylic Acid. *Int. J. Polym. Mater.* **55,** 413–424 (2006).

[74] Shokri, A. A., Bakhshandeh, G. & Farahani, T. D. An investigation of mechanical and rheological properties of NBR/PVC blends: Influence of anhydride additives, mixing procedure and NBR form. Iran Polym J. *Iran. Polym. J.* **15,** 227 (2006).

[75] Aravind, I., Albert, P., Ranganathaiah, C., Kurian, J. V. & Thomas, S. Compatibilizing effect of EPM-g-MA in EPDM/poly(trimethylene terephthalate) incompatible blends. *Polymer.* **45,** 4925–4937 (2004).

[76] Jo, W. H., Park, C. D. & Lee, M. S. Preparation of functionalized polystyrene by reactive extrusion and its blend with polyamide 6. *Polymer.* **37,** 1709–1714 (1996).

[77] Sekharan, R. V., Abraham, B. T. & Thachil, E. T. Utilization of waste expanded polystyrene: Blends with silica-filled natural rubber. *Mater. Des.* **40,** 221–228 (2012).

[78] Park, C. D., Jo, W. H. & Lee, M. S. Effect of molecular weight of functionalized polystyrene on the compatibility of blends of polyamide 6 and polystyrene. *Polymer.* **37,** 3055–3063 (1996).

[79] Nakason, C., Saiwaree, S., Tatun, S. & Kaesaman, A. Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate). *Polym. Test.* **25,** 656–667 (2006).

[80] Thomas, S. & Groeninckx, G. Reactive compatibilisation of heterogeneous ethylene propylene rubber (EPM)/nylon 6 blends by the addition of compatibiliser precursor EPM-g-MA. *Polymer.* **40,** 5799–5819 (1999).

[81] Wang, D., Li, Y., Xie, X.-M. & Guo, B.-H. Compatibilization and morphology development of immiscible ternary polymer blends. *Polymer.* **52,** 191–200 (2011).

[82] Kim, S.-J., Shin, B.-S., Hong, J.-L., Cho, W.-J. & Ha, C.-S. Reactive compatibilization of the PBT/EVA blend by maleic anhydride. *Polymer.* **42,** 4073–4080 (2001).

[83] Tayebi, H., Bigdeli, A., Torabinezhad, A. & Tayebi, S. Polypropylene /Polystyrene in situ nano reinforced blends fiber: Morphology and properties. *Int. J. Nano Dimens.* **6,** 305–314 (2015).

[84] Teli, M. D. & Desai, P. V. Effect of compatibilizer on the dyeability of polypropylene/ polytrimethylene terephthalate polyblend fibres. *Int. Res. J. Eng. Technol.* **2,** 396–402 (2015).

[85] Zhu, Y., Liang, C., Bo, Y. & Xu, S. Compatibilization of polypropylene/ recycled polyethylene terephthalate blends with maleic anhydride grafted polypropylene in the presence of diallyl phthalate. *J. Polym. Res.* **22,** 35 (2015).

[86] Supri, A. G., Fatimah, A. R. H. & Zainuddin, F. Recycled high density polyethylene/ethylene vinyl acetate/taro powder composites: The effect of polyethylene-grafted-maleic anhydride on tensile properties and thermal stability. *J. Teknol.* **74,** 131–136 (2015).

[87] *Physical Chemistry of Macromolecules: Macro to Nanoscales*. Eds. Chan, C. H., Chia, C. H. & Thomas, S. (Apple Academic Press, Inc., 2014).

[88] Olabisi, O., Robeson, L. M. & Shaw, M. T. *Polymer-Polymer Miscibility*. (Academic Press, New York, 1979).

[89] Muter, M. A. & Mugar, Q. K. The Study of the Development of Natural Rubber Blends using Different Types of Polymers and Fillers on the Mechanical and Chemical Properties of the Vulcanizates. *J. Nat. Sci. Res.* **4,** 60–73 (2014).

[90] Corish, P. J. & Powell, B. D. W. Elastomer Blends. *Rubber Chem. Technol.* **47,** 481–510 (1974).

[91] Ibrahim, A. & Dahlan, M. Thermoplastic natural rubber blends. *Prog. Polym. Sci.* **23,** 665–706 (1998).

[92] George, J. Dynamically vulcanised thermoplastic elastomer blends of polyethylene and nitrile rubber. *Polymer.* **41,** 1507–1517 (2000).

[93] Chatterjee, K. & Naskar, K. Development of thermoplastic elastomers based on maleated ethylene propylene rubber (m-EPM) and polypropylene (PP) by dynamic vulcanization. *Express Polym. Lett.* **1,** 527–534 (2007).

[94] Ngudsuntear, C., Limtrakul, S., Vatanatham, T. & Wichien, A. N. Effect of Blend Ratio on Cure Characteristics , Mechanical Properties , and Aging Resistance of Silica- filled ENR / SBR Blends. **5,** 11–24 (2014).

[95] Asaletha, R., Kumaran, M. G. & Thomas, S. Thermoplastic elastomers from blends of polystyrene and natural rubber: morphology and mechanical properties. *Eur. Polym. J.* **35,** 253–271 (1999).

[96] Asaletha, R., Kumaran, M. G. & Thomas, S. Thermal behaviour of natural rubber/polystyrene blends: thermogravimetric and differential scanning calorimetric analysis. *Polym. Degrad. Stab.* **61,** 431–439 (1998).

[97] Phummor, P., Riyajan, S. A. & Tangboriboonrat, P. Physical Properties of Polymer Blend: Natural Rubber Glove Waste/Polystyrene Foam Waste/ Cellulose Fiber via Brabender. *Adv. Mater. Res.* **844,** 57–60 (2013).

[98] Asaletha, R., Groeninckx, G., Kumaran, M. G. & Thomas, S. Melt rheology and morphology of physically compatibilized natural rubber-polystyrene blends by the addition of natural rubber-g-polystyrene. *J. Appl. Polym. Sci.* **69,** 2673–2690 (1998).

[99] Heidary, S. H., Amraei, I. A. & Payami, A. Carbon-black-reinforced natural rubber/polystyrene full interpenetrated polymer networks: Synthesis and properties. *J. Appl. Polym. Sci.* **113,** 2143–2149 (2009).

[100] Chuayjuljit, S., Moolsin, S. & Potiyaraj, P. Use of natural rubber-g-polystyrene as a compatibilizer in casting natural rubber/polystyrene blend films. *J. Appl. Polym. Sci.* **95,** 826–831 (2005).

[101] Mathew, A. P., Packirisamy, S. & Thomas, S. Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: thermogravimetric analysis. *Polym. Degrad. Stab.* **72,** 423–439 (2001).

[102] Asaletha, R. *et al.* Stress-relaxation behavior of natural rubber/polystyrene and natural rubber/polystyrene/natural rubber-graft-polystyrene blends. *J. Appl. Polym. Sci.* **108,** 904–913 (2008).

[103] Mathew, A. P. & Thomas, S. Izod impact behavior of natural rubber/ polystyrene interpenetrating polymer networks. *Mater. Lett.* **50,** 154–163 (2001).

[104] Das, B., Sinha, S. & Gangopadhyay, T. Natural rubber-polystyrene interpenetrating networks. Morphology and mechanical properties. *Eur. Polym. J.* **29,** 57–61 (1993).

[105] Mathew, A. P., Groeninckx, G., Michler, G. H., Radusch, H. J. & Thomas, S. Viscoelastic properties of nanostructured natural rubber/ polystyrene interpenetrating polymer networks. *J. Polym. Sci. Part B Polym. Phys.* **41,** 1680–1696 (2003).

[106] Ruamcharoen, J., Ratana, T. & Ruamcharoen, P. Bentonite as a reinforcing and compatibilizing filler for natural rubber and polystyrene blends in latex stage. *Polym. Eng. Sci.* **54,** 1436–1443 (2014).

[107] Boondamnoen, O., Azura, A. R., Ohshima, M., Chuayjuljit, S. & Ariffin, A. Effect of blend ratio and compatibilizer on solution casted treated waste natural rubber latex/polystyrene blends. *Songklanakarin J. Sci. Technol.* **35,** 547–555 (2013).

[108] Mathew, A.., Packirisamy, S., Radusch, H. . & Thomas, S. Effect of initiating system, blend ratio and crosslink density on the mechanical properties and failure topography of nano-structured full-interpenetrating polymer networks from natural rubber and polystyrene. *Eur. Polym. J.* **37,** 1921–1934 (2001).

[109] Goyanes, S., Lopez, C. C., Rubiolo, G. H., Quasso, F. & Marzocca, A. J. Thermal properties in cured natural rubber/styrene butadiene rubber blends. *Eur. Polym. J.* **44,** 1525–1534 (2008).

[110] Radhakrishnan, C. K., Kumari, P., Sujith, A. & Unnikrishnan, G. Dynamic mechanical properties of styrene butadiene rubber and poly (ethylene-co-vinyl acetate) blends. *J. Polym. Res.* **15,** 161–171 (2007).

[111] Arayapranee, W. *Rubber Abrasion Resistance. In Abrasion Resistance of Materials* . Ed. Adamiak M. (InTech, 2012). doi:10.5772/1083

[112] Martínez-Barrera, G., López, H., Castaño, V. M. & Rodríguez, R. Studies on the rubber phase stability in gamma irradiated polystyrene-SBR blends by using FT-IR and Raman spectroscopy. *Radiat. Phys. Chem.* **69,** 155–162 (2004).

[113] Martínez-Barrera, G., Menchaca, C., Pietkiewicz, D. & Brostow, W. Polystyrene + Styrene-Butadiene Blends: Mechanical and Morphological Properties. *Mater. Sci.* **10,** 166–172 (2004).

[114] 114. 1. Li, D. *et al.* Radiation preparation of nano-powdered styrene-butadiene rubber (SBR) and its toughening effect for polystyrene and high-impact polystyrene. *Radiat. Phys. Chem.* **76,** 1732–1735 (2007).

[115] Broltow, W., Castańo, V. M., Horta, J. & Martinez-Barrera, G. Gamma irradiation effects on impact strength and thermal properties of SBR-toughened polystyrene. *Polimery* **49,** 9–14 (2004).

[116] Siengchin, S. & Karger-Kocsis, J. Binary and ternary composites of polystyrene, styrene–butadiene rubber and boehmite produced by water-mediated melt compounding: Morphology and mechanical properties. *Compos. Part B Eng.* **45,** 1458–1463 (2013).

[117] Wang, Z., Zhao, H., Zhao, J. & Wang, X. Rheological, mechanical and morphological properties of thermoplastic vulcanizates based on high impact polystyrene and styrene-butadiene rubber. *J. Appl. Polym. Sci.* **117,** 2523–2529 (2010).

[118] Hanif, I., Zarina, M. & Azhar, A. B. The effect of dynamic vulcanization on properties of rice husk powder filled polystyrene/styrene butadiene rubber blends. *Iran. Polym. J.* **13,** 11–19 (2004).

[119] Mousa, A. The Effect of Exfoliated Graphite on the Thermal Properties of Dynamically Vulcanized PS/SBR Composites. in *Proceedings of the International Conference on Mining, Material and Metallurgical Engineering* 11(1–7) (Prague, 2014).

[120] Veilleux, J. & Rodrigue, D. Optimization of a Polymer Blend Based on Recycled Polystyrene And Styrene-Butadiene Rubber. in *Third US-Mexico Meeting "Advances in Polymer Science" and XXVII SPM National Congress* (2014).

[121] Dai, Y. & Feng, Z. Compatibility and phase behaviour of PS/SBR blend. I. Effect of molecular weight of PS. *Chinese J. Polym. Sci.* **8,** 321–329 (1990).

[122] Higazy, A. A., Afifi, H., Khafagy, A. H., El-Shahawy, M. A. & Mansour, A. M. Ultrasonic studies on polystyrene/styrene butadiene rubber polymer blends filled with glass fiber and talc. *Ultrasonics* **44 Suppl 1,** e1439–45 (2006).

[123] Taşdemir, M. & Uluğ, E. Mechanical, Morphological and Thermal Properties of SEBS, SIS and SBR-type Thermoplastic Elastomers Toughened High Impact Polystyrene. *Polym. Plast. Technol. Eng.* **51,** 164–169 (2012).

[124] Martínez, G., Vázquez, F., Alvarez-castillo, A., López-Castañares, R. & Castaño, V. M. Mechanical and Processing Properties of Polystyrene-(Styrene Butadiene) Blends. *Int. J. Polym. Mater.* **46,** 27–40 (2000).

[125] Ismail, H., Mohamad, Z. & Bakar, A. A. A Comparative Study on Processing, Mechanical Properties, Thermo-oxidative Aging, Water Absorption, and Morphology of Rice Husk Powder and Silica Fillers in Polystyrene/Styrene Butadiene Rubber Blends. *Polym. Plast. Technol. Eng.* **42,** 81–103 (2003).

[126] Ciesielska, D. & Liu, P. Mechanical, rheological and morphological properties of recycled expanded polystyrene/styrene butadiene rubber blends. *Kautschuk und Gummi, Kunststoffe* **53,** 273–276

[127] Yousefi, A. A. Segmental mobility in the vicinity of T g in PS/SBR blends: Nanodomain size prediction of the dispersed phase. *J. Appl. Polym. Sci.* **127,** 659–665 (2013).

[128] Prasad, V. S. & Pillai, C. K. S. Flame retardation of polyethylene: Effect of a phosphorus flame retardant having both hydrophobic and hydrophilic groups in the same molecule. *J. Appl. Polym. Sci.* **77,** 2631–2640 (2000).

[129] Johnson, K. G. & Yang, L. S. Preparation, Properties and Applications of Unsaturated Polyesters. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters* (Scheirs, J. & Long, T. E.) (John Wiley & Sons, Ltd, 2003). doi:10.1002/0470090685

[130] Fink, J. K. *Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers*. (William Andrew Publishing, 2005).

[131] Malik, M., Choudhary, V. & Varma, I. K. Current Status of Unsaturated Polyester Resins. *J. Macromol. Sci. Part C Polym. Rev.* **40,** 139–165 (2000).

[132] Kandola, B., Ebdon, J. & Chowdhury, K. Flame Retardance and Physical Properties of Novel Cured Blends of Unsaturated Polyester and Furan Resins. *Polymers.* **7,** 298–315 (2015).

[133] Enns, J. B. & Gillham, J. K. Time–temperature–transformation (TTT) cure diagram: Modeling the cure behavior of thermosets. *J. Appl. Polym. Sci.* **28,** 2567–2591 (1983).

[134] Kim, W. G., Lee, J. Y. & Park, K. Y. Curing reaction of o-cresol novolac epoxy resin according to hardener change. *J. Polym. Sci. Part A Polym. Chem.* **31,** 633–639 (1993).

[135] Martín, J. L., Cadenato, A. & Salla, J. M. Comparative studies on the non-isothermal DSC curing kinetics of an unsaturated polyester resin using free radicals and empirical models. *Thermochim. Acta* **306,** 115–126 (1997).

[136] Lu, M. G., Shim, M. J. & Kim, S. W. Curing behavior of an unsaturated polyester system analyzed by Avrami equation. *Thermochim. Acta* **323,** 37–42 (1998).

[137] Yousefi, A., Lafleur, P. G. & Gauvin, R. Kinetic studies of thermoset cure reactions: A review. Polym. Compos. 18, 157–168 (1997).

[138] Grunden, B. L. & Sung, C. S. P. Cure Characterization of Unsaturated Polyester Resin by Near-IR and Mid-IR Spectroscopy. *Macromolecules* 36, 3166–3173 (2003).

[139] Imai, T. Infrared study of the cure of unsaturated polyester. *J. Appl. Polym. Sci.* 11, 1055–1063 (1967).

[140] de la Caba, K., Guerrero, P., Mondragon, I. & Kenny, J. M. Comparative study by DSC and FTIR techniques of an unsaturated polyester resin cured at different temperatures. *Polym. Int.* **45,** 333–338 (1998).

[141] Cook, W. D., Lau, M., Mehrabi, M., Dean, K. & Zipper, M. Control of gel time and exotherm behaviour during cure of unsaturated polyester resins. *Polym. Int.* **50,** 129–134 (2001).

[142] Pang, K. P. & Gillham, J. K. Anomalous behavior of cured epoxy resins: Density at room temperature versus time and temperature of cure. *J. Appl. Polym. Sci.* 37, 1969–1991 (1989).

[143] Shah, D. U. & Schubel, P. J. Evaluation of cure shrinkage measurement techniques for thermosetting resins. *Polym. Test.* 29, 629–639 (2010).

[144] Xu, L. & Lee, L. J. Effect of nanoclay on shrinkage control of low profile unsaturated polyester (UP) resin cured at room temperature. *Polymer.* **45,** 7325–7334 (2004).

[145] Schoch, K. F., Panackal, P. A. & Frank, P. P. Real-time measurement of resin shrinkage during cure. *Thermochim. Acta* **417,** 115–118 (2004).

[146] Haider, M., Hubert, P. & Lessard, L. Cure shrinkage characterization and modeling of a polyester resin containing low profile additives. *Compos. Part A Appl. Sci. Manuf.* **38,** 994–1009 (2007).

[147] Kinkelaar, M., Muzumdar, S. & Lee, L. J. Dilatometric study of low profile unsaturated polyester resins. *Polym. Eng. Sci.* **35,** 823–836 (1995).

[148] Kinkelaar, M., Wang, B. & Lee, L. J. Shrinkage behaviour of low-profile unsaturated polyester resins. *Polymer.* **35,** 3011–3022 (1994).

[149] Huang, Y.-J. & Liang, C.-M. Volume shrinkage characteristics in the cure of low-shrink unsaturated polyester resins. *Polymer.* **37,** 401–412 (1996).

[150] Li, W. & Lee, L. J. Shrinkage control of low-profile unsaturated polyester resins cured at low temperature. *Polymer.* **39,** 5677–5687 (1998).

[151] Beheshty, M. H., Vafayan, M. & Poorabdollah, M. Shrinkage Control and Kinetics Behaviour of Clay-Unsaturated Polyester Nanocomposites. *Iran. Polym. J.* **15,** 841–849 (2006).

[152] Li, W. & Lee, L. J. Low temperature cure of unsaturated polyester resins with thermoplastic additives. II. Structure formation and shrinkage control mechanism. *Polymer.* **41,** 697–710 (2000).

[153] McMaster L. P. Aspects of Liquid-Liquid Phase Transition Phenomena in Multicomponent Polymeric Systems. In *Copolymers, Polyblends, and Composites* (Platzer, N. A. J.) **142,** 43–65 (American Chemical Society, 1975).

[154] Beheshty, M. H., Hayat, M. & Vafayan, M. Evaluation of Low-profile Additives in the Curing of Unsaturated Polyester Resins at Low Temperatures. *Iran. Polym. J.* **15,** 143–153 (2006).

[155] Ma, C. M., Hsieh, C., Kuan, H., Tsai, T. & Yu, S. Effects of molecular weight and molecular structure of low profile additives on the properties of bulk molding compound (BMC). *Polym. Eng. Sci.* **43,** 989–998 (2003).

[156] Huang, Y.-J. & Horng, J. C. Effects of thermoplastic additives on mechanical properties and glass transition temperatures for styrene-crosslinked low-shrink polyester matrices. *Polymer.* **39,** 3683–3695 (1998).

[157] Kim, S.-K., Kim, J. T., Kim, H.-C., Rhee, K.-Y. & Kathi, J. Miscibility of Solution Blends of Unsaturated Polyester Resin with Polystyrene and Polycarbonate. *J. Macromol. Sci. Part B* **49**, 750–756 (2010).

[158] Huang, Y.-J. & Chen, L.-D. Effects of chemical composition and structure of unsaturated polyester resins on the miscibility, cured sample morphology and mechanical properties of styrene/unsaturated polyester/low-profile additive ternary systems: 2. Mechanical properties. *Polymer.* **39,** 7049–7059 (1998).

[159] Teng, K.-C. & Chang, F.-C. Single-phase and multiple-phase thermoplastic/thermoset polyblends: 2. Morphologies and mechanical properties of phenoxy/epoxy blends. *Polymer.* **37,** 2385–2394 (1996).

[160] Qazvini, N. T. & Mohammadi, N. Segmental dynamics of reactively prepared polystyrene blends: Unsaturated polyester resin versus high impact polystyrene. *J. Appl. Polym. Sci.* **106,** 498–504 (2007).

[161] Koleva, M., Vassilev, V. & Vassilev, G. Polymer composites containing waste dust from power production. II. Strength characteristics of composites based on UPR/HIPS polymer system. *Maced. J. Chem. Chem. Eng.* **27,** 47–52 (2008).

[162] Mustafa, S. A. B. S., Mohamed, R., Bahira, W. & Rasidan, K. Flame Retardancy of Polymeric Building Material with Recycled Expanded Polystyrene Filler. In *Proceedings of the International Conference on Global Sustainability and Chemical Engineering* (Hashim, M. A.) 403–409 (Springer Singapore, 2014).

……

Chapter 2

EXPERIMENTAL TECHNIQUES

Contents

This chapter deals with the description of the materials used, the methods of sample preparation and the characterisation techniques adopted in the present investigations.

2.1 Materials

2.1.1 Polymers

Expanded Polystyrene

Expanded polystyrene used in this study with a density value of 15 Kg/m^{3}was purchased from S-tech Thermocool Industry, Cherthala, Kerala. Waste EPS was not selected for the study because of the need to get a clean material for the initial studies.

Natural rubber (ISNR-5)

Natural rubber was supplied by the Rubber Research Institute of India, Kottayam, India. The Indian standard specifications for this grade of rubber are given below.

Mooney Viscosity [ML (1+4) at 100°C]	82.00
Dirt content, % by mass, max	0.05
Volatile matter, % by mass, max	1.00
Nitrogen, % by mass, max	0.70
Ash, % by mass, max	0.60
Initial plasticity, min	30.00
Plasticity Retention Index (PRl) min	60.00

Styrene butadiene rubber (SBR synaprene1502)

Styrene butadiene rubber was obtained from Synthetics and Chemicals Ltd., Bareilly.

Mooney viscosity [ML (1+4) at 100 °C]	52.00
Bound styrene content, % by mass	23.30
Volatile matter, % by mass	0.23
Soap content, % by mass	0.01
Ash content, % by mass	0.16
Organic acid content, %	5.46

GP grade UP resin (HSR 8113M)

GP grade UP resin was supplied by M/s Sharon Engineering Enterprises, Kochi. Specifications of commercial UP resin are given below.

Acid number	10-30 mg KOH/g
Styrene content	25-45%
Viscosity at 25 °C	0.2-4.5 Pa.s
Specific gravity at 25°C	1.07-1.3
Refractive index at 25°C	1.524-1.559

2.1.2 Chemicals

Zinc Oxide (activator)

Zinc oxide was supplied by Mls Meta Zinc Ltd, Mumbai and had the following specifications.

Specific gravity	5.50
ZnO content (%)	98.00
Acidity(%)	0.40
Heat loss (%), max (2h at 100°C)	0.50

Stearic acid (co-activator)

Stearic acid was obtained from Goderej Soaps Pvt Ltd, Mumbai and had the following specifications.

Specific gravity	0.85
Melting point	50-69 °C
Acid number	185-210
Iodine number	9.5
Ash content (%)	0.1

N-cyclo hexyl 2-benzothiazole sulphenamide (CBS) (accelerator)

CBS was obtained from Merchem Ltd., Cochin, India. It had the following specifications.

Melting point (°C)	103.00
Flash point (°C)	177.00
Density (at 25°C, Kg/m^3)	1200.00

Tetramethylthiuram disulphide (TMTD) (accelerator)

TMTD was supplied by Merchem Ltd., Cochin, India. The specification of TMTD is given below.

Melting point (°C)	142.00
Flash point (°C)	150.00
Density (20°C, Kg/m^3)	1425.00

Precipitated silica

Precipitated silica used was of commercial grade supplied by Sameera Chemicals, Kottayam. The specifications are given below.

pH (5% aqueous solution)	6.30
Specific gravity	2.03
SiO_2 in dried sample (%)	90.00
Loss on heating at 105°C (%)	5.50

High Abrasion Furnace black (N330)

High abrasion furnace black used in the present study was supplied by M/s Philips Carbon Black India Ltd., Cochin, India. It had the following specifications.

Appearance	black granules
DBP absorption	102cc/100 g
Pour density	376 kg/m^3
Iodine number	82 mg/g

Cardanol

Cardanol was separated from commercial grade CNSL by distillation under reduced pressure (I mmHg). The pale yellow fraction collected at 206-208°C was cardanol. Refined CNSL conforming to Indian Standard I S: 840 (1964) was supplied by Vijayalaksmi Cashew Exports, Kollam, India.

Aromatic oil

Aromatic oil obtained from Hindustan Organic Chemicals Ltd. Kochi, had the following specifications.

Specific gravity	0.98
Aniline point	43.00
Ash content % by mass	0.01
Viscosity gravity constant	0.96

Naphthenic oil

Naphthenic oil was supplied by M/S Hindustan Petroleum Ltd., India and the specifications are as follows.

Colour	Light coloured oil
Viscosity gravity constant (VGC)	0.85 - 0.9

Sulphur (cross linking agent)

Sulphur was obtained from Standard Chemicals Co. Pvt. Ltd., Chennai and had the following specifications.

Specific gravity	2.05
Acidity (%), max	0.01
Ash content (%), max	0.015

Styrenated phenol (SP)

Styrenated phenol used in this study was obtained from Olympic Chemicals, Maharashtra, India

Diethylene glycol (DEG)

Diethylene glycol was supplied by S.D fine chemicals Ltd, Mumbai.

Accinox TQ

Commercial antioxidant TQ (1,2-dihydro-2,2,4-trimethyl quinoline, polymerized) was obtained from Bayer India Ltd. It had a specific gravity of 1.1.

Toluene

Toluene was supplied by Fine Chemicals Ltd., Mumbai and had the following specifications.

Boiling point	95 °C
Acidity	0 .012
Alkalinity	0.012
Non volatile matter	0.002%

Acetone (AR)

Acetone was supplied by Qualigens Fine Chemicals, India

Maleic anhydride

Maleic anhydride (MA) was obtained from Nice chemicals Pvt. Ltd, Cochin and had the following specifications.

Molecular weight	98.06 g/mol
Assay	99%
Boiling point	51-53 °C

Dicumyl peroxide

Dicumyl peroxide was supplied by Merck, India.

Methyl ethyl ketone peroxide (MEKP)

Catalyst MEKP is of commercial grade, supplied by Mls Sharon Engineering Enterprises, Kochi.

Cobalt naphthenate

Commercial grade cobalt naphthenate activator was obtained from Sharon Engineering Enterprises, Kochi

Styrene

Styrene monomer used was supplied by Sharon Engineering Enterprises, Kochi.

1, 2 Propylene glycol

1,2 propylene glycol used for synthesis was supplied by Spectrochem Pvt. Ltd., Mumbai and had the following specifications.

Molecular weight	76.1 g/mol
Assay	99.5%
Boiling point	184-189 °C
Density	1.035-1.040 g/cc

Phthalic anhydride

Phthalic anhydride was obtained from Merck India Ltd, Mumbai., with the following specifications.

Molecular weight	148.12 g/mol
Assay	98%
Melting point	131-133 °C

Xylene

Xylene was supplied by Merck India Ltd, Mumbai with the following specifications.

Molecular weight	106.17 g/mol
Assay	95%
Boiling point	137-143 °C
Density	0.85-0.87 g/cc

Triphenyl phosphate

Triphenyl phosphate was supplied by Sdfine-chem Ltd, Mumbai and had the following specifications.

Molecular weight	326.29 g/mol
Assay	99%
Melting point	48-50 °C

Hydroquinone

Hydroquinone was supplied by Merck India Ltd, Mumbai with the following specifications.

Molecular weight	110.11 g/mol
Assay	99.5%
Melting point	170-174 °C

Methanol

Methanol was supplied by Spectrochem Pvt. Ltd., Mumbai.

Potassium hydroxide

Potassium hydroxide was obtained from Universal Laboratories Private Ltd, Mumbai.

Methyl ethyl ketone (MEK)

Methyl ethyl ketone was supplied by Merck India Ltd, Mumbai.

2.2 Methods

Expanded polystyrene was initially size-reduced to 0.9 g/cm^3.

2.2.1 Preparation of Elasomer/EPSblend using a Brabender Plasticorder

A Brabender Plasticorder (torque rheometer) model PL 3S was used for the preparation of elastomer/ EPS blend. The mixing chamber of 40 cc capacity is the central part of the machine which is heated by oil circulating thermostat heating tanks. High temperature silicone oil is used as heating liquid and the temperature on the mixer can be varied up to 300 °C. The measuring head is equipped with a stock temperature thermocouple, coupled with a temperature recorder for temperature measurement. The mixing or shearing of the material in the mixing chamber is done by two rotors. A speed controlled DC drive thyristor allows the rotor speed adjustment between 0 to 150rpm. At first size reduced EPS was allowed to soften for 2 min, followed by rubber. The mixing temperature and mixing time were different for different rubbers. For preparing compatibilised blends, MA and DCP were also added before the addition of rubber.

2.2.2 Compounding and curing

The rubber compounding was done on a two-roll mill (16×33 cm^2) according to ASTM D 3184-11at a friction ratio of 1:1.22. The temperature of the rolls was maintained at 70 ± 5 °C during the mastication of rubber. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order of activators, accelerators and curing agents. After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. Mixing time and temperature were controlled during the process. The sheets were kept for 24 hours for maturation.

After determining the cure time of the mixes as per ASTM D 2084-07 using Rubber Processing Analyser, RPA 2000 supplied by Alpha Technologies, USA, the rubber compounds were vulcanized up to the optimum cure time in an electrically heated hydraulic press with 30cm × 30cm platens at 150 °C at a pressure of 200 Kg/cm^2. The moulded samples were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h prior to physical testing.

2.2.3 Preparation of polyester resin/EPS blend (UPR/EPS)

The size reduced EPS was dissolved in minimum quantity (5 g) of styrene and kept over a period of 12 h. To this 100 phr unsaturated polyester resin was added and stirring was done using a mechanical stirrer for 30 min to get a homogeneous liquid. The resulting blends were designated as unmodified blends (UPR/EPS).

For the modification, the size-reduced EPS was first grafted using 1phr maleic anhydride and dicumyl peroxide (10% of MA) initiator. Grafting was done on a Brabender Plasticorder at 200 °C for about 5min. The grafted EPS was dissolved in 5 g of styrene over a period of 12 h. Then 100 phr unsaturated polyester resin was added and stirred well for 30 min to get a homogeneous liquid. The resulting blends were assigned as modified blends (UPR/EPS(m)).

2.2.4 Curing of polyester resin/EPS blends

Neat UPR (without EPS) was first cured at room temperature using a catalyst (methyl ethyl ketone peroxide dissolved in dimethyl phthalate containing 60% peroxide) and accelerator (6% solution of cobalt napthenate in styrene) combination. These were used in concentrations of 1 and 0.5 phr of the weight of the resin, respectively. The resin was then poured into appropriate molds coated with a releasing agent. Curing was done at room temperature for 24 h, followed by post curing at 80 °C for 3 h. Curing of both unmodified and modified blends were also done by the same procedure.

2.3 Characterisation techniques

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used for confirming the MA grafting on the blends and characterising the cured resin samples. The FTIR spectra were recorded using a Thermo Nicolet FTIR Spectrometer Model Avtar 370 instrument. The scanning range was from 400 to 4000 cm-1.Infrared spectroscopy is the absorption measurement of different IR frequencies (400-4000 cm^{-1}) by a sample positioned in the path of an IR beam. IR spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. The IR spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wave length. This can be done with a monochromatic beam, which changes in wave length over time, or by using a Fourier Transform Instrument to measure all wavelengths at once.

From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. This technique works almost exclusively on samples with covalent bonds.

2.3.2 Cure characteristics and kinetics

The processing characteristics of the vulcanizates were monitored as per ASTM D 2084-07 using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) which is a computer controlled torsional dynamic rheometer with a unique test gap design, an advanced temperature control system and fully automated operation modes. The die type used was biconical and the die gap was 0.487 mm in order to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated at 50rpm and the torque transducer on the upper die senses the force being transmitted through the rubber. To determine the cure characteristics of the rubber compound, approximately 5 g of the sealed sample was placed in the lower die, under pressurized conditions and submitted to harmonic torsional strain by the oscillation of the lower die through a small deformation angle about 2° and the transmitted torque is measured. The optimum cure time; T_{90}, scorch time; T_{10}, maximum torque; M_H and minimum torque; M_L values were determined at 150 °C for 30 minutes.

1) Optimum cure time, T_{90}: This corresponds to the time to achieve 90% of the maximum torque and this torque is calculated using the formula:

   Torque at optimum cure = $0.9\ (M_H – M_L) + M_L$

2) Scorch time, T_{10}: It is time for attaining 10% of the maximum torque.

3) Maximum torque, M_H: It is the maximum torque recorded when curing of the mix is completed.

4) Minimum torque, M_L: It is the lowest torque shown by the mix atthe test temperature before the onset of cure.

5) Cure rate index (CRI) is a measure of the speed with which the cure reaction is taking place and is calculated using the equation,

   $CRI = 100/(t_{90}-t_{10})$ ....(2.1)

Cure Kinetics

The kinetic rate constant of cure reaction, were determined from the rheometric data [1-3]. The general equation for the kinetics of a first order chemical reaction is

$\ln(a - x) = -kt + \ln a$ ....(2.2)

where ‘a’ is the initial reactant concentration, ‘x’ is the reacted quantity of reactant at time ‘t’ and ‘k’ is the first-order rate constant. For the vulcanization of rubber, measuring the torque developed during vulcanization monitors therate of crosslink formation. The torque obtained is proportional to the modulus of rubber. Thus, the following substitutions can be made.

$(a - x) = M_H - M_t$

$a = M_H - M_L$

where ‘Mt’ is the torque at time t. Therefore, the equation can be written as

$$\ln (M_H - M_t) = -kt + \ln(M_H - M_L) \quad \text{..(2.3)}$$

A plot of ln (MH–Mt) against time t can be drawn and if it is a straight line, then the cure reaction follows first-order kinetics. The cure reaction rate constant (k) can be obtained from the slope of the corresponding straight lines [4].

2.3.4 Strain-sweep studies

The strain sweep measurements were conducted to study the rubber-filler interaction. Rubber Process Analyzer (RPA 2000- Alpha Technologies) is a purposely modified commercial dynamic rheometer [5]. Such instrument was modified for capturing strain and torque signals, through appropriate software. Filled rubber compounds exhibit strong non-linear viscoelastic behaviour, the well-known Payne effect, i.e. the reduction of elastic modulus with increasing strain amplitude [6]. RPA can do strain sweep tests in which the variation of storage modulus (G'), loss modulus (G") and complex modulus (G*) with change in strain amplitude are measured. With respect to its measuring principle, the RPA cavity must be loaded with a volume excess of test material. In agreement with ASTM D 5289, the manufacturer recommends to load samples of about 5.0 g (4.4 cm^3) for a standard filled rubber compound with a specific gravity of 1.14 g/cm^3. Samples for RPA testing were consequently prepared by die cutting 46 mm diameter disks out of around 2 mm thick sheets of materials. The testing temperature was selected as

100 °C; a temperature below the curing temperature and the shear strain was varied from 0.5 to 40% keeping the frequency measurements at 0.5 Hz.

2.3.5 Stress-strain measurements

The tensile properties were measured using Shimadzu Universal Testing Machine, UTM (model AG-I) with a load cell of 10 KN capacity. The dumb bell shaped samples were held tight by the two grips or jaws of the UTM after measuring the thickness of the narrow portion using a thickness gauge, the lower grip being fixed. The tests were carried out at 28±2 (^{o}C).

For testing of rubber samples, dumb bell specimens were punched out of the moulded sheet parallel to the mill grain direction using a dumb bell die (C-type). The testing was done at a crosshead speed of 500 mm/min and with a grip separation of 40 mm as per ASTM D412. The tensile strength, elongation at break and modulus were evaluated.

Testing of resin samples were done on dumb bell shaped casted specimens as per ASTM D638-99 at a constant rate of traverse of the moving grip of 5 mm/min. The cast specimens were polished using emery paper prior to testing. Tensile strength, elongation, modulus and energy absorbed were evaluated.

2.3.6 Tear strength

Tear strength of the rubber samples were measured as per ASTM D 624 using standard test specimens with 90° angle on one side and tab ends (Type C die). The test speed was 500 mm/min. Average of at least six sample measurements was taken to represent each data point.

2.3.7 Hot air aging studies

The tensile properties were measured after ageing at 70 °C and 100 °C for 72 h in a hot air oven to assess resistance of the sample to aging.

2.3.8 Specific gravity

The densities of the cured samples of both rubber and resin were estimated by the method of displacement of liquid (ASTM D792). According to the principle of Archimedes a specimen immersed in a liquid receives a pressure equal to the displaced liquid. The density, which is the inverse of specific volume, may be calculated after the determination of the specimen weight in the air and its occupied volume in a liquid of known density.

The specific gravity of the liquid resin was determined according to ASTM D1475 using a specific gravity bottle. Clean, dry and weigh (W_a) the specific gravity bottle together with the stopper. Fill it with distilled water up to the brim and insert the stopper firmly. Keep the bottle for not less than 30 minutes at room temperature and weigh again (W_b). After weighing the water empty the bottle and dry it. Fill it with the resin up to the brim and insert the stopper firmly. Keep the filled bottle at room temperature for few minutes and the weight (W_c) is noted. Specific gravity can be calculated by the equation,

$$Specific\ gravity = \frac{Weight\ \ of\ resin(W_c - W_a)}{Weight\ of\ water\ (W_b\ - W_a)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.4)$$

2.3.9 Hardness

The hardness (Shore A) of the moulded samples was determined using Mitutoyo Hardmatic hardness tester in accordance with ASTM D 2240-03. The tests were performed on unstressed samples of 12mm diameter and 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact has been established with the specimen.

2.3.10 Abrasion loss

The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53516). Samples having a diameter of 6 ± 0.2 mm and a thickness of 6 mm were kept on a rotating sample holder and a 10 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The abrasion loss in cc/hr. was calculated using the formula

$$Abrasion\ loss = \frac{weight\ loss \times 60}{specific\ gravity \times 2.2} \qquad \text{.............................}(2.5)$$

2.3.11 Rebound resilience

Rebound resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. It is expressed as percentage and is measured using a Vertical Rebound Resilience Tester as per ASTM D2632-01. A plunger weighing 28±0.5g is dropped from a height of 40 cm to the sample of thickness 12.5 mm and the rebound height is measured. The resilience scale was marked in 100 equally spaced divisions and hence the rebound height is equal to the resilience (%).

2.3.12 Compression set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate compressed to a constant deflection (25 %) were kept in an air oven at 70°C for 22h (ASTM D395-1998 method B). The samples were taken out, cooled to room temperature for half an hour and the final thickness measured. The compression set was calculated using the equation,

$$Compression\ set\ (\%) = \frac{T_i - T_f}{T_i - T_s} \times 100 \quad \text{..............................(2.6)}$$

where T_i and T_f are the initial and final thickness of the specimen and T_s is the thickness of the spacer bar used.

2.3.13 Swelling studies

Swelling studies on the vulcanizates were done in toluene and crosslink densities calculated. Circular specimens of diameter, 20 mm, were punched out from the central portion of the vulcanizate. Thickness and diameter of the specimens were measured by means of a thickness gauge and vernier calipers, respectively. Specimens of known weight were immersed in about 20 ml toluene in diffusion bottles, which were kept at constant temperature. Samples were removed from the bottles at periodic intervals, quickly dried using tissue paper and weighed by a four digit electronic balance. The samples were then immediately replaced into the diffusion bottle. The experimental procedure was repeated until equilibrium swelling was attained.

The results of diffusion experiments were expressed as diffusion curves, where mol% or wt% uptake is plotted against the square root of time in minutes. The mol % uptake of the solvent, Qt, for the composite samples was determined using the equation:

$$Q_t = \frac{(W_1 - W_0)/M_s}{W_0} \times 100 \quad \text{..}(2.7)$$

where 'W_0' and 'W_1' are the weights of the specimen before and after swelling, and 'Ms' the molar mass of the solvent.

In order to assess the extent of swelling behaviour of the composites, swelling index was evaluated. It is the ratio of swollen weight to original weight. Swelling index is a direct measurement of degree of crosslinking, smaller the ratio higher the degree of crosslinking.

$$Swelling\ index, Q(\%) = \frac{(W_1 - W_0)}{W_0} \times 100 \quad \text{..............................}(2.8)$$

The crosslink density (1/2Mc, where *Mc* is the number-average molecular weight of the rubber chains between crosslinks) was determined with an equilibrium swelling method with toluene as solvent. The swollen weight and deswollen weight (weight after drying the swollen sample in a vacuum to constant weight) of the sample was measured. The volume fraction of rubber (Vr) in the swollen network was calculated by the method reported by Ellis and Welding from the following equation [7].

$$V_r = \frac{(m_d - f m_i)\rho_r^{-1}}{(m_d - f m_i)\rho_r^{-1} + m_s \rho_s^{-1}} \quad \text{..}(2.9)$$

where m_d is the deswollen weight of sample, f is the weight fraction of insoluble components, m_i is the initial weight of sample, ρ_r is the density of polymer, ρ_s is the density of solvent, m_s is the amount of solvent absorbed by sample.

The volume fraction of rubber (V_r) is calculated assuming that the filler does not swell. It is then converted to Vr_0 (the value V_r would have in the absence of filler) according to Cunneen and Russel,

$$\frac{V_{r_0}}{V_r} = ae^{-z} + b \text{ ....} (2.10)$$

Here a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black filled systems are; a = 0.56 and b = 0.44. The corresponding values for silica filled systems are; a = l.4l and b = -0.41[8].

The crosslink density 1/2Mcwas determined from Vr_0 using the Flory–Rehner equation,

$$\frac{1}{2M_c} = -\left[\frac{ln(1 - V_r) + V_r + \chi V_r^2}{2V_s\rho_r\left(V_r^{1/3}\right)}\right] \text{ ....} (2.11)$$

whereρ_r is the density of rubber, V_s is the molar volume of the solvent (V_s toluene is 106.2 cm^3/mol), and χ is the parameter characteristic of the interaction between the blend and solvent. For the NR–toluene system, $\chi = 0.3795$ and for SBR-toluene system, $\chi = 0.391$.

2.3.14 Thermogravirmetric analysis

Thermogravimetric analysis is a type of testing that is performed onsamples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. TGA is commonly employed in research and testing to determine characteristics of polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, composition of blends and composites etc. The analyzer usually consists of a high precision balance with a pan loaded with the sample. The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. Analysis was carried out by raising the temperature gradually and plotting weight against temperature.

Thermogravimetric analysis was carried out on vulcanized samples using a Thermo Gravimetric Analyser Q-50, TA Instruments. It is a computer controlled instrument that permits the measurement of the weight changes in the sample material as a function of temperature. The sample (5-10mg) was placed in a temperature programmed furnace. It was then subjected to a temperature change from room temperature to 600 °C with a heating rate of 20 °C/minute in nitrogen atmosphere (flow rate of 40–60 cm^3/min). The corresponding weight changes were noted with the help of an ultra sensitive microbalance. The onset of degradation, the temperature at maximum degradation and residual weight in percentage were noted.

2.3.15 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference material to maintain both at the same temperature. Whether more or less heat must flow to the sample depends upon whether the sample is exothermic or endothermic. By observing the difference in heat flow between the sample and the reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

The sample was first heated under vaccum for 15 minutes at 85 °C (elimination of water) before it was sealed in an aluminium pan with a perforated lid. The sample pan was placed in a differential scanning calorimetry (DSC) cell (Q-100, TA instruments calorimeter) under a dry nitrogen purge. The samples (3-6 mg) were inserted into the apparatus an dimmediately heated from -80 °C to 150 °C at a rate of 10 °C/min and kept for one minute at this temperature in order to erase thermal history. The samples were quenched to -80 °C and then heated to 150 °C at a heating rate of 10 °C/min. in nitrogen atmosphere.

2.3.16 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out on a DMA Q800 dynamic mechanical analyzer (TA instruments) using film samples. Temperature sweep experiments were conducted at a ramp rate of 3 °C/min and a frequency of 1 Hz. Oscillating strain was set at 0.02% for all tests.

For testing rubber, specimens having a dimension of 30 mm × 3 mm × 2 mm were used in tension mode. Temperature sweep experiments of the composites were performed from -80 °C to +40 °C for NR and -60 °C to +40 °C for SBR. For blends the testing was performed to some elevated temperatures.

The damping qualities of resin samples were according to ASTM D 5418 – 01. Rectangular specimens 64 mm length, 12.7 mm breadth and 3.2 mm height were used. DMA tests were conducted at a constant frequency of 1 Hz. The above temperature ramp was run from room temperature to 200 °C to get an overview of the thermo mechanical behaviour of specimens.

2.3.17 Morphological studies- Scanning electron microscopy

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology. Scanning electron microscope (JEOL JSM 840A Scanning Microscope) was used to investigate the morphology of the fractured surfaces. In a typical SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film.

The SEM observations reported in the present study were made on the fracture surface of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sampleswere mounted on a metallic stub and an ultra thin (<10 nm) coating of electrically conducting material (gold) was deposited by low vacuum gold coating.This was done to prevent the accumulation of static electric fields at the specimen due to the electron irradiation during imaging and to improve contact. The gold coated sample was subjected to SEM.

2.3.18 Acid value and number average molecular weight ($\overline{M}n$)

Acid value determination is used for estimating the reaction extent and number average molecular weight indirectly. The experiment is done as per ASTM D2849. 100 cc of 50/50 methanol/toluene solvent was made mildly alkaline to phenolphthalein indicator by the addition of 0.2 N KOH solutions. About 2 g of polyester resin was then added to the flask containing the solvent. The resin was allowed to dissolve. The solution was then titrated against 0.2 N KOH solution until a pink colour (permanent for 5 minutes) was obtained. The volume of 0.2N KOH was noted.

$$Acid\ value = \frac{Volume\ of\ KOH \times Normality\ of\ KOH}{Weight\ of\ the\ sample} \times 56.1 \text{ ......(2.12)}$$

$$The\ number\ average\ molecular\ weight(\overline{M}_n) = \frac{56000}{Acid\ value} \text{ ...(2.13)}$$

2.3.19 Viscosity

The viscosity of the resin was measured at room temperature on a Brookfield viscometer model RVF as per ASTM D2393. The appropriate spindle was allowed to rotate in the resin for 30 sec and the dial reading was taken. The procedure was repeated for constant dial reading.

2.3.20 Gel time and peak exothermic temperature

Gel time and peak exothermic temperatures of the resin samples were determined as per ASTM D2471. About 45 ml of resin was taken in an aluminium foil dish, approximately 70 mm in diameterand 14 mm depth and placed in a temperature-controlled bath maintained at 23 ± 1.0 °C. A thermocouple was inserted at the geometric centre of the resin mass and stirred with a glass rod. 0.5 wt % of cobalt naphthenate and 1 wt% of MEKP were added and a stopwatch was started. When the reactant mass no longer adheres to the glass rod, the gel time was recorded as the elapsed time from the start of mixing. The time temperature recording was continued until the temperature started to drop. The highest temperature reached was recorded as the peak exothermic temperature.

2.3.21 Flexural properties

Flexural properties were measured using rectangular samples cured in a mould cavity of dimensions 127×12.7×3.2 mm. The flexural properties were tested on a Shimadzu Autograph (AG-I 50 kN) Universal Testing Machine (ASTM D790) at a constant rate of traverse of the moving grip of 1.3 mm/min. The cast specimens in the form of rectangular bars were polished using emery paper prior to testing. The depth and width of the specimen was measured nearest to 0.01 mm. The support span should be 16 times the depth of the specimen. The specimen was centred on the supports with the long axis of the specimen perpendicular to the loading nose and supports. The load was applied to the specimen and flexural strength and modulus were recorded. The load-deflection curve was also obtained. It is calculated at any point on the stress strain curve by the following equation

$$S = \frac{3PL}{2bd^2} \quad \text{...(2.14)}$$

where S = stress in the outer fibres at midpoint (MPa), P = Load at any point on the load -elongation curve (N), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm).

Flexural modulus is the ratio of stress to corresponding strain and is expressed in MPa. It is calculated by drawing a tangent to the steepest initial straight line portion of the load- deflection curve and using the equation

$$E_b = \frac{L^3 m}{4db^3} \quad \text{...(2.15)}$$

Where E_b = modulus of elasticity in bending (MPa), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm), m = slope of the tangent to the initial straight line portion of the load - deflection curve (N/mm of deflection).

2.3.22 Impact strength

Impact strength was measured using unnotched samples cured in a mould cavity of dimensions 64 × 12.7 × 3.2 mm according to ASTM D 4812-99. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. This test can be used as a quick and easy quality control check to determine if a material meets specific impact properties or to compare materials for general toughness. The test was done employing an impact testing machine, CEAST Resil Impact Junior with a pendulum capacity of 4 J and striking velocity of 3.46 m/s, at room temperature. The sample was clamped vertically into the pendulum impact test fixture with the thin edge facing the striking edge of the pendulum such that 31.5 mm of the specimen projected above the top surface of the vice. The pendulum is released and allowed to strike through the specimen. The energy required to fracture the sample was measured from the reading dial.

2.3.23 Water/Chemical resistance of resin

Water absorption was tested as per ASTM D570. Chemical resistance of the resin is determined as per ASTM D543-52. The standard specimens are in the form of disks with a diameter of 50.8 mm and a thickness on 3.175 mm. Three dimensional cross-link networks possess resistance to attack by corrosive chemicals, including weak alkalies, strong acids, and organic solvents. The chemical resistance of a completely cured resin is a function of its chemical composition, molecular weight and the degree of cross-linking. The samples were directly placed in a temperature-controlled oven. The temperature was kept constant at 50 °C for 24 hours. The samples were taken out and cooled in a desiccator and weighed. The weighed samples were immersed in the following solvents viz.,

(a) Water
(b) Hydrochloric acid (0.1 N)
(c) Sodium hydroxide Solution (0.1 N)
(d) Methyl ethyl ketone

for 24 hours at room temperature. The specimens were removed, wiped dry with a cloth and immediately weighed. The increase in weight was found out.

$$\text{Solvent absorption (\%)} = \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 10 \quad .....(2.16)$$

The same samples were immersed in the above chemicals for 5 days at room temperature and observed for a visible change in the condition of the films at a regular interval. The specimens were removed, wiped dry with a cloth and immediately weighed. The increase/decrease in weight was found out.

2.3.24 Crosslink density

Though there are several methods to determine the crosslink densities of highly crosslinked thermoset materials, the frequently employed method is the crosslink density calculation from the value of modulus according to the rubber elasticity theory [9]. The crosslink density is calculated using the following equation,

$$\nu_e = \frac{E'}{3RT} \text{ ....(2.17)}$$

where ν represents the crosslink density (number of moles of chains per cm^3), R is the gas constant (8.314 J/K.mole), T is the temperature in Kelvin, and E is the Young's modulus (elastic modulus).

2.3.25 Transparency studies

Transparency studies were carried out using UV-Vis-NIR Spectrophotometer, Varian, Cary 5000 with a spectral range of 175 – 3300 nm and limiting resolution of 0.05 nm. Cured samples were used for the study and the measurements were carried out at 300-800 nm range.

References

[1] Mathew, G. Multifiller-matrix Adhesion Effects in Epoxidized Natural Rubber. *J. Elastomers Plast.* **38,** 43–63 (2006).

[2] Fujimoto, K., T. Nishi, and T. Okamoto. "Devulcanisation of NB Based Latex Products For Tyre Applications. *Int. Polym. Sci. and Technol.* **8**, T/30 (1981).

[3] Mathew, G., Singh, R. P., Nair, N. R. & Thomas, S. Development and characterization of novel EPDM / NR prophylactic waste composites. *J. Mater. Sci.* **38**, 2469–2481 (2003).

[4] González, L., Rodríguez, A., Marcos, A. & Chamorro, C. Crosslink Reaction Mechanisms of Diene Rubber with Dicumyl Peroxide. *Rubber Chem. Technol.* **69**, 203–214 (1996).

[5] Leblanc, J. L. & Cartault, M. Advanced torsional dynamic methods to study the morphology of uncured filled rubber compounds. *J. Appl. Polym. Sci.* **80,** 2093–2104 (2001).).

[6] Payne, A. R. & Whittaker, R. E. Low Strain Dynamic Properties of Filled Rubbers. *Rubber Chem. Technol.* **44,** 440–478 (1971).

[7] Ellis, B. & Welding, G. N. Estimation, from Swelling, of the Structural Contribution of Chemical Reactions to the Vulcanization of Natural Rubber. Part II. Estimation of Equilibrium Degree of Swelling. *Rubber Chem. Technol.* **37,** 571–575 (1964).

[8] Chakraborty, S. K. & De, S. K. Silica- and Clay-Reinforced Carboxylated Nitrile Rubber Vulcanized by a Mixed Crosslinking System. *Rubber Chem. Technol.* **55,** 990–1003 (1982).

[9] Tyman, J. H. P., Wilczynski, D. & Kashani, M. A. Compositional studies on technical cashew nutshell liquid (cnsl) by chromatography and mass spectroscopy. *J. Am. Oil Chem. Soc.* **55,** 663–668 (1978).

* * *

Chapter 3

UTILIZATION OF EPS IN NR EMPLOYING GRAFTING REACTION

Contents

Part A

MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF UNFILLED AND FILLED NR/EPS BLENDS

3A.1 Introduction

Synthetic rubber has been commercialised for more than 50 years. Still natural rubber (NR) is stretching its muscles as a practically non equivalent elastomer with remarkable elasticity, resilience, resistance to temperature, extensibility and toughness. High tensile strength due to strain induced crystallization, superior building tack and good crack propagation resistance make NR suitable for a variety of industrial applications in which it cannot be replaced by synthetic alternatives. It remains; in fact the most often used type of elastomer, without which the survival of industry becomes difficult. Since the current world NR consumption is high (around 12 million metric tons in 2014), replacement of NR even by an inexpensive polymer material even in small percentages can have considerable impact on the economic viability of NR based product manufacturing. Polymer blending assumes significance in this context. A waste thermoplastic material such as expanded polystyrene is an ideal candidate for blending with NR considering the enormous nuisance it poses for the environment.

Blending of rubber and thermoplastics has, of recent, become a popular research activity in macromolecular science due to their ability to combine the properties of two different phases in a unique product. The final properties of polymer blends are directly related to their microstructure and morphology [1-2]. The major factors determining the blend morphology are the blend ratio, the shear viscosity of the components and shear rate during mixing [3]. The blending of plastic and rubber results in the improvement of physical, thermal and mechanical properties as well as modified processing characteristics and cost reduction of the final product. Higher the amount of the hard plastic phase, greater the usefulness as impact resistant plastic and with relatively large amount of rubber phase, the blend will be soft with elastomeric properties.

Expanded polystyrene (EPS) is a major constituent of plastic waste due to its global consumption which exceeds 3 million tons with an increase of approximately 6% a year [4,5]. Because of the low bulk density and voluminous nature the recycling of EPS is difficult and it usually ends up in landfills or is incinerated. Added to this are the high transportation costs associated with shipping low bulk density waste EPS [6]. In response to the high cost of disposal and decreasing space of landfills, a number of recycling strategies have been devised for EPS. If the waste EPS is incorporated in other polymers by cost effective methods, the recycling will be economically favorable. Hence, blending EPS with NR has been done in this study to gainfully utilize waste EPS, thereby exploring and extending the performance of a versatile general purpose polymer (NR) by blending with a low-cost material (EPS).

Although there is hardly any information in the literature about NR/EPS blends, there are some detailed references about studies on thermoplastic elastomers based on NR/PS blends [7-8]. Blends based on NR and PS has the potential to combine the superior processing characteristics of PS and the elastic properties of NR [9]. The properties of a blend are dependent on phase behaviour, blend ratio and cross linking levels [10-11]. In some cases immiscible blends are preferable over miscible blends because in miscible blends only an average of the individual properties is obtained [12]. However, very often many of the immiscible blends exhibit poor mechanical properties as well as unstable morphology.

This section compares the effect of EPS on the mechanical properties of gum, black filled and silica filled NR in order to select the best filler for the blend. Two different blend ratios of NR/EPS were selected and the studies were carried out by comparing with virgin NR.

3A.2 Experimental

3A.2.1 Materials

The materials used are given in Section 2.1 of Chapter 2.

3A.2.2 Methods

3A.2.2.1 Blending

The blending method is given in section 2.2.1. NR/EPS blends were prepared by melt mixing in a Brabender Plasticorder at 140 °C maintaining the rotor speed at 50 rpm. Total mixing time was fixed as 8min. Three batches of 35/5 blends of NR/EPS were prepared. Similarly, three batches of 30/10 (NR/EPS) blends were also prepared. Since this study has carried out in order two select the best filler for the blend higher percentages of EPS were not considered.

3A.2.2.2 Compounding and curing

The compounding and curing was done according to the procedure given in Section 2. 2. 2. At first 60g NR was masticated in a two roll mill for 3min and then mixed with the blend of NR and EPS already prepared in Brabender Plasticorder and the filler and other compounding ingredients so that a final 95/5 and 90/10 blends of gum, black filled and silica filled compounds were obtained. Gum, black filled and silica filled NR, without EPS were also prepared. The final formulation used is given below in Table 3A.1. It has been shown during earlier studies that cardanol separated from cashew nut shell liquid (CNSL) is a good substitute for petroleum based NR plasticisers [13]. Hence this study uses cardanol as plasticiser as an additional step to conserve fossil fuel based substances and utilizes a cheap agrobyproduct.

Table 3A.1. Final formulation

Vulcanizing ingredients	Quantity in phr		
	Gum	**Silica**	**Black**
NR	100	100	100
ZnO	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
CBS	0.6	0.6	0.6
TMTD	0.1	0.1	0.1
Sulphur	2.5	2.5	2.5
Silica/Black	-	15	40
Cardanol	-	1.5	4
DEG	-	1	-
SP/TQ	1	1	1

3 A.2.3 Characterisations

A detailed explanation of characterisation techniques are given in Section 2.3 of chapter 2.

3A.3 Results and discussion

3A.3.1 Cure characteristics

The cure characteristics are shown in Table 3A.2. Black filled compounds showed the highest torque values, followed by the silica filled and then the gum (unfilled) compounds. A reduction in torque values was observed for all the blends compared to their virgin compounds. The low torque values for the blends are associated with the low viscosity of the PS phase compared to NR at the vulcanization temperature since torque is a direct function of viscosity. Unattached PS chains can also reduce the cohesion of the rubber matrix by hindering the sulphur crosslinks and reducing the torque. The blends, except silica filled compounds, show substantial deviation in cure time. The cure properties of silica filled blends are comparable to silica filled NR without EPS.

Table 3A.2. Cure characteristics of gum, black and silica filled NR and NR/EPS blends

Cure properties	Gum			Black filled			Silica filled		
	NR	NR/EPS		NR	NR/EPS		NR	NR/EPS	
		95/5	90/10		95/5	90/10		95/5	90/10
Maximum torque (dNm)	2.58	2.56	2.35	6.47	4.24	5.63	4.13	3.06	3.24
Minimum torque (dNm)	0.02	0.01	0.01	0.24	0.17	0.87	0.01	0.01	0.01
Torque difference	2.56	2.55	2.34	6.23	4.07	4.76	4.12	3.05	3.23
Cure time (min)	6.48	4.47	7.57	6.06	6.17	5.14	3.37	3.46	3.34
Scroch time (min)	2.53	2.01	3.54	1.25	2.24	1.26	1.56	1.55	2.13
Cure rate index	25.32	40.65	24.81	20.79	25.45	25.77	55.25	52.36	82.64

3A.3.2 Tensile properties

The tensile properties of gum, black and silica filled NR and NR/EPS blends are shown in Fig. 3A.1(tensile strength), Fig. 3A.2 (elongation at break) and Fig. 3A.3 (modulus at 300% elongation). The incorporation of EPS directly to NR showed a reduction in tensile strength and elongation at break for all three sets; gum, black and silica filled systems. The drop in tensile strength of the blends is associated with the phase separation due to the presence of EPS. The reinforcement activity of the filler in blends depends on the affinity of the filler towards each component of the blend and also on the distribution and dispersion of the filler in each phase of the blend. Polymer chains under applied stress distribute stress by slippage and thus avoid chain breakage [14-16]. This results in energy dissipation and increases the strength of the filled elastomer. But in NR/EPS blends, EPS may resist such slippage resulting in the reduction of tensile strength. For unfilled compounds the phase separation is much less at lower PS content [17]. It seems that the presence of carbon black decreases the miscibility of NR and PS, causing phase separation even with lower PS content. Therefore, a large decrease in the tensile strength was observed for black filled system even at low PS content. In this case, PS acts as rigid incompatible filler, resulting in a drop in tensile strength of the blend.

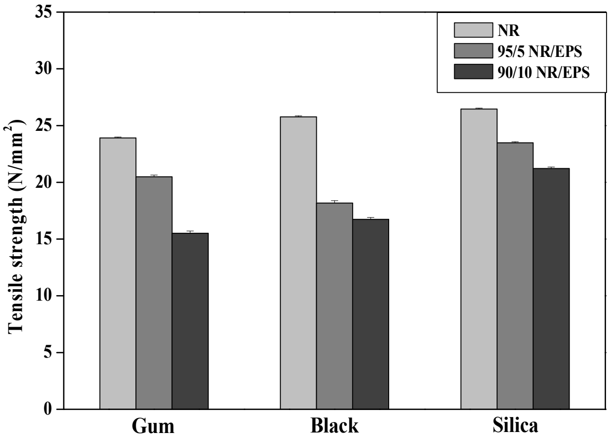


Fig. 3A.1. Tensile strength of gum, black and silica filled NR and NR/EPS blends

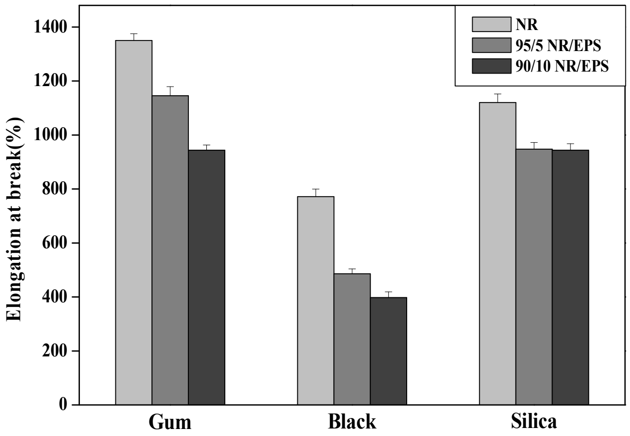


Fig. 3A.2. Elongation at break of gum, black and silica filled NR and NR/EPS blends

The reduction in tensile strength for silica filled NR/EPS blend is very small compared to gum and black filled systems. The interaction between styrene and silica is responsible for this behaviour. It has been already reported that copolymer rubbers like SBR have an added complexity that there are two comonomer elements with which filler particles can interact [18]. Interactions of each comonomer elements with the filler particles will affect the compound processing and properties. The interaction between SBR and fillers increases in the order, carbon black < silica < clay. Though there is some interaction between carbon black and styrene containing rubbers, the interaction is weaker than that of silicates [19-20]. Also according to Inverse Gas Chromatography (IGC) technique principles [21], the compatibility of polymers with silica can be classified as follows: NBR > SBR > NR > BR > high vinyl BR > EPDM >IIR. This tendency corresponds to the solubility parameter of each polymer [22]. NR/EPS blends emulate the behaviour of SBR towards silica showing better tensile strength for silica filled blends than black filled blends. Generally, as the PS content increases, the stress- strain curves show a decrease in the elongation at break. This is due to the rigid nature and lower elongation of PS in comparison with NR.

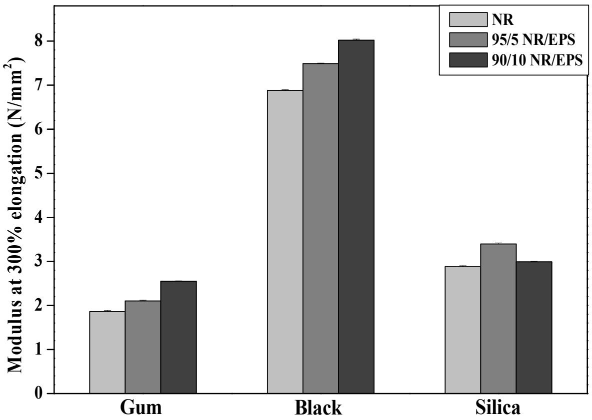


Fig. 3A.3. Modulus at 300% elongation of gum, black and silica filled NR and NR/EPS blends

The modulus at 300% elongation for the blends some shows an improvement compared to samples without EPS irrespective of the filler. This is due to the presence of thermoplastic PS phase with high modulus which acts as rigid filler and provides rigidity for the compounds. The PS resists the mobility of rubber chains, which increases blend stiffness [23]. The maximum modulus is observed for black filled compounds, followed by silica filled compounds. Gum compounds show the lowest modulii. This is because carbon filler offers much better stiffness compared to silica filler [24] because of the difference in reinforcement mechanism.

3A.3.3 Tear strength

The tear strength of gum, black and silica filled NR and NR/EPS blends are illustrated in Fig. 3A.4.The gum compounds exhibit the lowest tear strength while the filled systems show higher tear strength because an extra energy dissipating mechanism is operative for filled vulcanizates [25]. The blends showed better tear strength at low EPS content. This is due to the presence of hard PS domains which resists crack propagation in the blends. This is similar to the findings of Asaletha et al. [7], Joseph and Thomas [26] and Mathew et al. [27].

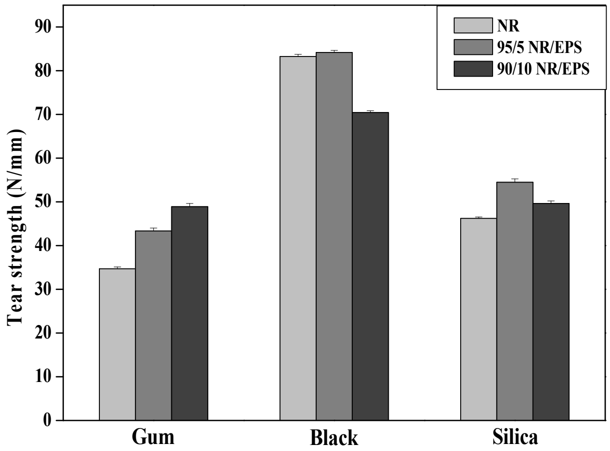


Fig. 3A.4. Tear strength of gum, black and silica filled NR and NR/EPS blends

But for the filled system at higher concentration of EPS the tear strength drops. This is due to incompatibility between the two phases and also the reduction in the reinforcement offered by the filler (black and silica) due to the presence of EPS. At higher concentrations severe phase separation occurs so that the specimen easily breaks under stress [23]. As there is no such filler effect in unfilled blends the tear strength shows gradual improvement on EPS addition.

3A.3.4 Thermogravimetric analysis

Fig. 3A.5 shows the TG (a)/DTG (b) curves of gum and black / silica filled NR and NR/EPS blend. Vulcanised NR and pure PS have almost the same thermal stability [28]. They both degrade in the temperature range of 300–400 °C. The curves indicate that the decomposition ranges from approximately 300 °C to 470 °C with a mass loss of about 95% for gum compounds, 85% for silica filled compounds and 70% for black filled compounds, which can be assigned to the thermal decomposition of natural rubber into monomers, dimers, trimers, etc. in inert atmosphere. A small shoulder can be observed in the DTG curves at approximately 410 °C attributable to cross linked and cyclised networks which degrade at higher temperature [29]. The improvement in onset of degradation upon addition of EPS is higher for silica filled system compared to gum or black filled system.

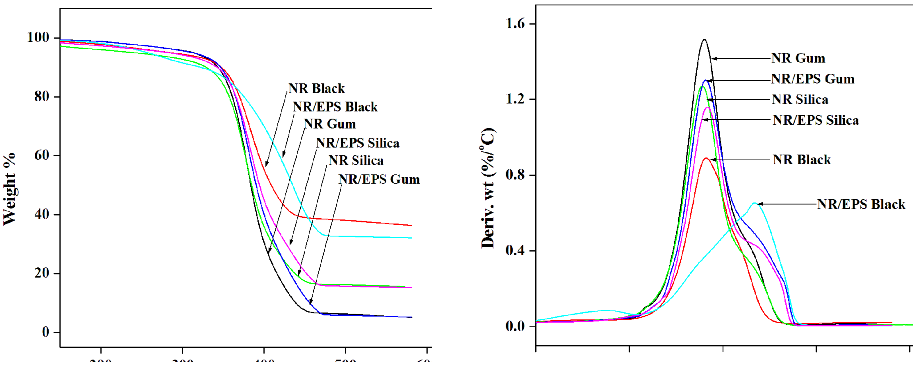


Fig. 3A.5. TG (a)/DTG (b) curves of gum and black / silica filled NR and 90/10 NR-EPS blend

The temperature of the maximum mass loss rate, the peak temperature of the DTG curves in Fig. 3A. 5 are around 380 °C for all cases, except for black filled NR/EPS blend which is 434.49 °C. The temperature at which 50% decomposition occurs is generally considered as an index of thermal stability. Our results have shown that this temperature is higher for the blends in all the three systems indicating an increase in thermal stability upon the addition of PS to NR. Except for black filled system, the percentage of residue for the blends is found to be on par with their corresponding NR formulation without EPS. The residual weight % of black filled NR/EPS blend is lower than black filled NR due to the preferential dispersion of carbon black in NR and the phase separation of components resulting in a complete degradation of PS component in the blend. Table 3A.3 shows the TGA data for gum and black / silica filled NR and 90/10 NR-EPS blend. The results suggest that blends have thermal stability either higher or comparable to NR.

Table 3A.3. TGA data for gum and black / silica filled NR and 90/10 NR/EPS blend

Thermal properties	**Gum**		**Black**		**Silica**	
	NR	**90/10 NR/EPS**	**NR**	**90/10 NR/EPS**	**NR**	**90/10 NR/EPS**
Onset degradation temperature (°C)	310.0	312.5	314.6	316.8	311.6	316.8
Maximum degradation temperature (°C)	380.2	381.4	382.4	434.5	378.1	383.6
End set degradation temperature (°C)	461.1	477.7	452.1	477.3	460.8	471.8
Temperature (°C) at 5% degradation	312.4	311.0	283.9	256.9	239.5	282.9
Temperature (°C) at 50% degradation	383.9	390.2	408.5	435.3	384.9	394.5
Residue (%)	5.1	5.3	36.4	32.2	15.6	15.3

3A.3.5 Morphological analysis

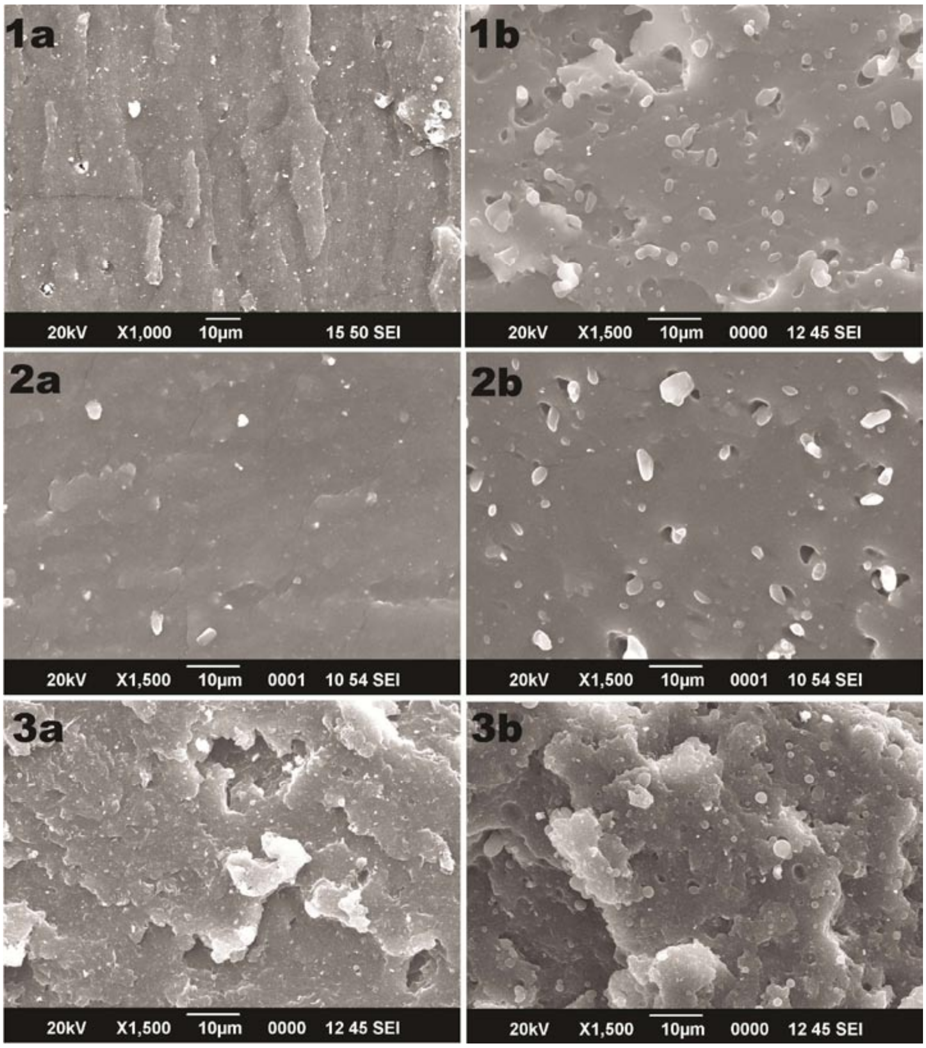


Fig 3A.6. Scanning electron micrographs of the tensile fractured surfaces of (1) gum and (2) black/ (3) silica filled NR (a) and NR-EPS blend (b)

The scanning electron micrographs of the tensile fractured surfaces of (1) gum and (2) black/ (3) silica filled NR (a) and NR/EPS blend (b) is shown in fig 3A.6. The blends of all the three systems consist of EPS as the dispersed objects. But silica filled NR/EPS blend showed more uniformity in the size and shape of the dispersed particles compared to other two blends signifying the greater compatibility between the components. Moreover, silica filled samples show greater extent of roughness in the fractured surface morphology both in pure NR and NR/EPS blend indicating better reinforcement. In the case of black filled compounds the roughness is seen only for pure NR and the blend exhibits smooth morphology indicating poor compatibility. These observations are in accordance with the mechanical properties.

3A.4 Conclusion

Black filled compounds showed the highest torque values, followed by silica filled and then by gum compounds. A reduction of torque values was observed for all the blends compared to their virgin compounds. The blends, except silica filled compounds show some deviation in cure time and scorch time for different samples of the same batch. The cure properties of silica filled blends of NR/EPS are comparable to those of the virgin compound.

The incorporation of EPS to NR caused a reduction in tensile strength and elongation at break for gum, black and silica filled systems. As the PS content increases the properties tend to be lowered. The reduction in tensile strength for silica filled NR/EPS blend is very small compared to other systems. The modulus at 300% elongation for the blends shows some improvement compared to NR irrespective of the filler. The highest modulus is observed for black filled compound followed by the silica filled one where as gum compounds show the lowest modulus.

Filled systems show improved tear strength compared to unfilled systems. But higher concentration of EPS causes a reduction in tear strength.

The improvement in onset of degradation upon addition of EPS is higher for silica filled system compared to gum or black filled system. The temperature of the maximum mass loss rate is around 380 °C for all the cases, except for black filled NR/EPS blend in which it is 434.49 °C. The 50% decomposition temperature is higher for blends in all the three systems indicating an increase in thermal stability upon the addition of PS to NR. Except for black filled system, the percentage of residue for the blends is found to be on par with their corresponding NR compounds without EPS. The residual weight percentage of black filled NR/EPS blend is lower than that of black filled NR. The TGA data suggest that blends have thermal stability either higher or comparable to NR.

From the overall performance, it can be concluded that silica is best suited for NR/EPS blends as a filler.

References

[1] Pticek, V., Hrnjak-Murgic, Z. & Jelencic, J. Effect of the structure of ethylene-propylene-diene-graftpolystyrene graft copolymers on morphology and mechanical properties of SAN/EPDM blends. *Express Polym. Lett.* **1,** 173–179 (2007).

[2] Khalf, A. I., Nashar, D. E. El & Maziad, N. A. Effect of grafting cellulose acetate and methylmethacrylate as compatibilizer onto NBR/SBR blends. *Mater. Des.* **31,** 2592–2598 (2010).

[3] Joseph, S. & Thomas, S. Morphology, morphology development and mechanical properties of polystyrene/polybutadiene blends. *Eur. Polym. J.* **39,** 115–125 (2003).

[4] Philip, N. & Manfred, W. New perspectives in thermal insulation and product design: Economic added value. *Sulzer Tech. Rev.* **1,** 6–8 (2009).

[5] Myint, S., Zakaria, M. S. B. & Ahmed, K. R. Paints Based on Waste Expanded Polystyrene. *Prog. Rubber, Plast. Recycl. Technol.* **26,** 21–30 (2010).

[6] Shin, C., Chase, G. G. & Reneker, D. H. Recycled expanded polystyrene nanofibers applied in filter media. *Colloids Surfaces A Physicochem. Eng. Asp.* **262,** 211–215 (2005).

[7] Asaletha, R., Kumaran, M. G. & Thomas, S. Thermoplastic elastomers from blends of polystyrene and natural rubber: morphology and mechanical properties. *Eur. Polym. J.* **35,** 253–271 (1999).

[8] Asaletha, R., Groeninckx, G., Kumaran, M. G. & Thomas, S. Melt rheology and morphology of physically compatibilized natural rubber–polystyrene blends by the addition of natural rubber-g-polystyrene. *J. Appl. Polym. Sci.* **69,** 2673–2690 (1998).

[9] Khalf, A. I. & Ward, A. A. Use of rice husks as potential filler in styrene butadiene rubber/linear low density polyethylene blends in the presence of maleic anhydride. *Mater. Des.* **31,** 2414–2421 (2010).

[10] Paul, D. & Newman, S. *Polymer blends*. vol. 2. *Acad. New York* (1978).

[11] Findik, F., Yilmaz, R. & Köksal, T. Investigation of mechanical and physical properties of several industrial rubbers. *Mater. Des.* **25,** 269–276 (2004).

[12] Olabisi O, Robeson LM, Shaw MT. *Polymer–polymer miscibility*. New York: Academic Press, 1978.

[13] Alexander, M., Kurian, P., Thachil, E. T. & . Effectiveness of Cardanol as Plasticizer for Silica-Filled Natural Rubber. *Prog. Rubber, Plast. Recycl. Technol.* **23,** 43–55 (2007).

[14] Jha, V. Carbon black filler reinforcement of elastomers. PhD Thesis, Queen Mary, University of London, (2008).

[15] Boonstra, B. B. Mixing of carbon black and polymer: Interaction and reinforcement. *J. Appl. Polym. Sci.* **11,** 389–406 (1967).

[16] Dannenberg, E. M., Molecular slippage mechanism of reinforcement. *Trans. Inst. Rubber. Ind*. **42**, 26, (1966).

[17] Heidary, S. H., Amraei, I. A. & Payami, A. Carbon-black-reinforced natural rubber/polystyrene full interpenetrated polymer networks: Synthesis and properties. *J. Appl. Polym. Sci.* **113,** 2143–2149 (2009).

[18] Vo, L. T., Anastasiadis, S. H. & Giannelis, E. P. Dielectric study of Poly(styrene- co -butadiene) Composites with Carbon Black, Silica, and Nanoclay. *Macromolecules* **44,** 6162–6171 (2011).

[19] Kraus, G. & Dugone, J. Adsorption of Elastomers on Carbon Black. *Ind. Eng. Chem.* **47,** 1809–1816 (1955).

[20] Dutta, N. . *et al.* High resolution solid-state n.m.r. investigation of the filler-rubber interaction: 1. High speed 1H magic-angle spinning n.m.r. spectroscopy in carbon black filled styrene-butadiene rubber. *Polymer.* **35,** 4293–4299 (1994).

[21] Conzatti, L. *et al.* Morphology and Viscoelastic Behaviour of a Silica Filled Styrene/Butadiene Random Copolymer. *Macromol. Mater. Eng.* **293,** 178–187 (2008).

[22] Mihara, S. Reactive Processing of Silica-Reinforced Tire Rubber: New Insight into The Time- And Temperature-Dependence of Silica Rubber Interaction. Ph.D thesis, University of Twente, Enschede, the Netherlands, (2008).

[23] Boondamnoen, O. & Azura, A. EFFECT of blend ratio and compatibilizer on solution casted treated waste natural rubber latex/polystyrene blends. *Songklanakarin J. Sci. Technol* **35,** 547–555 (2013).

[24] Rattanasom, N., Prasertsri, S. & Ruangritnumchai, T. Comparison of the mechanical properties at similar hardness level of natural rubber filled with various reinforcing-fillers. *Polym. Test.* **28,** 8–12 (2009).

[25] Bhowmick, A. K., Neogi, C. & Basu, S. P. Threshold tear strength of carbon black filled rubber vulcanizates. *J. Appl. Polym. Sci.* **41,** 917–928 (1990).

[26] Joseph, S. & Thomas, S. Morphology, morphology development and mechanical properties of polystyrene/polybutadiene blends. *Eur. Polym. J.* **39,** 115–125 (2003).

[27] Mathew, G., Singh, R. ., Nair, N. . & Thomas, S. Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber. *Polymer.* **42,** 2137–2165 (2001).

[28] Mathew, A. P., Packirisamy, S. & Thomas, S. Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: thermogravimetric analysis. *Polym. Degrad. Stab.* **72,** 423–439 (2001).

[29] Sircar, A. K. Characterization of isomeric elastomers using thermal analysis. *J. Therm. Anal.* **49**, 293–301 (1997).

Part B

COMPATIBILIZATION OF SILICA FILLED NR/EPS BLENDS USING MALEIC ANHYDRIDE

3B.1 Introduction

Blending of elastomer and thermoplastic is an emerging field in polymer processing as the product could combine the desirable properties of individual polymers. However, most of the polymers are immiscible with poor adhesion to each other which results in unstable morphology. This leads to worsening of overall performance of the blend compared to individual polymers. Therefore, compatibilization of the blend is necessary to improve its properties to usable levels. Comatibilization is the technique which makes the blend components miscible or less immiscible to improve the performance of the blend. Compatibilized blends are characterized by technologically desirable properties due to the existence of a finely dispersed phase, good adhesion between blend phases and strong resistance to phase coalescence [1].

Addition of compatibilizers/interfacial agents to polymer blends affects the flow behaviour because of the interactions between the blend components via the blend compatibilization. This results in technologically useful engineering materials with improved physiomechanical properties [2-4]. The block and graft copolymers can be made separately before adding into the blend or can be generated in situ during the blend preparation [5-6]. However the usage of preformed copolymer limits the economic viability of blending.

Grafting reactions of reactive compatibilizers could induce significant changes in the chemical composition, polymer chain structure and molecular mass of the polymer chain. These parameters are responsible for the interactions between polymers. Maleic anhydride is one of the most widely used reactive compatibilizers due to good chemical reactivity, low toxicity, and low tendency to polymerize itself under free radical grafting conditions [7]. Other functional monomers used for this purpose are acrylic acid, methacrylic acid, glycidyl methacrylate, sulfonic acid etc. The effect of the addition of different compatibilizers such as bromobutyl rubber (BIIR) and maleic anhydride has been studied by Hamza et al. [8]. Grafting of natural rubber and nitrile rubber on to low density polyethylene has been performed successfully using acrylic acid and maleic anhydride [9]. The grafted compounds were found to be superior compared to nongrafted compounds in mechanical properties, chemical resistance, aging, and so on [10]. The incorporation of MA-functionalized polypropylene (PP-g-MA) as a compatibilizer in PP/ rubber blends [11] and toughening of PET using maleic anhydride grafted styrene-ethylene-butadiene-styrene (MA-g-SEBS) rubber were found to be the most effective [12-13]. The grafting performance by MA on SBS was reported by Lasalle et al. [14].

Though both NR and EPS are nonpolar materials, they exhibit poor adhesion between the interfaces and in this case compatibilization of the blend is required. Hence MA grafting was done for this purpose. From the previous section it is clear that silica is the best choice for NR/EPS blends because silica filled NR/EPS blend shows the best properties compared to black filled or gum NR-EPS blends. Also on employing MA in the blend, silica- polymer interaction [15] can be improved.

In this section, EPS has been incorporated in NR in two stages. First is the reactive blending of NR and EPS using maleic anhydride and second is the subsequent blending of this preformed copolymer with more of NR containing silica during vulcanisation. This study also uses cardanol as plasticiser [16], as an additional step to conserve fossil fuel based substances and utilizes a cheap agrobyproduct.

3B.2 Experimental

3B.2.1 Materials

The materials used are given in Section 2.1 of Chapter 2.

3B.2.2 Methods

3B.2.2.1 Compatibilization

The blending and compatibilization method is given in section 2.2.1. Mixing time, temperature and rpm are same as section 3A.2.2.1. Varying proportions (weight %) of MA with respect to the blend was used at a constant DCP concentration (12.5% with respect to MA). Then the amount of DCP was varied (weight % with respect to MA) at an optimum MA concentration. Finally, the blend ratio was changed by varying the EPS concentration. Blend with 0% MA and DCP referred to as nongrafted and others, grafted blends. Table 3B.1 is the blend formulation.

Table 3B.1. Blend formulation

Ingredients	Compositions		
	MA optimisation	**DCP optimisation**	**Blend ratio**
NR (phr)	35	35	35, 30, 15, 20
EPS (phr)	5	5	5, 10, 15, 20
MA (wt% of blend)	0*, 0.5, 1, 1.5, 2	1	1
DCP (wt% of MA)	12.5	7.5, 10, 12.5, 15, 17.5	15

* Non grafted blend without MA and DCP

3B.2.2.2 Compounding and curing

The compounding and curing was done according to the procedure given in Section 2. 2. 2 of chapter 2. At first 60g NR was masticated in a two roll mill for 3min and then mixed with the blend of NR and EPS already prepared in Brabender Plasticorder and the filler and other compounding ingredients. The compounding formulation used is given below in Table 3B. 2. The final blend compositions (NR/EPS) would be 95/5 for MA optimization, 95/5 for DCP optimization and 95/5, 90/10, 85/15 and 80/20 for EPS optimization.

Table 3B.2. The compounding formulation

Ingredients	Quantity (phr)
Natural rubber	100
ZnO	5
Stearic acid	2
Precipitated silica	15
Cardanol	1.5
DEG	1
SP	1
CBS	0.6
TMTD	0.1
Sulphur	2.5

A compound consisting of pure NR (without EPS, MA and DCP) and other ingredients was also prepared (known as the silica filled NR). Final cured compound containing grafted blend is referred to as compatibilized blend and that containing non-grafted blend is referred to as non-compatibilized blend. The compounds were cured in a hydraulic press at 150 °C after estimating the cure time in a Rubber Processing Analyzer (RPA 2000 Alpha Technologies, USA), as per ASTM D 2084-07 [17].

3B.2.2.3 Sample preparation for FTIR analysis

A detailed explanation of Fourier Transform Infrared Spectroscopy was given in Section 2.3.1.The blends obtained from Brabender Plasticorder were Soxhlet extracted for 48hours in water to remove unreacted MA. The nongrafted sample was solution cast using toluene as solvent. The solvent was evaporated in a hot air oven at 60 °C for 30 min before recording the IR spectra. The grafted sample was found to only swell in toluene. It was directly used for IR study after drying.

3B.2.3 Characterisations

A detailed explanation of characterisation techniques are given in Section 2.3 of chapter 2.

3B.3 Results and discussion

3B.3.1 Structure of MA grafted NR/EPS blend

The possible functionalization reaction of EPS and NR with MA are given below in Fig. 3B.1.

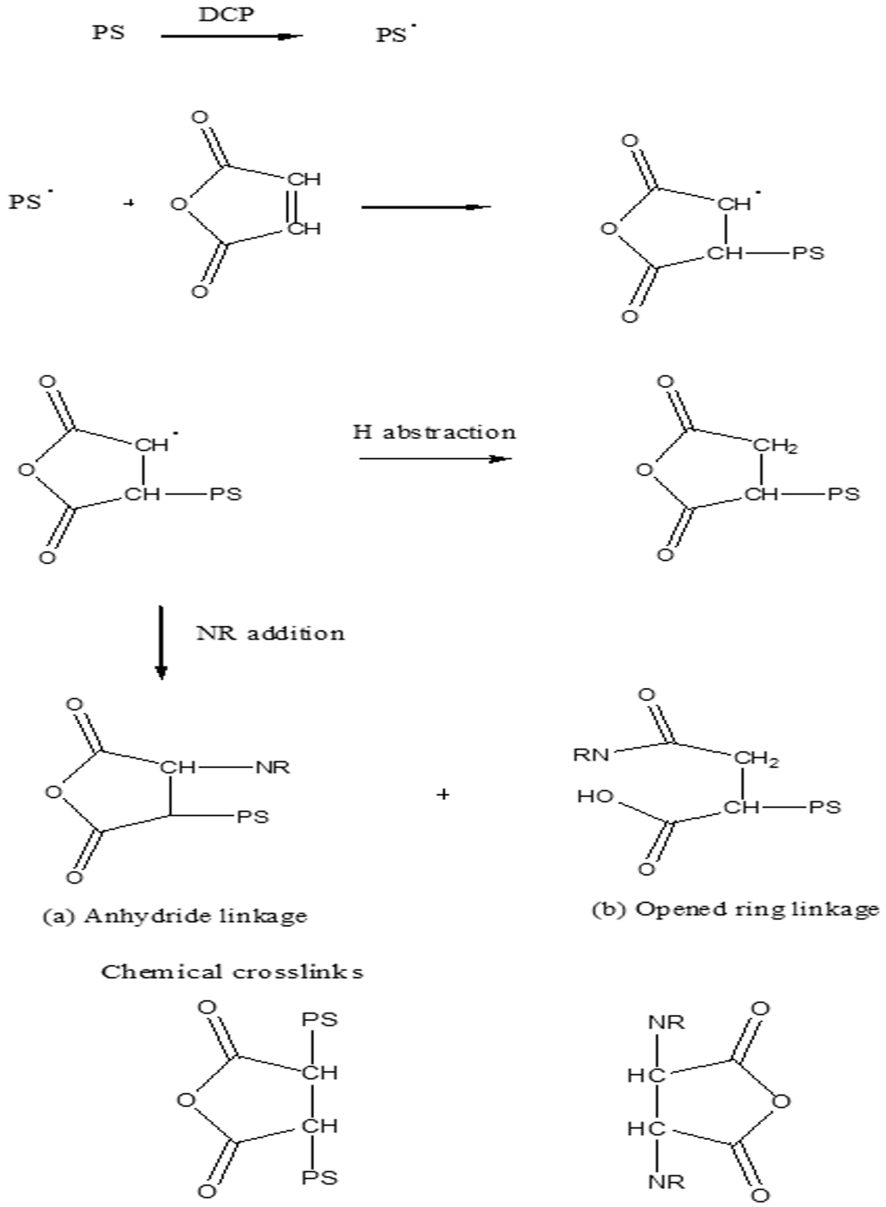


Fig. 3B.1. Possible functionalization reactions of EPS and NR with MA

A representative infrared spectra of the non-grafted and grafted NR/EPS blends with 1% MA are shown in Fig. 3B.2. An intense characteristic band at 1778 cm^{-1} and a weak absorption band at 1854 cm^{-1} are observed. These bands can be assigned to grafted anhydride rings. They are due to symmetric (strong) and asymmetric (weak) carbonyl (>C=O) stretching vibrations of succinic anhydride rings grafted on PS (polystyrene) and NR [18-20]. This proves the presence of grafted anhydride groups on the NR and PS chains.

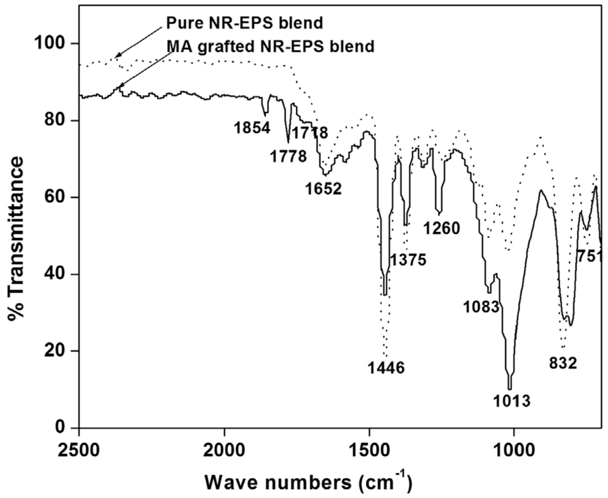


Fig. 3B.2. Infrared spectra of non-grafted NR/EPS blend and grafted NR/EPS blend with maleic anhydride

The small shoulder at 1718 cm^{-1} (the carbonyl stretching frequency of the acid group) in the spectrum of the grafted blend arises from the acid peak resulting from maleic anhydride modification. In general, the anhydride modification may result in anhydride or acid forms depending upon the addition or removal of water. Normal carbonyl group stretching frequency is 1760 cm^{-1} [21]. According to literature, the acid peak is indicated by 1714 cm^{-1} whereas the anhydride shows the absorption peaks at wavenumbers of 1789 cm^{-1} (strong) and 1864 cm^{-1} (weak) [22]. We can also notice the peaks corresponding to absorbances at 1652 cm^{-1} and 832 cm^{-1} due to the stretching of the -C=C- bond of the NR. The peak at 3026 cm^{-1} and 2868 cm^{-1} (not shown here) were assigned to the aromatic -C-H stretching of polystyrene. These peaks corresponding to -C-H stretching are slightly shifted and the intensities are reduced on addition of MA. The signals at 1375 cm^{-1} and 1446 cm^{-1} can be attributed to the aliphatic -C-H stretching in natural rubber [23]. The band at 1260 cm^{-1} corresponds to the -C-O-C- stretching in the ester moiety. These peaks suggest that the mechanism of grafting involves both the (a) anhydride linkage and (b) opened ring linkage [24]. Some possible chemical crosslinks are also shown in Fig. 3B.1, although a good many other reactions arising from the presence of one/two NR/PS chains cannot be ruled out in the grafted product with the anhydride ring intact or opened by cleavage.

Optimization of maleic anhydride in silica filled NR/EPS blends

3B.3.2 Cure characteristics

The rheographs of silica filled NR and NR/EPS blends with varying MA concentrations at 150 °C are shown in Fig. 3B.3. The highest torque is exhibited by pure silica filled NR and the torque decreases for the blends. The low torque value for the blends is associated with the low viscosity of the PS phase compared to NR at the cure temperature. Unattached PS chains can also reduce the cohesion of the rubber matrix by hindering the sulphur crosslinks although at some stage the compatibilized blend may attain somewhat higher torques because of the interlinking of different polymer chains. The latter effect is presumably of low magnitude considering that NR exhibits a still higher value of torque.

The degradation during the blending process lowers the molecular weight of rubber. This can also be a reason for the lower torque associated with the blend.

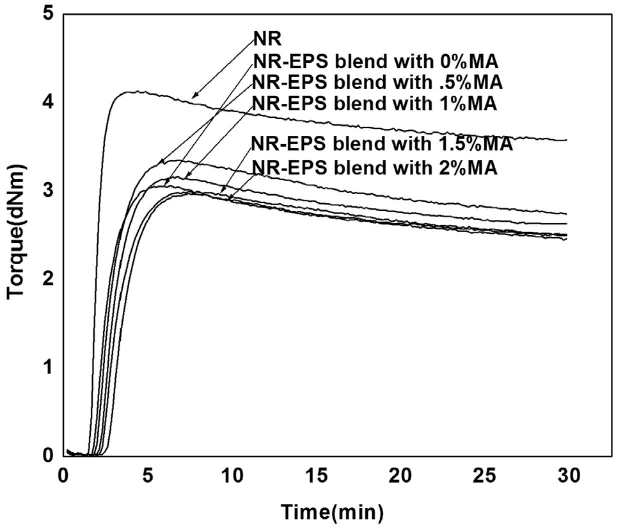


Fig. 3B.3. The rheographs of silica filled NR and NR/EPS blends with varying MA concentrations at 150 °C

The processing characteristics of silica filled NR and silica filled NR/EPS blends are given in Table 3B.3. The cure time and scorch time are higher for blends than for NR and increase with increasing MA content. The compatibilized compounds display significantly longer scorch and cure times compared to NR, as shown in Table 2 due to (1) the presence of acid groups from the ring opening of succinic anhydride groups (2) the presence of PS chains and (3) the possible interlinking of polymer chains. The acid groups can deactivate the accelerators and the zinc complex. Therefore, the vulcanization reaction is retarded [25]. The decreased cure rate index for the blends compared to pure NR also suggest a deceleration of the crosslinking reaction.

Table 3B.3. Processing characteristics of silica filled NR and silica filled NR/EPS blends.

Cure characteristics	NR	NR/EPS (0%MA)	NR/EPS (0.5%MA)	NR/EPS (1%MA)	NR/EPS (1.5%MA)	NR/EPS (2%MA)
Min Torque, M_L (dNm)	0.01	0.01	0.01	0.01	0.02	0.01
Max Torque, M_H (dNm)	4.13	3.06	3.35	3.16	3.00	2.97
Scorch time, t_2 (min)	1.56	1.55	2.05	2.19	2.28	2.48
Cure time, T_{90} (min)	3.37	3.46	4.13	4.21	4.50	4.59
Cure rate index (min^{-1})	55.25	52.36	48.08	49.51	45.05	47.39

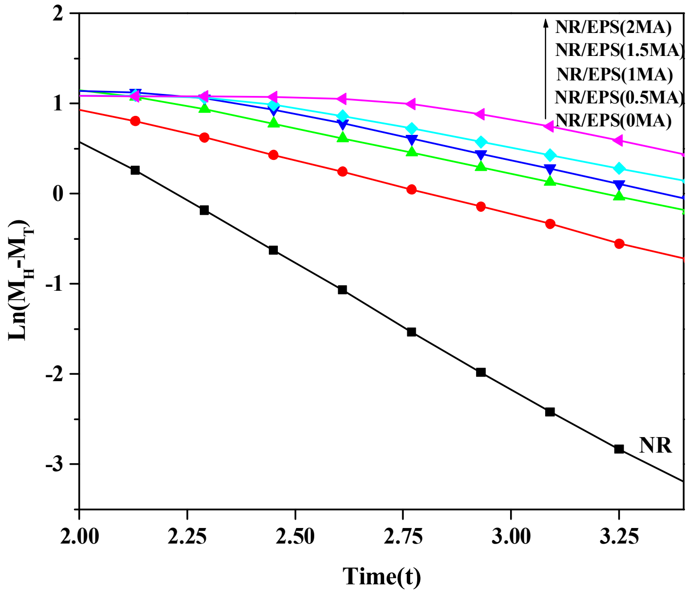


Fig. 3B.4. Cure kinetics plot of Ln (M_H –M_t) vs. time for silica filled NR and NR/EPS blends with varying MA concentrations

A cure kinetics plot of Ln ($M_H - M_t$) vs. time for silica filled NR and NR-EPS blends with varying MA concentrations at 150 °C is presented in Fig. 3B.4. The plots are found to be linear which proves that the cure reactions proceed according to first order kinetics. The nature of slopes shows some reduction in cure rate constant upon addition of EPS. The compatibilization further decreases the kinetic rate constants suggesting the deceleration of cure reaction [26].

3B.3.3 Strain-sweep studies

Storage modulus Vs strain curves of uncured silica filled NR and 95/5 NR/EPS blends with varying MA concentrations are depicted in Fig. 3B.5. All compounds exhibit low modulus value due to the incompatibility between polar silica and non-polar rubber.

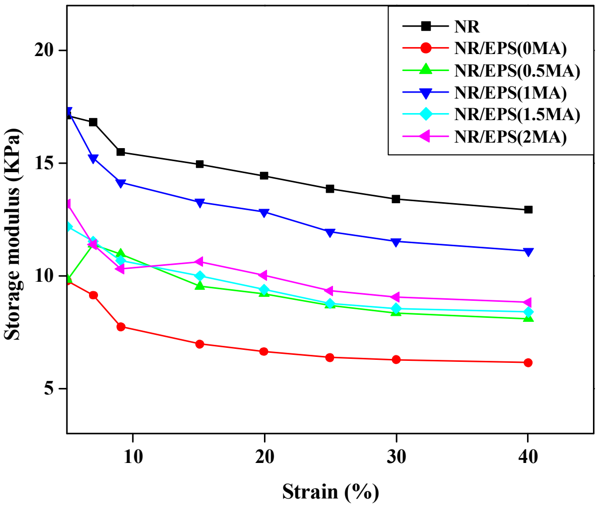


Fig. 3B.5. Storage modulus Vs strain curves **of uncured silica filled NR and 95/5 NR/EPS blends with varying MA concentrations**

Silica filled NR shows the maximum modulus over the entire range of strain (%) compared to blends. This is due to the presence of EPS in the blends. The silica filled NR/EPS blend without MA shows the least modulus. The inclusion of MA increases the modulus and higher modulus is observed at an optimum 1% MA. The enhanced modulus at high strain indicates a better filler-polymer interaction [27]. The presence of MA in the blend develops some polarity and this leads to better interaction with the polar filler.

3B.3.4 Mechanical properties

3B.3.4.1 Tensile properties

Fig. 3B.6 is the typical stress-strain curves for the NR and NR/EPS blends with various MA concentrations. The variation of tensile properties with MA content in the blends is shown in Fig. 3B.7. The properties of silica filled NR, non-compatibilized blend and compatibilized blend with optimum MA is given in Table 3B.4.

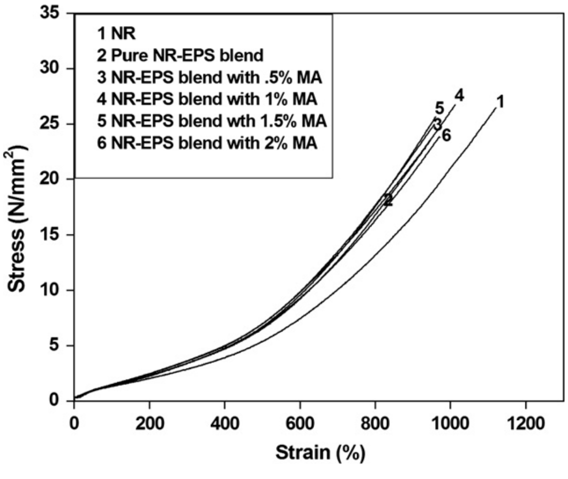


Fig. 3B.6. Stress-strain curves for NR and NR/EPS blends with various MA concentrations.

The incorporation of EPS directly to NR showed a reduction in tensile strength and elongation at break. The elongation for blends is less than that of pure NR due to some loss of elasticity. But, for the compatibilized blends the above properties are enhanced.

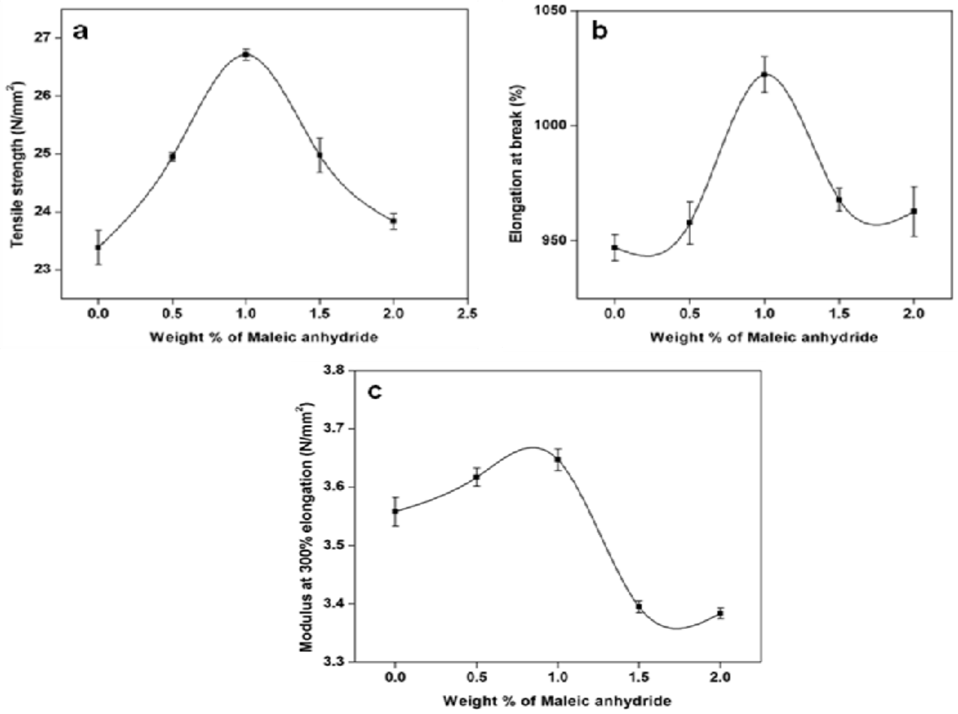


Fig. 3B.7. Tensile properties of compatibilized and non-compatibilized blends

The tensile properties reflect an improved degree of silica dispersion in the case of compatibilized blend as evidenced in the morphology (Fig. 3B.13). The addition of 1% MA in the blend improves the tensile strength (Fig.3B.7a) by about 14% and the elongation at break by 8% (Fig.3B.7b) compared to blends without MA. These values are comparable with that of NR alone. The probable reasons for this have already been cited under the discussion on FTIR results.

The addition of the compatibilizer enhances the favourable interactions at the interface. The interfacial tension reduces, thereby improving adhesion between the components as well as between the filler and the polymer matrix which enhances the tensile strength of the blends [4,10]. Moreover, it has been reported that silica filled NR shows better properties on MA grafting [15]. The modulus at 300% elongation (Fig.3B.7c) of the blends shows an improvement compared to NR. The blends show a maximum of 26.45% improvement in the modulus at 300% over that of NR. The tensile properties for the blends reach a maximum at an optimum concentration of ca.1%. It is observed that tensile properties of the blends at higher MA concentrations decrease. This may be due to an excess of MA at the interface which creates an energetically unbalanced design [4]. This will affect the interfacial adhesion between the components. A higher loading of MA can cause some adverse reactions such as homopolymerisation, resulting in the decrease of mechanical properties [28]. However, if the loading of MA is less than 1%, sufficient maleic free radicals would not be present for the grafting reaction.

Table 3B.4. Mechanical properties of silica filled NR and silica filled NR/EPS blends

Properties	**Silica filled NR**	**Non-compatibilized blend**	**Compatibilized blend**
Tensile strength(N/mm^2)	26.45	23.39	27.72
Elongation at break (%)	1120.08	947.16	1096.67
Modulus at 300% (N/mm^2)	2.88	3.56	2.96
Tear strength(N/mm)	46.23	51.18	58.18

It is interesting to note that at the optimum MA concentration, the tensile strength of the compatibilized blend is equal to that of NR even when the blend contains 5% EPS. The succinic anhydride groups grafted onto NR and EPS molecules enhance the polarity of the blend and an interaction between the succinic anhydride groups and the hydroxyl groups on silica surface is quite likely [15]. Similar interactions between the hydroxyl and maleic anhydride groups have previously been proposed such as in the cases of PP-g-MA/nano-silica [29] and maleated NR/paper sludge filler [30] systems. The polar interactions due to hydrogen bonds between the hydroxyl groups on the silica surface and the carboxyl groups of the grafted molecules or the hydroxyl group of the succinic acid improve the compatibility between rubber and silica and reduce filler aggregation. As a consequence there is an increase in the degree of filler dispersion which aids in improving the properties.

3B.3.4.2 Tear strength

Fig.3B.8 shows the variation of tear strength with MA content in NR/EPS blends. There is considerable improvement (~28%) at 1% MA compared to silica filled NR (not containing MA and EPS). As the filler agglomeration is less for compatibilized blends, the filler particles can be properly wet by macromolecules and hence adhesion between the filler and matrix improves. Thus, the energy required to propagate a crack increases, resulting in higher tear strength [31]. Improved dispersion of filler particles offers increased resistance to crack propagation. The values show a decreasing tendency as the MA concentration further goes up.

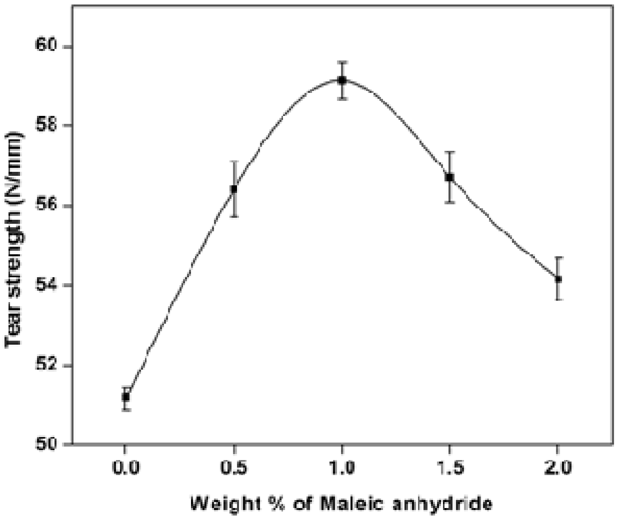


Fig. 3B.8. Variation of tear strength with MA content in NR/EPS blends

3B.3.4.3 Aging studies

Fig. 3B.9 shows the tensile properties of the unaged and aged samples of NR, and non-compatibilized and compatibilized NR/EPS blends. The aging data of tensile properties is shown in Table 3B.5. The data imply that aging deteriorates the properties of NR and NR/EPS blends (both compatibilized and non-compatiblized) practically to the same extend in all cases, especially the samples aged at 100 ^{o}C indicating thermal degradation. This is because of the oxidation reactions in rubber resulting in chain scission [32].

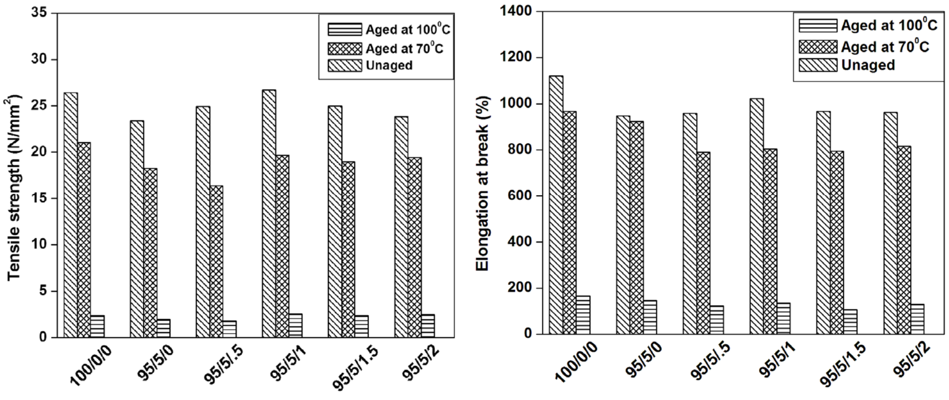


Fig. 3B.9. Tensile properties of the unaged and aged samples of NR, and non-compatibilized and compatibilized NR/EPS blends

Table 3B.5. Aging data of NR, non-compatibilized and compatibilized NR/EPS blends

Samples	**% reduction of tensile strength**		**% reduction of elongation at break**	
	Aged at 70°C	**Aged at 100°C**	**Aged at 70°C**	**Aged at 100°C**
NR	20.41	91.00	13.62	85.14
NR/EPS (0% MA)	21.95	91.63	12.56	84.53
NR/EPS (0.5% MA)	34.43	92.70	17.59	87.19
NR/EPS (1% MA)	26.34	90.39	21.36	86.77
NR/EPS (1.5% MA)	23.96	90.51	17.92	88.94
NR/EPS (2% MA)	18.50	89.73	15.31	86.50

3B.3.4.4 Miscellaneous properties

Compression set, abrasion loss, resilience and hardness of NR along with non-compatibilized and compatibilized NR/EPS blends are tabulated below (Table 3B.6). The ability to retain the elastic properties under prolonged action of compressive stress at some higher temperature is an important property to be considered for certain applications. Majority of applications prefer materials with low compression set values. The percentage of compression set was found to be higher for the blends compared to NR. There was no significant variation among the blends. The high compression set values for the blends were attributed to the presence of EPS, which affects the mobility of rubber chains, inducing some resistance to recovery in the material [33].

Abrasion resistance is the ability of a material to resist mechanical action such as rubbing or erosion [34]. The abrasion properties of vulcanizates depend on their physiomechanical properties, such as strength, hysteresis, hardness, fatigue, modulus of elasticity, etc. An enhancement of 27% in abrasion resistance was observed for the blend containing 1% MA over that of silica filled NR alone. When compared with non-compatibilized blend this represents an improvement of 36.5%. This improved abrasion resistance is associated with better filler-rubber interaction. Fine particles with uniform distribution give rise to greater interface between the filler and the rubber matrix and, hence, provide a better abrasion resistance [35].

A significant improvement in surface hardness was observed for all the blends due to the higher hardness of PS. The compatibilized blends showed much better hardness than the non- compatibilized blend because the PS phase was well incorporated in the rubber matrix.

The resilience values of the blends were found to be comparable with NR though the non-compatibilized blend shows a slight reduction. The is because, the chance of energy dissipation is more in the case of non-compatibilized blends compared to compatibilized blends [36]. The overall properties suggest that MA can be used as a reactive compatibilizer in NR/EPS blends there by facilitating the incorporation of EPS to NR without sacrificing the properties of NR.

Table 3B.6. Compression set, Abrasion loss, Resilience and Hardness of NR, non-compatibilized and compatibilized NR/EPS blends

NR/NR-EPS blends	Miscellaneous properties			
	Compression set (%)	Abrasion loss (cc/hr)	Resilience (%)	Hardness (Shore A)
NR	24.0	4.74	57	47
NR/EPS (0% MA)	32.3	5.44	56	51
NR/EPS (0.5% MA)	30.8	4.88	57	53
NR/EPS (1% MA)	29.2	3.45	58	53
NR/EPS (1.5% MA)	32.7	5.55	58	52
NR/EPS (2% MA)	30.4	5.87	58	52

3B.3.5 Swelling studies

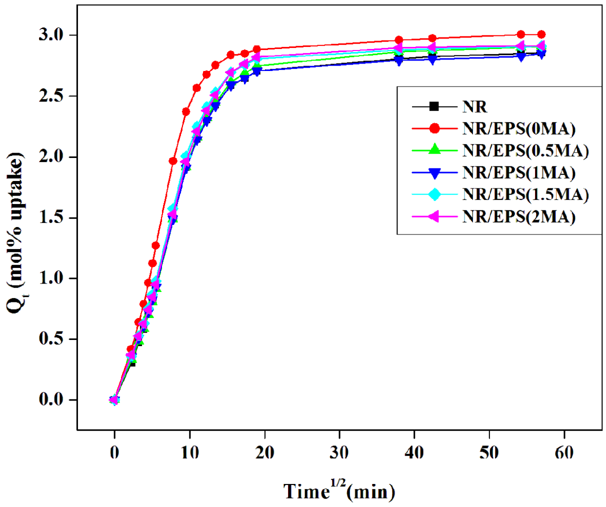


Fig. 3B.10. The mol% uptake of solvent by silica filled NR and NR/EPS blends with varying MA content

The mol% uptake of toluene by silica filled NR and NR/EPS blends with varying MA content is presented in Fig. 3B.10. The percentage of swelling index and crosslink densities are given in Table 3B.7. Composition, miscibility and phase morphology are the determining parameters of solvent transport through polymer blends [37]. Initially, the toluene uptake was high for all the compounds and after a certain time equilibrium is achieved resulting in slower sorption. NR and compatibilized blends show lower toluene uptake compared to non-compatibilized blends. The mol % uptake of the blend with 1% MA is found to be close to silica filled NR.

Table 3B.7. The percentage of swelling index and crosslink densities of silica filled NR and NR/EPS blends with varying MA content

Samples	Swelling index (%)	Crosslink density ($\times 10^{-5}$ gmol/cc)
NR	290.30	9.79
0% MA	312.47	8.73
0.5% MA	295.20	9.40
1% MA	289.76	9.75
1.5% MA	296.13	9.35
2% MA	296.02	9.30

Decrease in solvent (toluene) sorption of the compatibilized blend compared to non-compatibilized blend is evident from swelling index data. The presence of MA in the blend restricts the penetration of nonpolar solvent and hence lowers the swelling index. At 1%MA the blend shows the lowest swelling index and the value is comparable to NR. The crosslink density is also lowest for the non-compatibilized blend.

These results are in agreement with the stress-strain properties discussed earlier.

3B.3.6 Thermogravimetric analysis

Fig. 3B.11 shows the TG (a) and DTG (b) curves of NR, non-compatibilized NR/EPS blend and compatibilized NR-EPS (1%MA). Vulcanised NR and pure PS have almost the same thermal stability [38]. They both degrade in the temperature range of 300–400 °C.

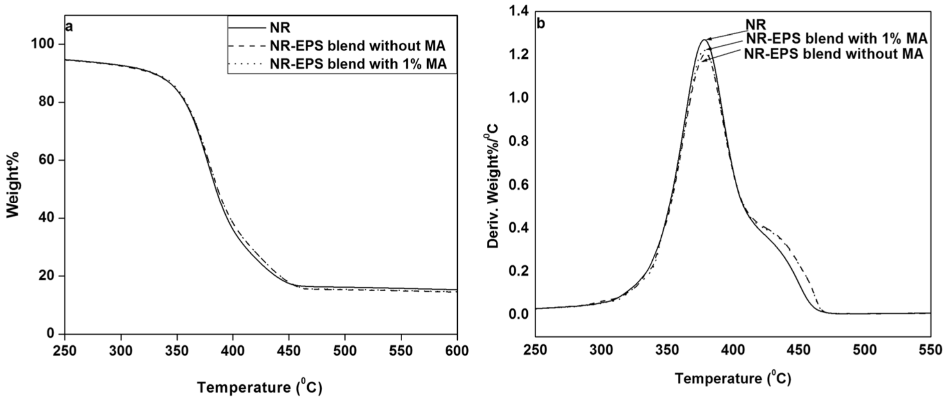


Fig. 3B.11. TG (a) and DTG (b) curves of NR, non-compatibilized NR/EPS blend and compatibilized NR-EPS (1%MA).

The curves indicate that the decomposition ranges from approximately 300 °C to 450 °C with a mass loss of about 85%, which can be assigned to the thermal decomposition of natural rubber into monomers, dimers, trimers, etc. in inert atmosphere. A small shoulder can be observed in the DTG curves at approximately 410 °C attributable to cross linked and cyclised networks which degrade at higher temperature [39]. The temperature of the maximum mass loss rate from the DTG curves is around

378 °C for all the three cases. The temperature at which 50% decomposition occurs is generally considered as an index of thermal stability. Our results have shown that this temperature for NR is 384 °C and for blends it is 386.5 °C indicating a comparable thermal stability upon the addition of EPS to NR. Table 3B.8 shows the TGA data for NR, non-compatibilized NR/EPS blend and compatibilized NR/EPS blend (1%MA). The results suggest that blends have thermal stability on par with NR.

Table 3B.8. TGA data for NR, non-compatibilized NR/EPS blend and compatibilized NR/EPS blend (1%MA)

Property	**NR**	**Non-compatibilized NR/EPS blend**	**Compatibilized NR/EPS blend**
Onset degradation temperature (^{0}C)	310.9	311.4	313.9
Maximum degradation temperature (^{0}C)	379.4	379.4	379.4
End set degradation temperature (^{0}C)	468.7	468.6	468.8
Temperature (^{0}C) at 5% degradation	240.0	235.9	238.4
Temperature (^{0}C) at 50% degradation	384.8	386.5	386.5
Residue (%) at 650 ^{o}C	14.9	14.1	14.2

3B.3.7 Differential scanning calorimetry

Fig. 3B.12 shows DSC curves of NR, non-compatibilized blend and compatibilized blend. Many of the important technical properties of elastomers such as resilience and abrasion resistance can be correlated to *T*g [40]. DSC provides information concerning the glass transition, a second order event which manifests itself in a DSC curve as a step change corresponding to the change in the heat capacity of the system. The DSC curves exhibit shift in baseline corresponds to a temperature of approximately −61 ◦C, which are attributable to the glass transition temperature of natural rubber. There are no significant differences among the *T*g values of NR and NR-EPS blends.

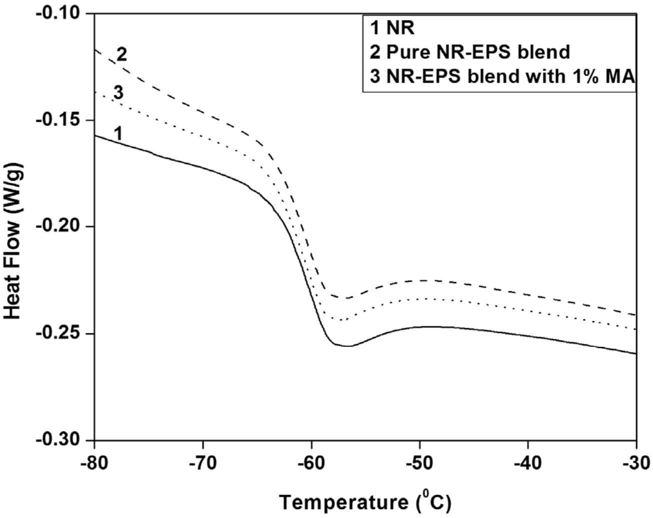


Fig. 3B.12. DSC curves of NR, non-compatibilized blend and compatibilized blend (1% MA).

3B.3.9 Scanning electron microscopy (SEM)

The SEM images of the tensile fractured surfaces of silica filled (a) NR, (b) non-compatibilized and (c) compatibilized (1% MA) NR/EPS blends are presented in Fig. 3B.13. The dispersed objects present in the images can be silica particles. In the case of non-compatibilized and compatibilized NR/EPS blends some additional particles are present due to the EPS phase. Here the minor EPS phase with a lower viscosity compared to NR is dispersed in the NR matrix as small spherical particles [41].

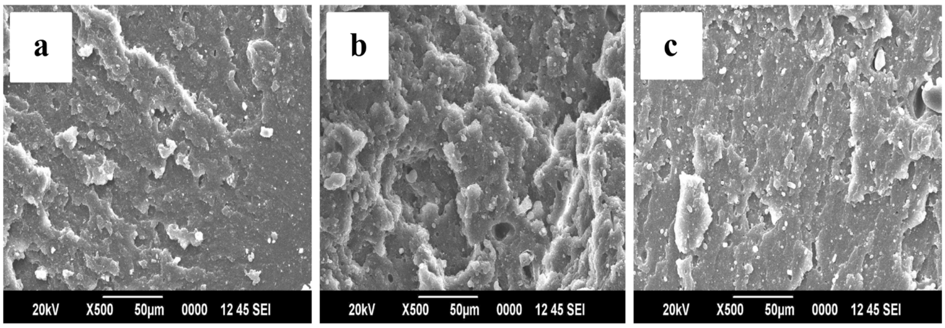


Fig. 3B.13. SEM images of the tensile fractured surfaces of silica filled (a) NR, (b) non-compatibilized and (c) compatibilized (1% MA) NR/EPS blends

A surface roughness associated with a non uniform phase morphology is observed in non-compatibilized blend. But a fine and more uniform phase distribution is exhibited by the MA compatibilized blend sample. In compatibilized blend, uniform distribution, size reduction and less pull out of the minor phase are found [4]. Because of the fine dispersion of EPS phase in the NR matrix alters the crack path giving resistance to crack propagation. The unidirectional ripples present in the SEM of compatibilized blend are an indication of compatibility between the components [42]. The SEM results are in conformity with the improvement in mechanical properties of the compatibilized NR/EPS blends.

The overall properties suggest an MA concentration of 1% to be optimum for NR/EPS blends.

Optimisation of DCP as initiator

3B.3.10 Cure characteristics

The rheographs of silica filled (95/5) NR/EPS blends (with optimum MA, 1% and varying DCP concentrations based on MA content) at 150 °C are shown in Fig. 3B.14. The decreasing plateaus of the torque for all compounds indicate the thermal instability of the crosslinks formed. The torque value increases with DCP concentration due to increasing crosslinks. This reaches a maximum and then decreases. The highest torque is exhibited by the blend contains 15% DCP and is considered as the optimum radical concentration, which depends on monomer/initiator ratio. Beyond this, the graft content levels off and termination starts [43] and hence a drop in torque is observed.

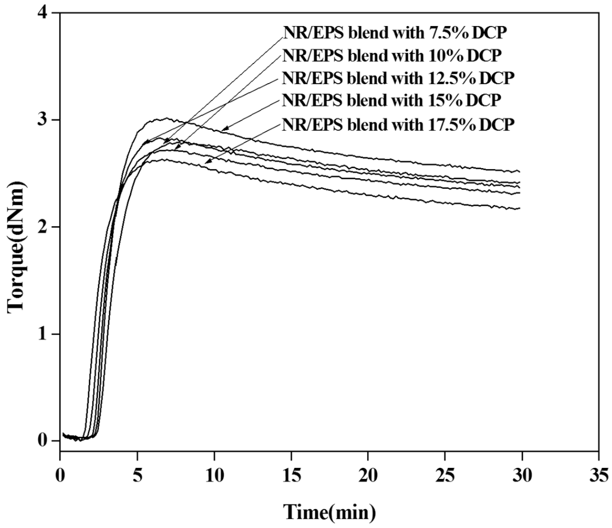


Fig. 3B.14. Rheographs of silica filled (95/5) NR/EPS blends (with optimum MA, 1% and varying DCP concentrations based on MA content) at 150°C

The processing characteristics of silica filled (95/5) NR/EPS blends (with optimum MA) at varying DCP concentrations at 150 °C is given in Table 3B.9. The cure time decreases with DCP concentration. Higher the amount of DCP, greater the free radicals formed for grafting, and improved compatibility between NR and EPS results. Moreover, at higher initiator level the excess unreacted DCP facilitates the peroxide curing of NR results in an enhanced cure rate suggesting the acceleration of the crosslinking reaction.

Table 3B.9. The processing characteristics of silica filled (95/5) NR/EPS blends (with optimum MA) at varying DCP concentrations at 150 °C

Cure characteristics	NR/EPS (7.5% DCP)	NR/EPS (10% DCP)	NR/EPS (12.5% DCP)	NR/EPS (15% DCP)	NR/EPS (17.5% DCP)
Min Torque, M_L (dNm)	0.02	0.01	0.01	0.02	0.01
Max Torque, M_H (dNm)	2.73	2.79	2.83	3.02	2.63
Scorch time, t_{10} (min)	2.26	2.05	2.20	2.31	1.46
Cure time, T_{90} (min)	5.07	4.21	4.22	4.19	3.59
Cure rate index (min^{-1})	35.58	46.30	49.51	53.19	46.95

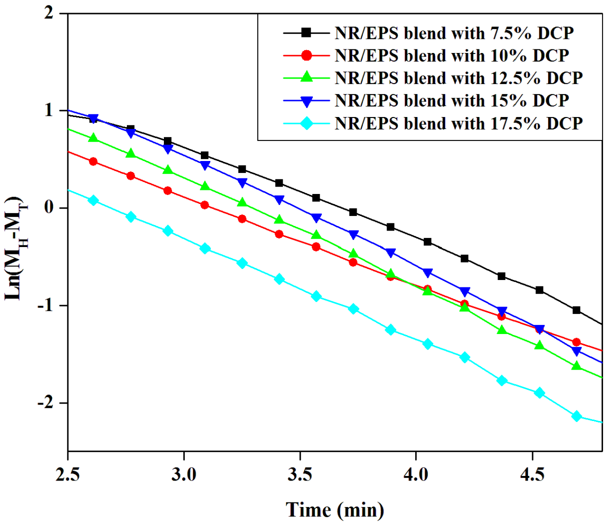


Fig. 3B.15. Plot of Ln (M_H –M_t) vs. time for silica filled NR/EPS blends with varying DCP concentrations

The cure kinetics plot of Ln (M_H –M_t) vs. time for silica filled NR/EPS blends with varying DCP concentrations at 150 °C is presented in Fig. 3B.15. The plots are found to be linear which proves that the cure reactions can be approximated to first order kinetics. The nature of slopes reveals the improvement of cure rate at higher DCP content suggests an accelerating effect on cure reaction [26].

3B.3.11 Strain-sweep studies

Storage modulus Vs strain curves of uncured silica filled (95/5) NR/EPS blends with varying DCP concentrations are depicted in Fig. 3B.16. On increasing the strain, a large decrease in modulus was observed at lower DCP concentrations. At 15% DCP concentration the blend shows enhanced modulus compared to others indicating a better filler-polymer interaction [27].

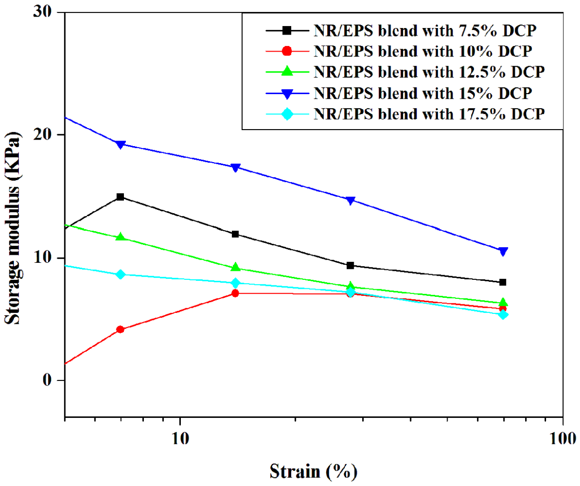


Fig. 3B.16. Storage modulus Vs strain curves of uncured silica filled (95/5) NR/EPS blends with varying DCP concentrations

3B.3.12 Mechanical properties

3B.3.12.1 Tensile properties

The tensile properties of silica filled (95/5) NR/EPS blends with varying DCP concentrations are shown in Fig. 3B.17 (tensile strength and elongation at break) and Fig. 3B.18 (modulus at 300% elongation). The tensile properties were found to increase, reach a maximum and then deccrease on further addition of DCP. A significant increase in tensile strength (12%), and modulus (26%) were observed for the blend with15% DCP. Elongation at break showed a marginal improvement.

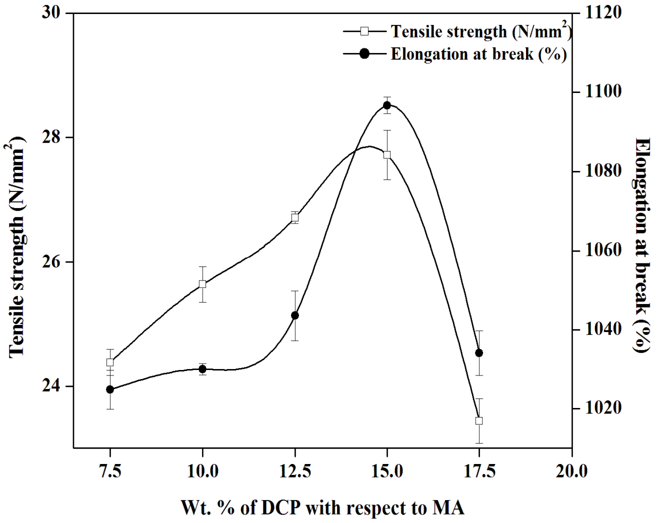


Fig. 3B.17. Tensile strength and elongation at break of silica filled (95/5) NR/EPS blends with varying DCP concentrations

During blending the peroxide initiator facilitates the maleic anhydride grafting/crosslinking of NR/EPS blend *in situ*. This results in improved compatibility between the phases. Improved properties are associated with enhanced interaction between the phases. But higher loading of DCP decreases the tensile properties. This is because of the degradation of the polymer chain induced by high levels of initiator loading and resultant lowering of the molecular weight [28]. On the other hand, if concentration of the initiator used is too low, it would be difficult to produce adequate amount of free radicals required for effective grafting/crosslinking. Consequently, poor interaction between the blend components occurs and the properties worsen.

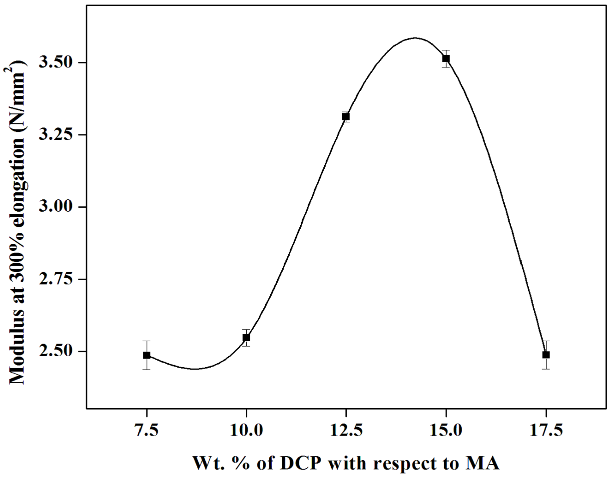


Fig. 3B.18. Modulus at 300% elongation of silica filled (95/5) NR/EPS blends with varying DCP concentrations

3B.3.12.2 Tear strength

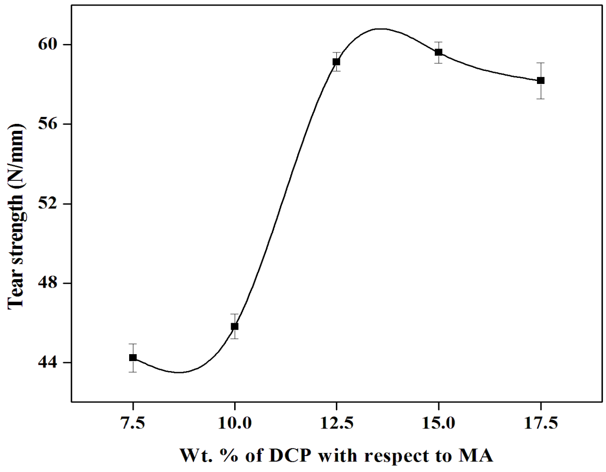


Fig. 3B.19. Tear strength of silica filled (95/5) NR/EPS blends with varying DCP concentrations

The effect of DCP loading on the tear strength of silica filled (95/5) NR/EPS blends is shown in Fig. 3B.19. The tear strength was found to be increasing on DCP loading upto 15% and then decreasing. A drastic elevation in tear strength was observed at 10% DCP. An impressive 35% improvement in tear strength was attained for the blend with 15% DCP loading. Better interaction between the phases due to sufficient amount of free radicals is the reason for superior properties at a particular initiator level. A detailed explanation is given under tensile properties.

3B.312.3 Aging studies

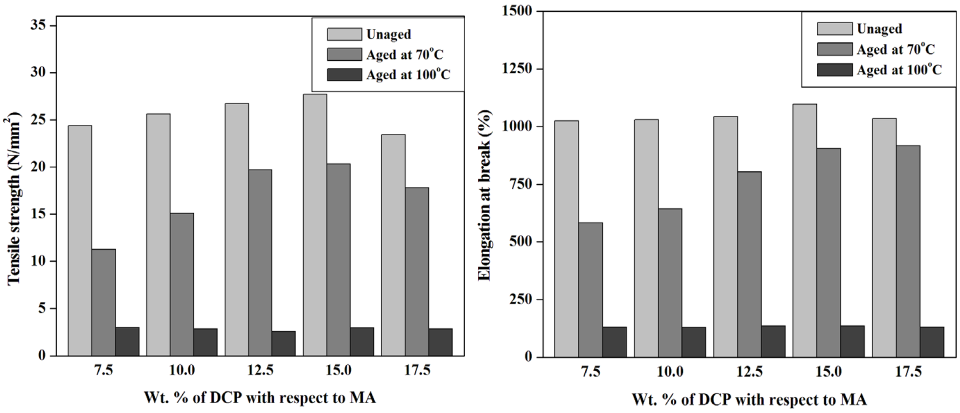


Fig. 3B.20. Tensile properties of the unaged and aged samples of compatibilized 95/5 NR/EPS blends with varying DCP concentrations.

Fig. 3B.20 is the graphical representation of tensile properties of the unaged and aged (at 70 °C and 100 °C for 72h) samples of compatibilized 95/5 NR/EPS blends with varying DCP concentrations. The percentage reduction of tensile properties is shown in Table 3B.10. The data implies that aging deteriorates the properties of all the compounds indicating thermal degradation of the crosslinks, especially at elevated temperature.

This is because rubber undergoes oxidation reactions resulting in chain scission [32]. The percentage reduction of tensile strength and elongation at break on aging at 70 °C was found to be decreasing with DCP loading. This can be explained on the basis of improved compatibility between the phases through improved grafting/crosslinking.

Table 3B.10. The percentage reduction in tensile properties of aged samples of 95/5 NR/EPS blends

Amount of DCP (wt. % of MA) in NR/EPS blend	% reduction of tensile strength		% reduction of elongation at break	
	Aged at 70°C	Aged at 100°C	Aged at 70°C	Aged at 100°C
7.5%	53.72	87.57	43.09	87.22
10%	41.13	88.86	37.59	87.46
12.5%	26.34	90.39	22.96	87.04
15%	26.68	89.26	17.49	87.61
17.5%	24.08	87.75	11.35	87.36

3B.3.12.4 Miscellaneous properties

Table 3B.11. Effect of DCP loading on compression set, abrasion loss, resilience and hardness of silica filled compatibilized NR/EPS blends

Concentration of DCP with respect to MA	Miscellaneous properties			
	Compression set (%)	Abrasion loss (cc/hr)	Resilience (%)	Hardness (Shore A)
7.5%	34.3	4.75	57	53
10%	32.2	4.10	57	53
12.5%	29.2	3.45	58	53
15%	26.4	3.41	59	54
17.5%	38.6	3.61	57	52

Effect of DCP loading on compression set, abrasion loss, resilience and hardness of silica filled compatibilized NR/EPS blends are tabulated above (Table 3B.11). The percentage of compression set was found to be decreasing with DCP. This is due to the improvement in compatibility between the phases. At higher DCP level the compound become stiffer and the compression set increases due to low mobility of polymer chains. During compression, the crosslinked chains try to resist the force and hence some of the crosslinks may break [33]. When the force is released there will be only a few crosslinks responsible for the strain recovery. Therefore, the compound cannot recover its initial thickness. If there is sufficient crosslinks for strain recovery the percentage of compression set will be lower.

An improvement in abrasion resistance was observed with DCP content and it reaches a maximum at 15% DCP concentration. This is because there is an optimum DCP percentage to produce sufficient free radicals for grafting, which results in better compatibility between NR and EPS through maleic anhydride, forming a polar blend. Hence silica filler can effectively interact with the matrix and consequently, the abrasion loss was found to be improved [35].

A marginal variation in surface hardness was observed for the blends on DCP loading of 15% and 17.5%. This variation is due to the difference in crosslink density of the blends. The highest percentage of resilience was observed at the optimum 15% DCP level. Higher elasticity due to better crosslinking may be the reason for this.

3B.3.13 Swelling studies

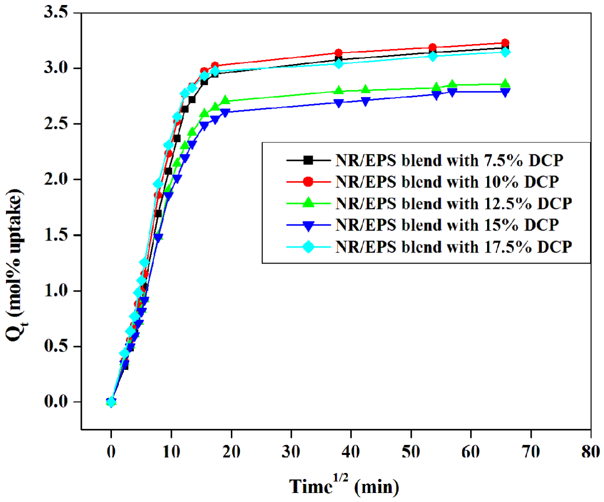


Fig. 3B.21. Solvent uptake by 95/5 compatibilized NR/EPS blends with varying DCP content

The solvent uptake by 95/5 compatibilized NR/EPS blends with varying DCP content is shown in Fig. 3B.21. The percentage of swelling index and crosslink densities are given in Table 3B.12. The initial toluene uptake was high for all the compounds, but becomes less with time finally reaching an equilibrium. The trend is similar for all DCP concentrations. The blend with15% DCP loading showed the lowest mol% uptake during the period. This is attributed to the crosslink density and enhanced interaction between the phases [44]. The enhanced matrix –filler interaction and NR-EPS compatibility reduces the mobility of matrix chain and makes it more difficult for toluene to penetrate [45]. Though there is not much variation in crosslink densities, a slight improvement was noticed at the 15% DCP level. The swelling index was found to decrease with DCP %. This proves the lower solvent uptake at higher

DCP levels. These results are in agreement with the stress-strain properties discussed earlier.

Table 3B.12. The percentage of swelling index and crosslink densities of 95/5 compatibilized NR/EPS blends with varying DCP content

Wt. % of DCP with respect to MA	Swelling index	Crosslink density ($\times 10^{-5}$ mol/cc)
7.5DCP	297.62	9.41
10DCP	296.85	9.51
12.5DCP	289.76	9.75
15DCP	289.35	9.98
17.5DCP	293.86	9.53

3B.3.14 Thermogravirmetric analysis

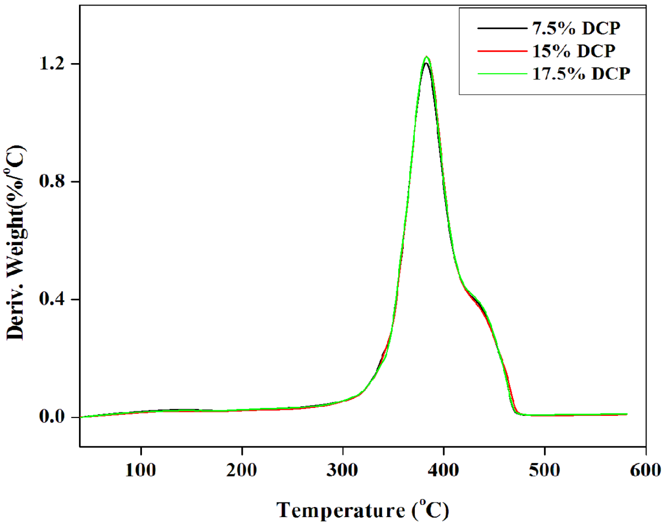


Fig. 3B.22. DTG curves of silica filled NR/EPS blend containing three DCP concentrations

Fig. 3B.22 shows the DTG curves of silica filled NR/EPS blend containing three DCP concentrations. The temperature of the maximum mass loss rate obtained from the DTG curves 383 °C for all the three cases. The temperature at which 50% decomposition occurs, which is generally considered as an index of thermal stability is the same for all three cases indicating no change in thermal stability upon DCP variation. Table 3B.13 shows the TGA data for silica filled NR/EPS blend with various DCP %. The results suggest that variation of DCP content in compatibilized NR/EPS blend do not alter the thermal degradation.

Table 3B.13. TGA data for silica filled compatibilized NR/EPS blend with various DCP content

Property	NR/EPS blend (7.5%DCP)	NR/EPS blend (15%DCP)	NR/EPS blend (17.5%DCP)
Onset degradation temperature (°C)	313.5	313.9	313.9
Maximum degradation temperature (°C)	382.9	383.1	383.3
End set degradation temperature (°C)	467.4	468.8	467.1
Temperature (°C) at 5% degradation	260.6	283.9	266.5
Temperature (°C) at 50% degradation	391.4	392.1	391.3
Residue (%)	15.5	15.8	14.8

3B.3.15 Scanning electron microscopy

The scanning electron micrographs of the tensile fractured surfaces of silica filled NR/EPS blends at two different DCP concentrations viz. (a) 12.5% and (b) 15% are presented in Fig. 3B.23. Since the minor phase is EPS with a lower viscosity compared to NR, it is dispersed in the NR matrix as small spherical particles [41]. Silica particles are also present in both the SEM images.

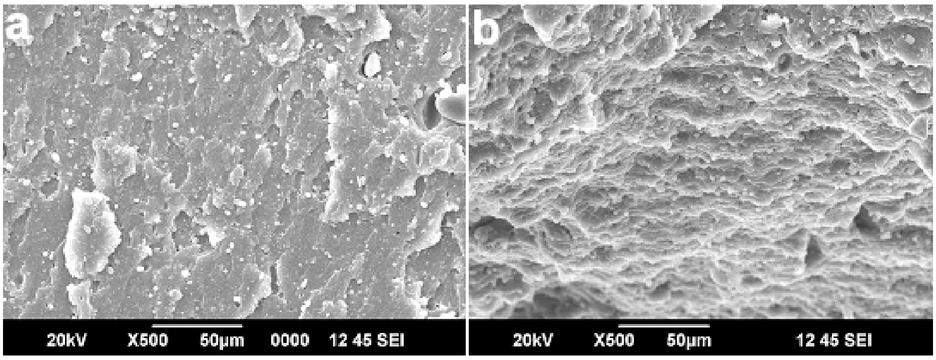


Fig. 3B.23. The scanning electron micrographs of the tensile fractured surfaces of silica filled NR/EPS blends at 12.5% (a) and 15% (b) DCP concentrations.

A considerable difference was observed in the morphology of both samples. Brittle fracture morphology was found for the blend with 12.5% DCP, but the morphology of the blend with15% DCP is found to be of a ridged pattern with rough surface. Though a uniform distribution of EPS domains was seen in both cases, the blend with 15% DCP showed a fine and more uniform phase distribution. The fine dispersion of EPS phase in the NR matrix alters the crack path giving resistance to crack propagation. Size reduction of EPS particles and less pull out of the minor phase were also noticed the case of the blend containing 15% DCP [4]. These observations are an indication of the compatibility between the components [42]. The SEM analysis is in conformity with the improvement in mechanical properties of the NR/EPS blend with 15% DCP.

Blend ratio optimization of compatibilized NR/EPS blends

3B.3.16 Cure characteristics

The rheographs at 150 °C of silica filled compatibilized NR/EPS blends at different blend ratio are shown in Fig. 3B.24. A gradual decrease in torque was observed with changing the NR/EPS ratio. The highest torque is exhibited by pure silica filled NR samples. Incorporation of EPS lowers the torque of the blends and as the EPS content increases a gradual decrease in torque is observed. The low torque value for the blends is associated with the low viscosity of the PS phase compared to NR at curing temperature. The degradation during blending process lowers the molecular weight of rubber can also be a reason for the lower torque associated with the blend.

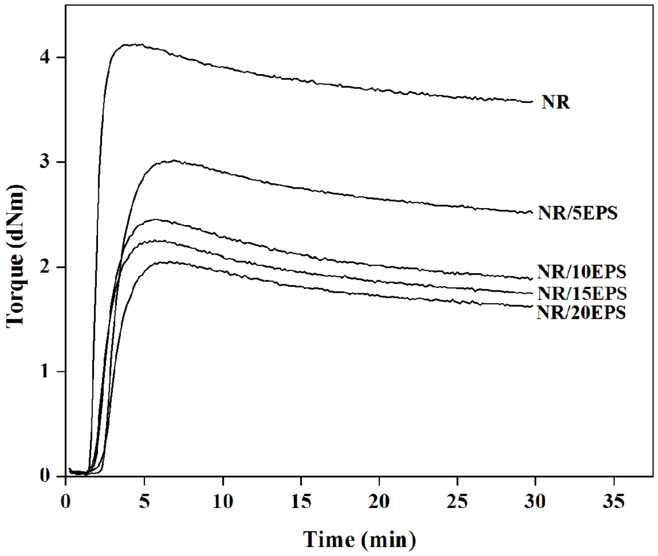


Fig. 3B.24. The rheographs at 150 °C of silica filled compatibilized NR/EPS blends at different blend ratio

The processing characteristics of silica filled compatibilized NR/EPS blends at different blend ratio at 150 °C is given in table 3B.14. An increase in cure time was observed for the blends due to presence of acidic groups, which retards the cure reaction. Again the increase of EPS decreases the cure time as the rubber content decreases. But at higher EPS concentration retardation effect of acidic groups become prominent again. The cure rate index is also in agreement with the curing reaction.

Table 3B.14. The processing characteristics of silica filled compatibilized NR/EPS blends at different blend ratio at 150 °C

Cure characteristics	NR	95/5 NR/EPS	90/10 NR/EPS	85/15 NR/EPS	80/20 NR/EPS
Min Torque, M_L (dNm)	0.01	0.02	0.02	0.03	0.03
Max Torque, M_H (dNm)	4.13	3.02	2.46	2.26	2.06
Scorch time, t_{10} (min)	1.56	2.31	1.58	1.53	2.25
Cure time, T_{90} (min)	3.37	4.19	3.50	3.43	4.27
Cure rate index (min^{-1})	55.25	53.19	52.08	52.63	49.50

A cure kinetics plot of Ln (M_H –M_t) vs. time for silica filled NR/EPS blends with varying blend ratios at 150 °C is presented in Fig. 3B.25. The plots are found to be linear which proves that the cure reactions proceed according to first order kinetics. The decrease in slope of cure kinetics plot in the case of blends compared to NR indicates a low cure rate for the blends.

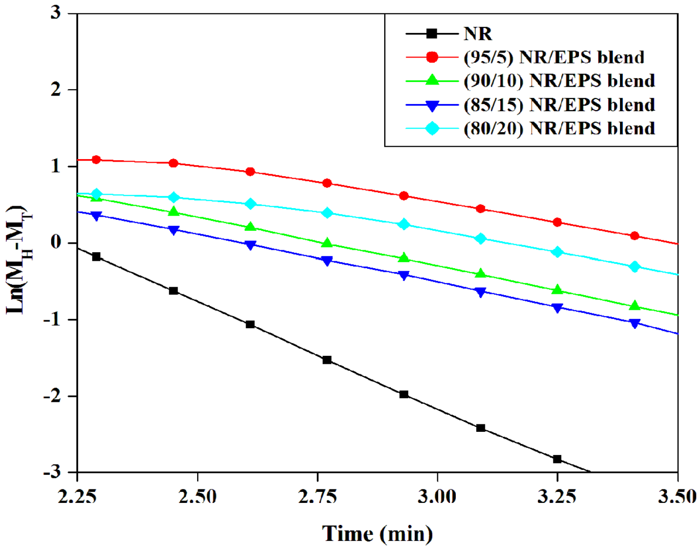


Fig. 3B.25. A cure kinetics plot of Ln (M_H –M_t) vs. time for silica filled NR/EPS blends with varying blend ratios at 150 °C

3B.3.17 Strain-Sweep Studies

Storage modulus Vs strain curves of silica filled NR/EPS blends with varying blend ratios are depicted in Fig. 3B.26. The blends show higher storage modulus compared to NR and the modulus increases with EPS content. This is due to the presence of high modulus EPS phase in the blends. In the previous section we have concluded that storage modulus of 95/5 blend is lower than NR. But optimum amounts of both MA and DCP in the blend results an improvement in storage modulus, which is higher than NR. The enhanced modulus indicates a better filler-polymer interaction [27]. The presence of MA in the blend develops some polarity and this leads to better interaction with the polar filler.

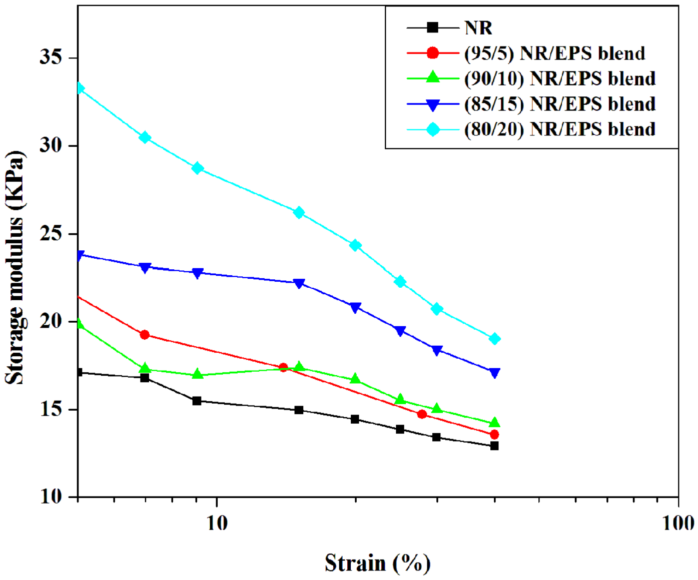


Fig. 3B.26. Storage modulus Vs strain curves **of silica filled NR/EPS blends with varying blend ratios**

3B.3.18 Mechanical properties

3B.3.18.1 Tensile properties

The tensile properties of silica filled compatibilized NR/EPS blend with different blend ratios are shown in Fig. 3B.27 (tensile strength) and Fig .3B.28 (elongation at break and modulus at 300% elongation). The incorporation of EPS to NR showed a reduction in tensile strength and elongation at break. But the 95/5 blend showed a slight improvement due to compatibility. There have been reports showing incorporation of a thermoplastic phase to an elastomer increases the tensile strength and decreases the elongation at break [41,46]. But in this study utilization of EPS in NR was done by preparing a blend of NR and EPS using a compatibilization technique which further it was subjected for conventional vulcanisation in order to get a product with properties comparable to NR.

Therefore we cannot expect the tensile strength to be higher than NR at high loadings of EPS. Here the tensile strength shows a gradual reduction on EPS loading. But when the EPS level is too low, due to compatibility (through MA grafting) [4,10] EPS appeared as small droplets with uniform distribution as evidenced in the SEM. These droplets with probable interlinking of phases at the interfaces present a strongly bound blend. Hence a raise in tensile strength was observed at 95/5 blend ratio. At higher loadings the chance of phase separation is soaring and the crosslinking occurs only in NR phase, which remains as a separate phase. Therefore the extent of interaction between the two phases decreases. This may be the reason why the tensile strength drops at higher loadings of EPS. Unattached PS chains can reduce the cohesion of the rubber matrix by hindering the sulphur crosslinks can also be a reason for the drop off tensile strength.

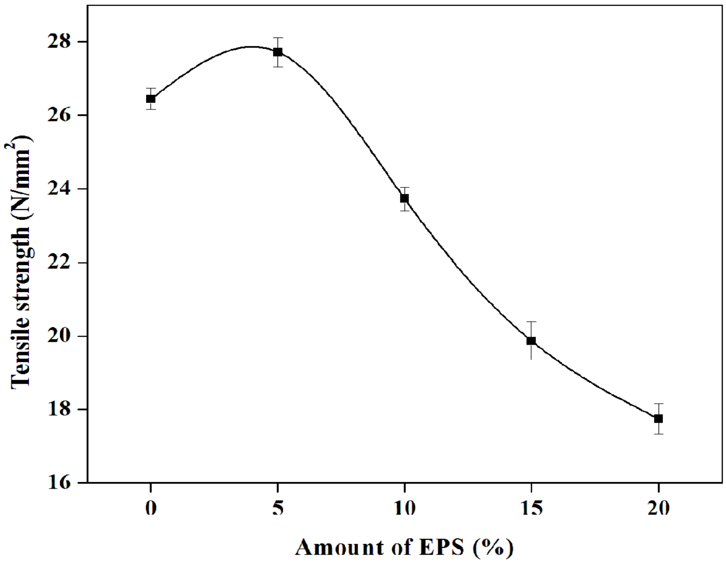


Fig. 3B.27. Tensile strength of silica filled compatibilized NR/EPS blend with different blend ratios

The elongation for blends is less than that of pure NR due to some loss of elasticity with the addition of EPS. Hence a gradual decrease of elongation with increase in the EPS content is effected. As EPS loading increases phase separation becomes a severe problem causing an early failure of the sample. This results in the reduction of elongation at break. Also when the brittle PS phase increases, the chain flexibility of the system may restrict and as a result the elongation drastically reduces [47].

The modulus at 300% elongation of the blends shows an improvement compared to NR and it increases with EPS content. This is due to the high modulus associated with the thermoplastic phase. The 95/5 blend showed comparable modulus with NR due to compatibility as well as small percentage of EPS. At higher PS level a large improvement in modulus was noticed.

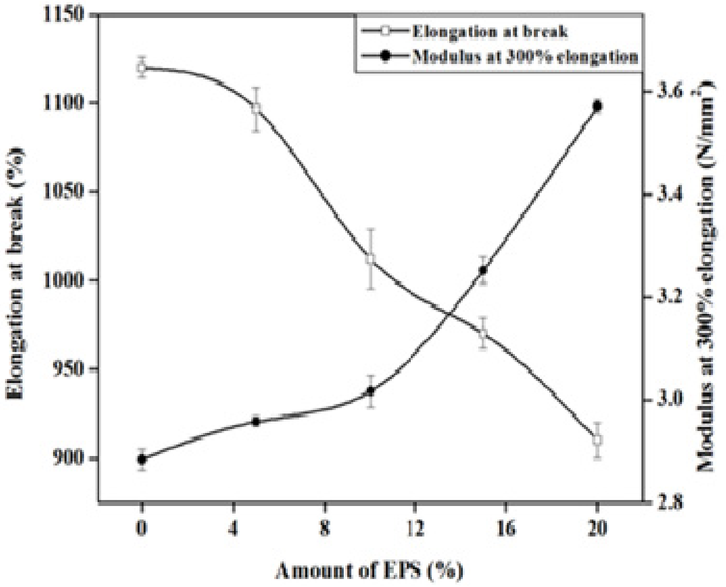


Fig. 3B.28. Elongation at break and modulus at 300% elongation of silica filled compatibilized NR/EPS blend with different blend ratios

3B.3.18.2 Tear strength

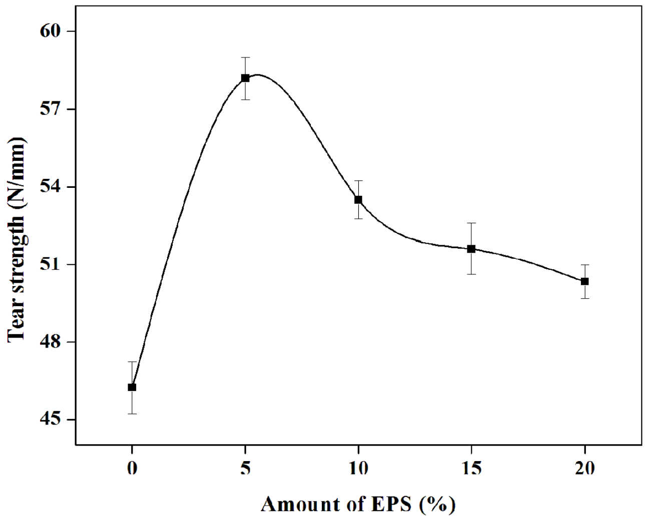


Fig. 3B.29. Tear strength of silica filled compatibilized NR/EPS blend with different blend ratios

Fig. 3B.29 shows the tear strength of silica filled compatibilized NR/EPS blend with different blend ratios. Tear strength is improved on EPS incorporation, but at higher levels it showed a decreasing tendency. A remarkable 26% improvement was shown by 95/5 blend. Here due to compatibility filler particles can be properly wetted by macromolecules and hence adhesion between the filler and matrix improves. Thus, the energy required to propagate a crack increases, resulting in higher tear strength [31]. When EPS content increases, phase separation in the blend presents an easier path for crack propagation and the tear strength shows a decreasing tendency.

3B.3.18.3 Aging studies

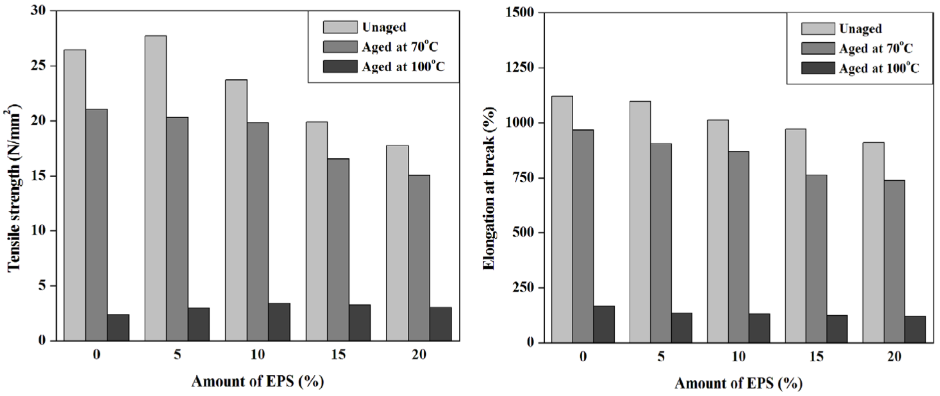


Fig. 3B.30. Tensile properties of the unaged and aged samples of silica filled NR/EPS blend with various blend ratios

Fig. 3B.30 shows the tensile properties of the unaged and aged samples of silica filled NR/EPS blend with various blend ratios. The percentage reduction of tensile properties is shown in Table 3B.15. The data implies that aging deteriorate the properties of all the compounds indicating thermal degradation of the crosslinks, especially at elevated temperature. This is because rubber undergoes oxidation reactions resulting in chain scission [32]. Since rubber is more prone to oxidative degradation because of the presence of double bonds the percentage reduction of tensile strength on aging at 70°C was found to be less at higher EPS ratio.

Table 3B.15. The percentage reduction of tensile properties of silica filled NR/EPS blend with various blend ratios

NR/EPS blend ratio	% reduction of tensile strength		% reduction of elongation at break	
	Aged at 70 °C	Aged at 100 °C	Aged at 70 °C	Aged at 100 °C
100/10	20.41	91.00	13.62	85.14
95/5	26.68	89.26	17.50	87.61
90/10	16.45	85.63	14.37	87.07
85/15	16.76	83.56	21.42	87.31
80/20	15.14	82.98	18.97	86.81

3B.3.18.4 Miscellaneous properties

Effect of blend ratios on compression set, abrasion loss, resilience and hardness of silica filled compatibilized NR/EPS is tabulated below (Table 3B.16). The % of compression set was found to be higher for the blends compared to NR. There was a regular increment in compression set for higher EPS content. The presence of EPS affects the mobility of rubber chains, induces some stiffness in the material [33]. A low value of compression set for 95/5 blend reflects the compatibility. But higher EPS loading lowers matrix elasticity, facilitate irreversible flow under stress [36]. Abrasion resistance was reduced upon loading of EPS, except for 95/5 blend where it is associated with the better filler-rubber interaction showed an improved abrasion resistance. Fine particles with uniform distribution causes greater interface between the filler and the rubber matrix and, hence, provide a better abrasion resistance [35]. A significant improvement in surface hardness was observed for all the blends compared to NR and a gradual increment is found with increasing the EPS content. This is due to the higher hardness of PS.

The resilience values of the blends were found to be comparable with NR though the uncompatibilized blend shows a slight reduction. This is attributed to the better reinforcing effect by the filler due to polar interactions [36]. The overall properties suggest that MA can be used as a reactive compatibilizer in NR/PS blends and there by facilitating the incorporation of EPS to NR without deteriorating the properties of NR.

Table 3B.16. Effect of blend ratios on compression set, abrasion loss, resilience and hardness of silica filled compatibilized NR/EPS

NR/EPS blend ratio	Miscellaneous properties			
	Compression set (%)	Abrasion loss (cc/hr)	Resilience (%)	Hardness (Shore A)
100/0	24.0	4.74	57	47
95/5	26.5	3.41	59	54
90/10	43.7	5.18	62	58
85/15	43.8	6.37	64	60
80/20	47. 5	7.44	65	64

3B.3.19 Swelling studies

Fig. 3B.31 is the graphical representation of the mol% uptake of toluene by silica filled compatibilized NR/EPS blend with different blend ratios. The percentage of swelling index and crosslink densities are given in Table 3B.17. The initial toluene uptake was high for all the compounds, after some time the uptake become slower and finally reaches at equilibrium. Here the lowest toluene uptake was shown by 95/5 blend with a slight improvement compared to NR. For other blends the uptake was higher than NR. This is due to the fact that toluene can penetrate into the matrix also through the unattached PS chains.

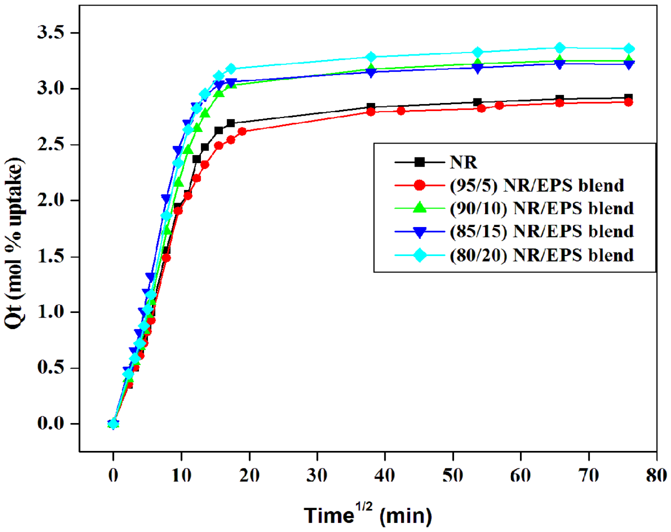


Fig. 3B.31. The mol% uptake of toluene by silica filled compatibilized NR/EPS blend with different blend ratios.

The solvent sorption is found to be increasing with EPS content, except for 95/5 blend. A similar trend was observed for swelling index. The slight improvement in solvent resistance is found for the 95/5 blend compared to NR. Sufficient monomer/initiator ratio for grafting (greater compatibility) and low EPS content in the blend are the constructive factors which grounds the slight increment of crosslink density in the 95/5 blend. When the EPS content increase, chance of phase separation (because of reduced crosslinking) becomes more and the solvent can easily penetrate through the matrix. Consequently, an increase of swelling index with a reduction of crosslink density arises. The results are in good agreement with the stress-strain properties discussed earlier.

Table 3B.17. The percentage of swelling index and crosslink densities of silica filled compatibilized NR/EPS blend with different blend ratios.

NR/EPS blend ratio	Swelling index	Crosslink density ($\times 10^{-5}$ mol/cc)
100/0	290.30	9.80
95/5	289.35	9.98
90/10	302.63	9.41
85/15	304.37	9.50
80/20	312.83	9.18

3B.3.20 Thermogravirmetric analysis

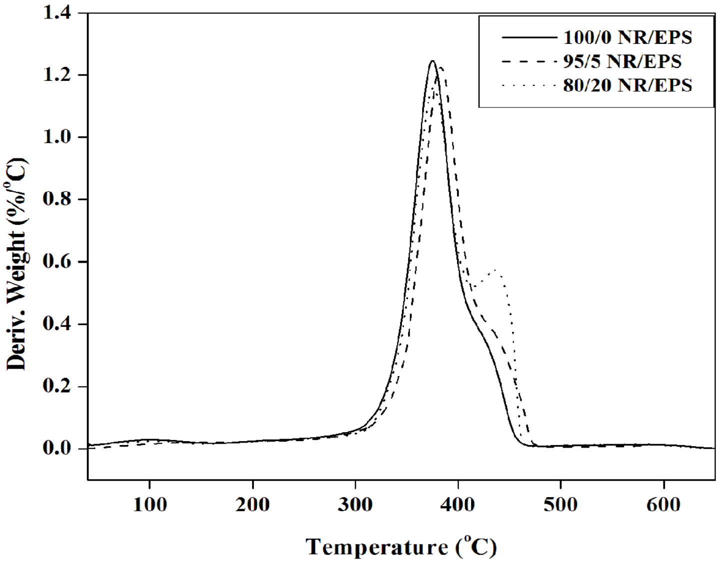


Fig. 3B.32. DTG curves of NR, 95/5 and 80/20 NR/EPS blends

DTG curves of NR, 95/5 NR/EPS and 80/20 NR/EPS are shown in Fig.3B.32 and thermal properties are given in Table. 3B.18. NR and 95/5 NR/EPS blend showed similar degradation behaviour. But an additional peak at 437.5 °C was appeared in the 80/20 blend due to higher amount of EPS and enhanced phase separation. A slight improvement in most of the thermal properties was observed for the 95/5 NR/EPS compatibilized blend. The overall data suggests the better thermal stability of the compatibilized blend containing 5% EPS compared to NR and 80/20 NR/EPS blend.

Table 3B.18. Thermal properties of NR, 95/5 and 80/20 NR/EPS blends

Property	NR	95/5 NR/EPS	80/20 NR/EPS
Onset degradation temperature (°C)	310.9	315.1	316.2
Maximum degradation temperature (°C)	378.0	383.1	377.2, 437.5
Final degradation temperature (°C)	468.8	471.8	468.9
Temperature (°C) at 5% degradation	251.2	283.9	264.9
Temperature (°C) at 50% degradation	382.5	392.1	387.1
Residue (%) at 600 °C	16.0	15. 8	8.2

3B.3.21 Scanning electron microscopy

Fig. 3B.33 is the SEM images of the tensile fractured surfaces of (a) NR, (b) 95/5 NR/EPS blend and (c) 80/20 NR/EPS blend. Phase homogeneity is obvious in the morphology of NR, except some silica particles were embedded. In the case of blends a heterogenous morphology with rough surface could be seen.

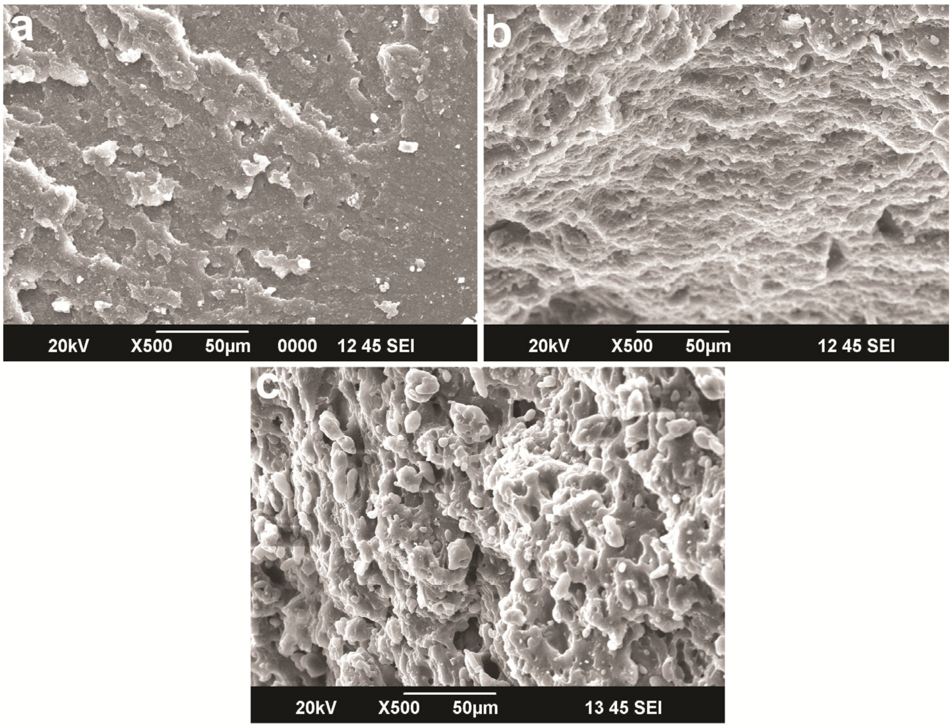


Fig. 3B.33. SEM images of the tensile fractured surfaces of (a) NR, (b) 95/5 NR/EPS blend and (c) 80/20 NR/EPS blend.

The 95/5 blend showed a ridged pattern where as the 80/20 blend is more close to a brittle fractured surface morphology. The 95/5 NR/EPS blend showed a fine and more uniform phase distribution compared to the 80/20 blend. The fine dispersion of EPS phase in the NR matrix alters the crack path giving increased resistance to crack propagation. These observations are an indication of compatibility between the components [4,42]. Size reduction and lower pull out of the minor phase also indicate the phase compatibility. This is in conformity with the enhanced mechanical properties associated with 95/5 blend. For the 80/20 blend the minor phase appeared as large domains resulting in the incompatibility between the phases.

3B.4 Conclusion

In this work, non-degradable and not easily recyclable waste EPS has been substituted for 5% NR by a compatibilization method during NR processing. Most properties of the blend show remarkable improvement on compatibilization with MA. For optimum concentrations of 1% MA and 15% DCP (based on MA), the tensile strength is comparable with that of silica filled NR. Properties like modulus at 300% elongation and compression set were the best for compatibilized blends. Tear strength showed an impressive 25% improvement in the case of compatibilized blends. Greater degrees of dispersion of PS have been confirmed by SEM in the case of compatibilized blends. The inclusion of PS does not lead to any deterioration of thermal properties. The overall data suggest that 5% waste expanded polystyrene can be incorporated into NR compounds as a waste management measure with some improvement in mechanical properties as bonus. This is also economically significant for NR processors.

References

[1] L. A. Utracki, *Polymer Alloys and Blends,* Hanser, New York, 1989.

[2] Pticek, V., Hrnjak-Murgic, Z. & Jelencic, J. Effect of the structure of ethylene-propylene-diene-graftpolystyrene graft copolymers on morphology and mechanical properties of SAN/EPDM blends. *Express Polym. Lett.* **1,** 173–179 (2007).

[3] Khalf, A. I., Nashar, D. E. El & Maziad, N. A. Effect of grafting cellulose acetate and methylmethacrylate as compatibilizer onto NBR/SBR blends. *Mater. Des.* **31,** 2592–2598 (2010).

[4] Khalf, A. I. & Ward A. A. Use of rice husks as potential filler in styrene butadiene rubber/linear low density polyethylene blends in the presence of maleic anhydride. *Mater. Des.* **31,** 2414–2421 (2010).

[5] Liu, N. C. & Baker, W. E. Reactive polymers for blend compatibilization. *Adv. Polym. Technol.* **11,** 249–262 (1992).

[6] Jo, W. H., Park, C. D. & Lee, M. S. Preparation of functionalized polystyrene by reactive extrusion and its blend with polyamide 6. *Polymer (Guildf).* **37,** 1709–1714 (1996).

[7] Raquez, J.-M., Narayan, R. & Dubois, P. Recent Advances in Reactive Extrusion Processing of Biodegradable Polymer-Based Compositions. *Macromol. Mater. Eng.* **293,** 447–470 (2008).

[8] Hamza, S. S., El-sabbagh, S. & Shokr, F. Elastic Behavior of NR/IIR Rubber Blend Loaded with Different Compatibilizers. *Int. J. Polym. Mater.* **57,** 203–215 (2008).

[9] Patel, G. V., Patel, H. B., Sharma, P., Patel, H. a. & John, N. A Study on Grafting of Natural Rubber and Nitrile Rubber on Thermoplastic Low Density Polyethylene Using Maleic Anhydride and Acrylic Acid. *Int. J. Polym. Mater.* **55,** 413–424 (2006).

[10] Johns, J. & Rao, V. Mechanical properties of MA compatibilised NR/CS blends. *Fibers Polym.* **10,** 761–767 (2009).

[11] Yoon, L. K., Choi, C. H. & Kim, B. K. Reactive extrusion of PP/natural rubber blends. *J. Appl. Polym. Sci.* **56,** 239–246 (1995).

[12] Yu, Z.-Z., Yang, M.-S., Dai, S.-C. & Mai, Y.-W. Toughening of recycled poly(ethylene terephthalate) with a maleic anhydride grafted SEBS triblock copolymer. *J. Appl. Polym. Sci.* **93,** 1462–1472 (2004).

[13] Fung, K. L. & Li, R. K. Y. A study on the fracture characteristics of rubber toughened poly(ethylene terephthalate) blends. *Polym. Test.* **24,** 863–872 (2005).

[14] Lasalle, V. L. *et al.* Chemical modification of styrene – butadiene – styrene (SBS) rubber by reactive grafting with maleic anhydride. *J. Adhes. Sci. Technol.* **17,** 1713–1726 (2003).

[15] Sahakaro, K. & Beraheng, S. Reinforcement of maleated natural rubber by precipitated silica. *J. Appl. Polym. Sci.* **109,** 3839–3848 (2008).

[16] Alexander, M., Kurian, P., Thachil, E. T. & . Effectiveness of Cardanol as Plasticizer for Silica-Filled Natural Rubber. *Prog. Rubber, Plast. Recycl. Technol.* **23,** 43–55 (2007).

[17] ASTM D2084-07. Standard test method for rubber property-vulcanization using oscillating disk cure meter. 09.01. ICS number code 83.060 (rubber).

[18] Nakason, C., Kaesaman, A. & Supasanthitikul, P. The grafting of maleic anhydride onto natural rubber. *Polym. Test.* **23,** 35–41 (2004).

[19] Li, H. M., Chen, H. B., Shen, Z. G. & Lin, S. Preparation and characterization of maleic anhydride-functionalized syndiotactic polystyrene. *Polymer (Guildf).* **43,** 5455–5461 (2002)

[20] Nakason, C., Saiwaree, S., Tatun, S. & Kaesaman, a. Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate). *Polym. Test.* **25,** 656–667 (2006).

[21] Chino, K. & Ashiura, M. Themoreversible Cross-Linking Rubber Using Supramolecular Hydrogen-Bonding Networks. *Macromolecules* **34,** 9201–9204 (2001).

[22] Premphet, K. & Chalearmthitipa, S. Melt grafting of maleic anhydride onto elastomeric ethylene-octene copolymer by reactive extrusion. *Polym. Eng. Sci.* **41,** 1978–1986 (2001).

[23] Nampitch, T. & Buakaew, P. The Effect of Curing Parameters on the Mechanical Properties of Styrene-NR Elastomers Containing Natural Rubber-Graft- Polystyrene. *Kasetsart J. Nat. Sci.* **40,** 7–16 (2006).

[24] Ismail, H., Supri & Yusof, a. M. M. Blend of waste poly(vinylchloride) (PVCw)/acrylonitrile butadiene-rubber (NBR): The effect of maleic anhydride (MAH). *Polym. Test.* **23,** 675–683 (2004).

[25] Sae-Oui, P., Sirisinha, C., Thepsuwan, U. & Hatthapanit, K. Comparison of reinforcing efficiency between Si-69 and Si-264 in a conventional vulcanization system. *Polym. Test.* **23,** 871–879 (2004).

[26] Poh, B. T., Ismail, H., Quah, E. H. & Chin, P. L. Cure and mechanical properties of filled SMR L/ENR 25 and SMR L/SBR blends. *J. Appl. Polym. Sci.* **81,** 47–52 (2001).

[27] Fröhlich, J., Niedermeier, W. & Luginsland, H. D. The effect of filler-filler and filler-elastomer interaction on rubber reinforcement. *Compos. Part A Appl. Sci. Manuf.* **36,** 449–460 (2005).

[28] Song, Y. M., Wang, Q. W., Han, G. P., Wang, H. G. & Gao, H. Effects of two modification methods on the mechanical properties of wood flour/recycled plastic blends composites: Addition of thermoplastic elastomer SEBS-g-MAH and in-situ grafting MAH. *J. For. Res.* **21,** 373–378 (2010).

[29] Bikiaris, D. N., Vassiliou, A., Pavlidou, E. & Karayannidis, G. P. Compatibilisation effect of PP-g-MA copolymer on iPP/SiO2 nanocomposites prepared by melt mixing. *Eur. Polym. J.* **41,** 1965–1978 (2005).

[30] Ismail, H., Rusli, A. & Rashid, A. A. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. *Polym. Test.* **24,** 856–862 (2005).

[31] Siriwardena, S., Ismail, H., Ishiaku, U. S. & Perera, M. C. S. Mechanical and morphological properties of white rice husk ash filled polypropylene/ethylene-propylene-diene terpolymer thermoplastic elastomer composites. *J. Appl. Polym. Sci.* **85,** 438–453 (2002).

[32] Arayapranee, W. & Rempel, G. L. Effects of Polarity on the Filler-Rubber Interaction and Properties of Silica Filled Grafted Natural Rubber Composites. *J. Polym.* **2013,** (1-9) (2013).

[33] Mostafa, a., Abouel-Kasem, a., Bayoumi, M. R. & El-Sebaie, M. G. Effect of carbon black loading on the swelling and compression set behavior of SBR and NBR rubber compounds. *Mater. Des.* **30,** 1561–1568 (2009).

[34] Arayapranee, W. *Rubber Abrasion Resistance. In Abrasion Resistance of Materials*. Ed. Adamiak M. (2007).

[35] Arayapranee, W., Na-Ranong, N. & Rempel, G. L. Application of rice husk ash as fillers in the natural rubber industry. *J. Appl. Polym. Sci.* **98,** 34–41 (2005).

[36] Nelson, P. A. & Kutty, S. K. N. Studies on Maleic anhydride grafted reclaimed rubber/acrylonitrile butadiene rubber blends. *Prog. rubber, Plast. Recycl. Technol.* **19,** 171–188 (2003).

[37] George, S. C. & Thomas, S. Transport phenomena through polymeric systems. *Prog. Polym. Sci.* **26,** 985–1017 (2001).

[38] Mathew, A. P., Packirisamy, S. & Thomas, S. Studies on the thermal stability of natural rubber/polystyrene interpenetrating polymer networks: Thermogravimetric analysis. *Polym. Degrad. Stab.* **72,** 423–439 (2001).

[39] Sircar, A. K. Characterization of isomeric elastomers using thermal analysis (IR). io. *J. Therm. Anal.* **49,** 293–301 (1997).

[40] Martins, M. A. *et al.* Thermooxidative study of raw natural rubber from Brazilian IAC 300 series clones. *Thermochim. Acta* **474,** 62–66 (2008).

[41] Joseph, S. & Thomas, S. Morphology, morphology development and mechanical properties of polystyrene/polybutadiene blends. *Eur. Polym. J.* **39,** 115–125 (2003).

[42] Das, A., Ghosh, A. K., Pal, S. & Basu, D. K. The role of thiophosphoryl disulfide on the co-cure of CR-EPDM blends: Effect of white fillers. *Polym. Adv. Technol.* **15,** 197–208 (2004).

[43] Park, K. N. & Park, J.-W. Modification of cellulase by synthesized copolymer with polyethylene oxide and maleic acid anhydride. *J. Appl. Polym. Sci.* **77,** 368–373 (2000).

[44] Ismail, H., Supri & Yusof, a. M. M. Blend of waste poly(vinylchloride) (PVCw)/acrylonitrile butadiene-rubber (NBR): The effect of maleic anhydride (MAH). *Polym. Test.* **23,** 675–683 (2004).

[45] Med, K., NiAhzami, S., Raza, N. & Mahmood, K. Mechanical, swelling, and thermal aging properties of marble sludge-natural rubber composites. *Int. J. Ind. Chem.* **3,** 21 (2012).

[46] Asaletha, R., Kumaran, M. G. & Thomas, S. Thermoplastic elastomers from blends of polystyrene and natural rubber: morphology and mechanical properties. *Eur. Polym. J.* **35,** 253–271 (1999).

[47] Mathew, A. P., Packirisamy, S., Radusch, H. J. & Thomas, S. Effect of initiating system, blend ratio and crosslink density on the mechanical properties and failure topography of nano-structured full-interpenetrating polymer networks from natural rubber and polystyrene. *Eur. Polym. J.* **37,** 1921–1934 (2001).

……

Chapter 4

UTILIZATION OF EPS IN SBR COMPOUNDING

Contents

4.1 Introduction

Among the synthetic rubbers styrene-butadiene rubber (SBR) produced by both emulsion and solution processes accounts for the largest volume and is one of the most widely used elastomers worldwide. This nonpolar rubber is derived from styrene and butadiene [1]. It has good abrasion resistance, thermal aging properties, high filler loading capacity, good flex resistance and crack-initiation resistance. However, its ageing resistance is poor, due to the unsaturation in the butadiene component [2]. The major application of solid SBR is in the automotive and tire industry, accounting for approximately 70 percent of the use. Due to superior traction and tread wear, the largest application is concentrated in tread compounds. Footwear, foamed products, wire and cable jacketing, belting, hoses, and mechanical goods are the other areas in which SBR is extensively used [3].

This part of the project explores the possibility of utilizing waste EPS in SBR compounding by a blending process. In the present study vulcanised SBR/EPS blend (with SBR as major component) was prepared and the properties analysed. There is hardly any previous literature on this aspect, but some research has been done in the area of PS/SBR blends [4-5], where the objective was the modification of PS using SBR. Both SBR and EPS contain styrenic segments which can lead to interaction between the polymers. Hence some miscibility can be expected on blending [6]. Due to the partial miscibility between these two polymers an enhancement in mechanical properties can be anticipated at certain blend ratios.

4.2 Experimental

4.2.1 Materials

The materials used are described in Section 2.1 of Chapter 2.

4.2.2 Methods

4.2.2.1 Blending

Blends of SBR and EPS were prepared by melt mixing. Melt mixing was carried out in a Brabender Plasticorder at 170 °C maintaining the rotor speed at 50 rpm. EPS was allowed to soften in the Brabender Plasticorder initially for 2 min. Then SBR was added to the molten EPS and the mixing was continued for another 4 min. Total mixing time was fixed as 6 min. Thus SBR/EPS blends in different ratios (35/5, 30/10, 25/15 and 20/20 percentage by weight) were prepared and were used as gum compounds. Two more batches of 25/15 SBR/EPS blends were prepared for the filled compounds. The blend compositions are given in Table 4. 1.

Table 4.1. Composition of SBR/EPS Blends Ingredients

	Compositions (weight in gm)			
SBR	35	30	25	20
EPS	5	10	15	20

4.2.2.2 Compounding and curing

The compounding and curing was done according to the procedure given in Section 2.2.2 of Chapter 2. At first 60g of SBR was masticated and then it was mixed with the blend of SBR and EPS already prepared in a Brabender Plasticorder so that finally, 95/5, 90/10, 85/15 and 80/20 blends were obtained. These blends were compounded with vulcanizing ingredients. The gum, black filled and silica filled SBR compounds without EPS were also prepared. The formulation used is given below in Table 4.2. The composition of final blends after compounding is shown in Table 4.3.

Table 4.2. Compounding formulation

Components	Quantity (phr)		
	Gum	Silica	Black
SBR	100	100	100
ZnO	4.5	4.5	4.5
Stearic acid	2.0	2.0	2.0
CBS	1	1	1
TMTD	0.2	0.2	0.2
Sulphur	2	2	2
Silica/Black	-	30	40
Paraffinic/Aromatic oil	-	6	7.5
DEG	-	1.5	-
SP/TQ	1	1	1

Table 4.3. Composition of final blends after compounding

Ingredients	Compositions (%)								
	Gum					Silica		Black	
SBR	100	95 (60+35)	90 (60+30)	85 (60+25)	80 (60+20)	100	85 (60+25)	100	85 (60+25)
EPS	0	5	10	15	20	0	15	0	15

4.2.3 Characterisation techniques

A detailed explanation of characterisation techniques are given in Section 2.2 of Chapter 2.

4.3 Results and discussion

4.3.1 Cure characteristics

The rheographs of SBR and SBR/EPS blends at 150 °C are shown in Fig.4.1. Gum compounds are shown in Fig. 4.1(a) and while Fig. 4.1(b) shows black/silica filled compounds with optimum EPS loading. In all the three systems (gum, silica and black), the blends were found to yield inferior torque values compared to the corresponding neat SBR. This is because of the low viscosity associated with EPS at the vulcanization temperature. The degradation during the melt blending process at high temperature that lowers the molecular weight of rubber also reduces the torque values. A gradual reduction of torque is observed on EPS loading for gum compounds.

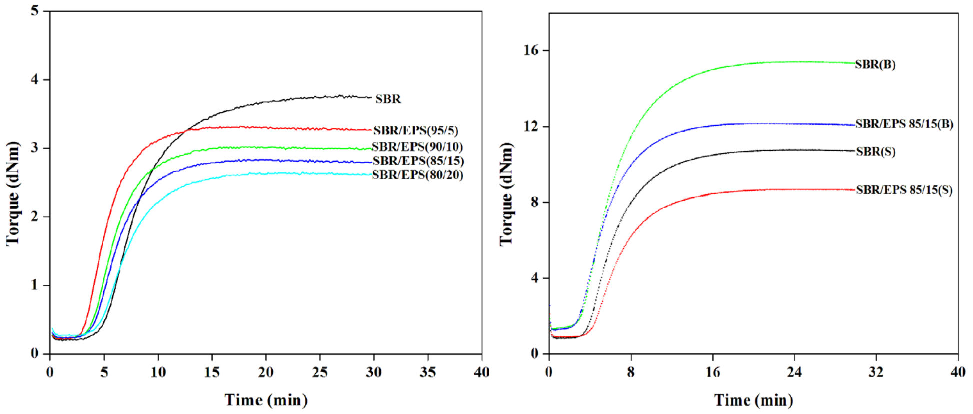


Fig.4.1 Rheographs of SBR and SBR/EPS blends (a) gum compounds and (b) silica/black filled compounds (SBR(B): Carbon black filled, SBR(S): Silica filled)

Cure characteristics of gum SBR and its blends with various percentages of EPS are given in Table 4.4(a). Table 4.4(b) gives cure characteristics of filled (silica/black) SBR and 85/15 SBR/EPS blends with fillers. In the case of gum compounds, pure SBR shows the maximum values of cure time and scorch time. The lower cure time and scorch time for blends compared to gum SBR is due to the decrease in rubber content in the blends. These characteristics initially showed a decrease on incorporation of EPS. But a gradual increase is noticed on further loading of EPS. Maximum torque was found to be decreasing gradually on EPS addition whereas a marginal increase is observed for the minimum torque. The cure rate index of the blends suggests an acceleration of the cure reaction. It is interesting to note that the cure reaction of silica filled system is not much affected by the presence of EPS. This may be due to the interaction between the polystyrene part and silica particles which reduces the retarding effect of silica particles on curing reaction. But for the black filled system the cure time has been slightly decreased. The interaction between SBR and fillers is reported to be increasing in the order, carbon black < silica < clay [7]. The lower interaction between carbon black and polystyrene part is reflecting in the variation of cure time.

Table 4.4a. Cure characteristics of gum SBR/EPS blends

Cure characteristics	Gum compounds				
	SBR/0% EPS	(95/5) SBR/ EPS	SBR/10% EPS	SBR/15% EPS	SBR/20% EPS
Cure time(min)	14.10	8.59	9.59	10.25	11.39
Scorch time(min)	5.13	3.25	4.02	4.11	4.46
Max Torque (dNm)	3.78	3.32	3.03	2.83	2.65
Min Torque (dNm)	0.19	0.21	0.24	0.23	0.27
Cure rate index	11.15	18.73	17.95	16.29	14.43

Table 4.4b. Cure characteristics of filled SBR/EPS blends Cure characteristics

	Filled compounds			
	Silica		Black	
	SBR/0% EPS	SBR/15% EPS	SBR/0% EPS	SBR/15% EPS
Cure time (min)	11.35	11.58	11.52	10.10
Scorch time (min)	4.02	4.28	3.31	3.11
Max Torque (dNm)	10.77	8.69	15.43	12.17
Min Torque (dNm)	0.84	0.90	1.31	1.27
Cure rate index	13.64	13.70	12.18	14.31

4.3.2 Tensile properties

Fig. 4.2(a) shows the stress-strain curves of gum SBR and SBR/EPS blends with different blend ratios Fig. 4.2(b) compares stress – strain curves of gum SBR with filled samples of SBR and SBR/EPS blends with optimum blend ratio. The presence of EPS in the blends results in a change in stress–strain behavior of all the three systems. Polystyrene is a rigid and brittle polymer and its incorporation in ductile SBR improves the stiffness and therefore causes a change in stress-strain behaviour of the blends.

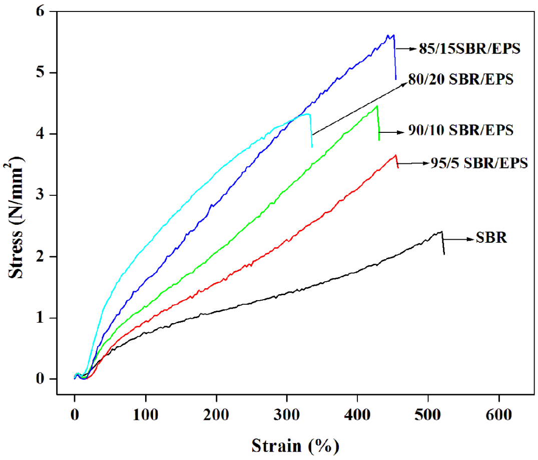


Fig. 4.2(a). Stress-strain curve of gum SBR and SBR/EPS blends with different blend ratios

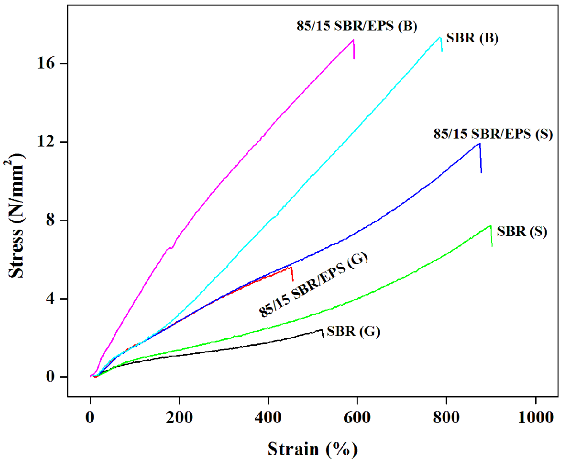


Fig. 4.2(b). Comparative stress – strain behaviour of gum SBR with filled samples of SBR and SBR/EPS blend with optimum blend ratio

Tensile properties such as tensile strength, modulus at 300% elongation and elongation at break of gum SBR and SBR/EPS blends with different blend ratios are shown in Fig. 4.3(a), 4.3(b) and 4.3(c) respectively. Tensile strength increases with EPS content and reaches a maximum at 15% loading whereafter it decreases. A significant improvement of 146% was observed for optimum loading of EPS (15%). Better stress transfer occurs at the PS-SBR interface as the PS molecules act as mechanical anchoring points and improve compatibility. This can be explained by intermolecular interactions. Specific interactions such as π-π electron transfer (an important noncovalent intermolecular force that facilitates the formation of extended architectures from building blocks with aromatic moieties [7-8] are responsible for the compatibility of PS/SBR system. Due to this, the chain segments get aligned to maximize association [9]. After 15% loading there is a rapid fall in tensile strength due to increased phase separation. The results suggest moderate compatibility between PS and SBR due to physical entanglements, similarity in chemical structure (styrene parts) [10] and the intramolecular repulsive effect (internal copolymer segmental “repulsion” can be dominant favouring the mixing of a homopolymer and a copolymer) [11-12]. Unlike NR, SBR lacks self-reinforcing ability and therefore fine state of dispersion of fillers and strong interfacial interaction are the main factors which improve the mechanical properties of SBR compounds [13].

The modulus shows an increasing tendency with EPS content. This is due to the high modulus associated with the thermoplastic phase. A gradual improvement up to 15% EPS is clearly seen from the graph. A significant improvement of 186% is observed at this optimum EPS loading. This can be explained on the basis of compatibility. Due to π-π interaction the chains get aligned to maximize the interaction resulting in stiffening of the chains [9]. As a consequence, the resistance to deformation increases or in other words the interchain friction increases. This reduces the molecular mobility and is responsible for the gradual increment in modulus. The effect is similar to antiplasticization [14-15] in which plasticizers fill the free volume of polymer chain, hinders molecular mobility and subsequently modulus and tensile strength increases. Therefore efficient interfacial adhesion between the blend components accounts for the observed high modulus.

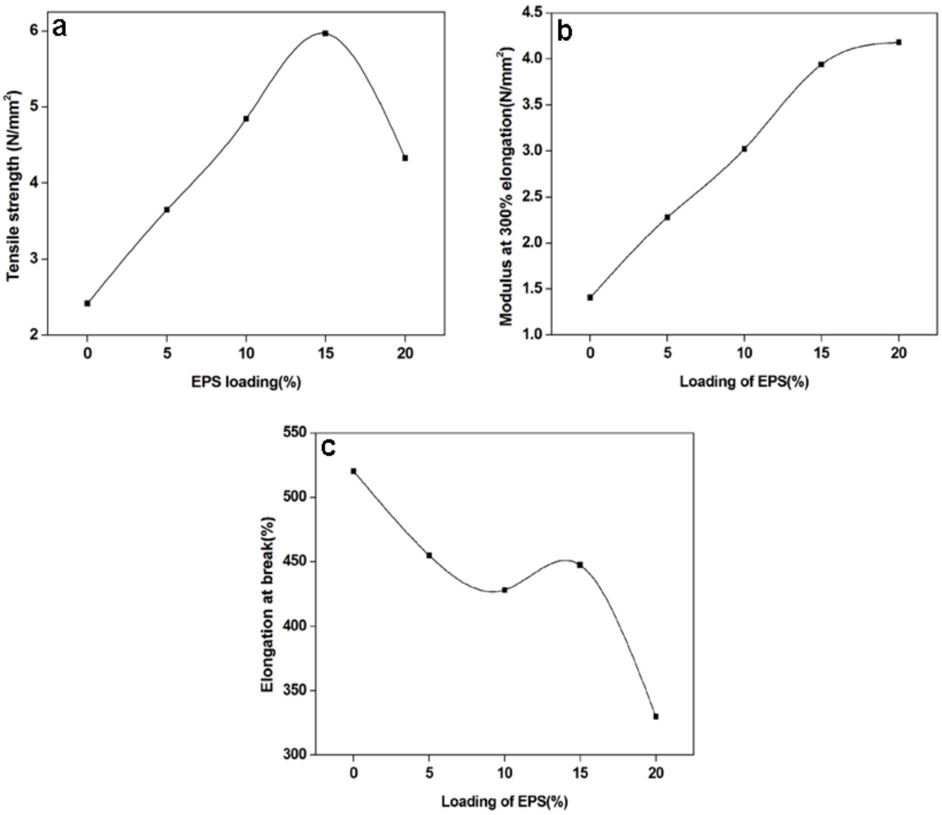


Fig. 4.3. Tensile properties (a) tensile strength, (b) modulus at 300% elongation and (c) elongation at break of gum SBR and SBR/EPS blends with different blend ratios

The elongation at break decreases with increasing PS content. PS is a hard and brittle thermoplastic polymer that breaks at relatively low strain. When it is incorporated in SBR it lowers the elongation of the blend. The low strain break of PS is more pronounced when the tensile test is performed at a high crosshead speed of 500 mm/min. Another explanation on this observation is based on intermolecular interaction and subsequent chain stiffening. On increasing the amount of PS, there is a decrease in the SBR content so that proportion of styrenic part of rubber decreases. As a result interaction between the two phases weakens [16] resulting in an early failure and reduced elongation at break. Moreover, a decrease in the elastomeric content in the blend also accounts for lowering of elongation.

From the above discussion, tensile properties of compatible /partially compatible blends can be explained generally in terms of the specific intermolecular interactions between the constituent components. The favourable interactions bring efficient packing and chain stiffening. Therefore an interaction-induced chain stiffening accounts for the remarkably improved properties of SBR/EPS blends. Though the blend is heterogeneous as evidenced in the microscopic image, there is some compatibility at least in the vicinity of the phase boundary and that will account for the improved properties [17].

Fig. 4.4 is the comparative variation of tensile strength (a), modulus at 300% elongation (b) and elongation at break (c) of SBR and 85/15 SBR/EPS blend in gum, silica and black filled systems. On comparing the three systems, the black filled system showed the highest tensile strength and modulus, followed by silica and the gum system. This is because of the difference in crosslink density of the three systems which is maximum for the black filled system. Though the interaction between SBR and different fillers is higher for silica than carbon black [6], the tensile properties of the silica filled system is poorer compared to those obtained with carbon black due to the tendency of silica to form aggregates with itself. Since in this study the silica filled system does not use coupling agents, silica dispersion is inadequate resulting in tensile strength and modulus lower than that of the carbon black system.

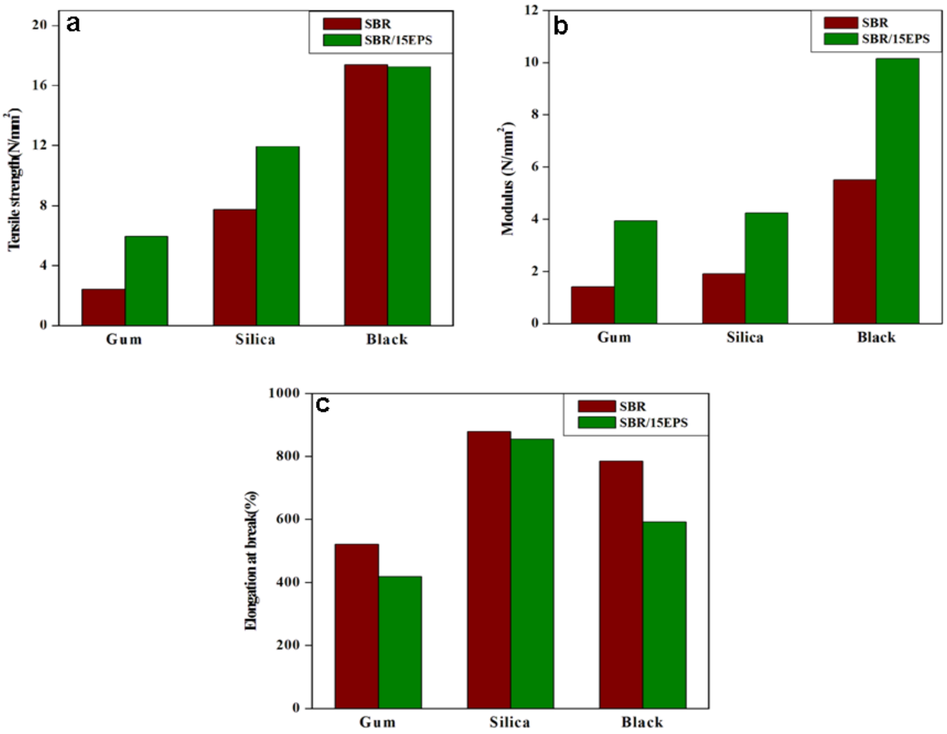


Fig. 4.4. Tensile strength (a), modulus at 300% elongation (b) and elongation at break (c) of SBR and 85/15 SBR/EPS blend in gum, silica and black filled systems

SBR like coploymers have two components and the filler particles can interact favourably with any one of the component polymers[18]. As a result, the filler particles reside only in one phase and there will be poor filler dispersion in the polymer a whole. Compared to carbon black silica interacts better with SBR and filler particles may concentrate in the styrenic part. This can also be a reason for low tensile strength and modulus.

The percentage elongation is found to be higher for the filled systems and is maximum in the case of silica filled system. There was an impressive improvement of 146% (in gum compound) and 54% (in silica filled compound) in tensile strength by 15% EPS loading, but a comparable result was could not be achieved in the case of the carbon black system.

4.3.3 Tear strength

Variation of tear strength with the loading of EPS in SBR/EPS blends is shown in Figure 4. 5. Comparative tear strength of unfilled (gum) and filled SBR and 85/15 SBR/EPS blends is shown in Fig.4.6. The blends of unfilled as well as filled compounds showed better tear strength than the corresponding SBR compounds. The blends provide more restrictions to tearing [19] because, PS particles are hard regions, and act as rigid filler particles which resist crack propagation. In the case of gum compounds, the tear strength is found to improve considerably up to 10% EPS loading. Thereafter the improvement was minimum may be due to the higher extent of phase separation in the blends.

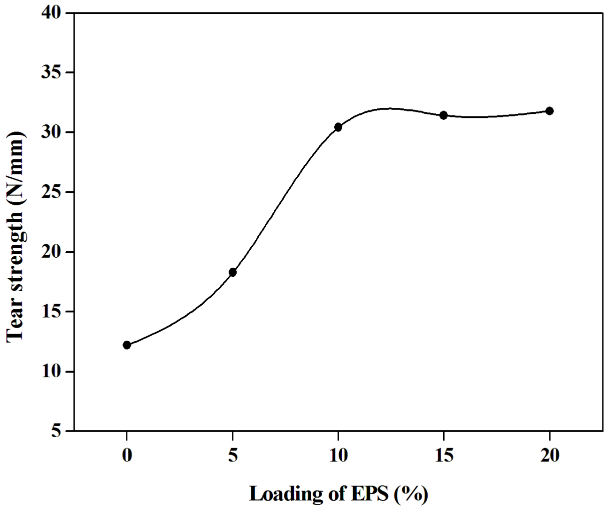


Fig. 4.5. Variation of tear strength with the loading of EPS in SBR/EPS blends

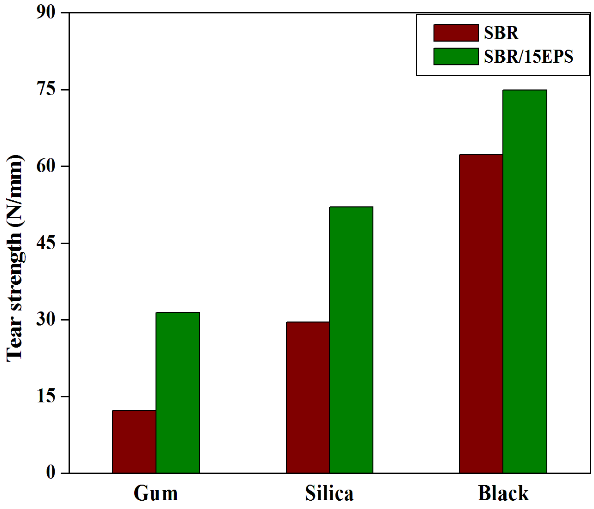


Fig. 4.6. Tear strengths of unfilled and filled SBR and 85/15 SBR/ EPS blends

The filled systems showed higher tear strength compared to the gum compounds due to the reinforcement imparted by the fillers and the resistance to crack propagation offered by the filler particles. Black filled systems showed the maximum tear strength. At the optimum loading of 15% EPS, the blends of gum, silica and black filled systems showed an improvement of 157%, 76% and 20% respectively.

4.3.4 Aging studies

Fig. 4.7 shows the tensile properties (a. tensile strength and b. elongation at break) of the unaged and aged samples as a function of EPS content in SBR/EPS blends and Fig. 4.8 depicts the unaged and aged tensile properties of unfilled and filled SBR and SBR/EPS 85/15 blends. The aging was done both at 70 ºC and 100 °C for 72 hours. An improvement in properties was found for the blends after aging. The aging resistance is better for blends compared to pure SBR since the presence of EPS improves resistance to the attack of heat, oxygen and ozone and also because of the interaction between SBR and EPS due to pi-pi adhesion. Tensile strength of the samples aged at 100 ºC was greater than those aged at 70 ºC but elongation generally showed poor retention due to further crosslinking. In the case of filled systems, the blends show some reduction in properties on aging compared to virgin SBR, elongation showing a much greater reduction.

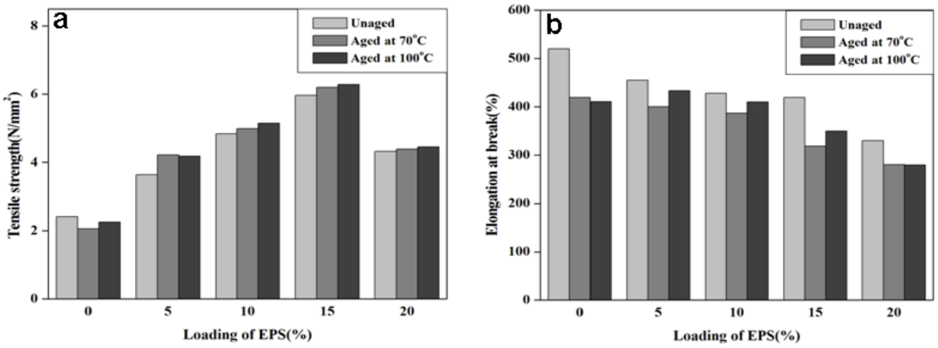


Fig.4.7. Variation of tensile properties (a) tensile strength and (b) elongation at break of unaged and aged samples with EPS content of SBR/EPS blends

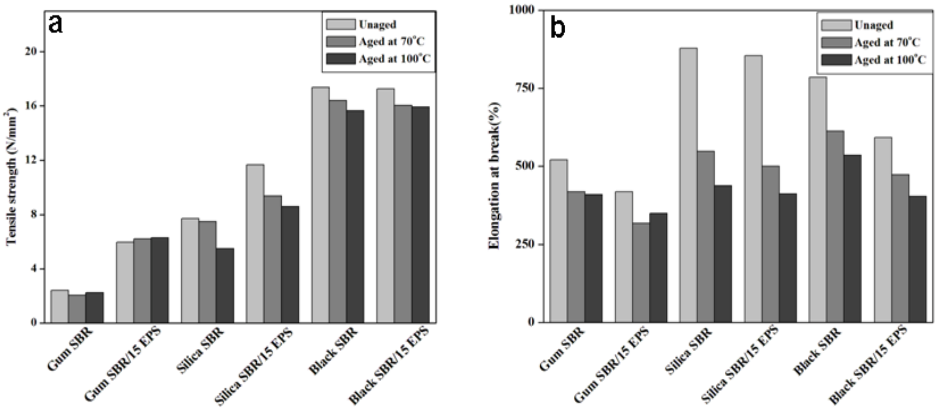


Fig.4.8. Tensile properties (a) tensile strength and (b) elongation at break of the unaged and aged samples of SBR and SBR/EPS 85/15 blends of gum, silica and black filled systems.

4.3.5 Miscellaneous properties

Compression set, abrasion loss, resilience and hardness of gum SBR and SBR/EPS blends with different blend ratios are given in Table 4.5 and those of filled (silica/black) SBR and 85/15 SBR/EPS blends are tabulated in Table 4.6. The ability to retain the elastic properties under prolonged action of compressive stress at higher temperature is one of the major advantages in the field of rubber application. The blends show higher percentages of compression set compared to SBR, except in black filled system. The high compression set values for the blends are attributed to the presence of EPS, which affects the mobility of rubber chains, inducing some stiffness in the material after release of stress [20]. In the case of gum compounds, a gradual increment in compression set is observed on EPS loading, because of the lowering of matrix elasticity which facilitates irreversible flow under stress [21]. The percentage of compression set is higher for filled systems compared to corresponding gum compounds. It has already been reported that increased in crosslink density in the filled compounds decreases the chain mobility and consequently, induces stiffness in the compounds [22]. During compression to a particular strain, the increased stiffness offer higher resistance And and this resistance causes the crosslinks to be broken. When the load is relieved the number of crosslinks responsible for the strain recovery is much less [20] compared to the number of crosslinks resisted deformation. As a result, the specimen cannot recover its original thickness giving high compression set. In the case of silica filled system, the interaction between the blend components is higher than black filled system, resulting in a higher % of compression set.

Table 4.5. Compression set, Abrasion loss, Resilience and Hardness of gum SBR and SBR/EPS blends with different blend ratios

Properties	**Gum compounds**				
	SBR	**SBR/EPS 95/5**	**SBR/EPS 90/10**	**SBR/EPS 85/15**	**SBR/EPS 80/20**
Compression set (%)	24.2	28.4	29.5	30.3	32.7
Abrasion loss (cc/hr)	3.98	3.44	3.25	2.56	3.25
Resilience(%)	63	61	60	57	53
Hardness (Shore A)	51	55	59	64	70

Table 4.6. Compression set, Abrasion loss, Resilience and Hardness of filled (silica/black) SBR and 85/15 SBR/EPS blends

Properties	**Silica filled compounds**		**Black filled compounds**	
	SBR	**SBR/EPS 85/15**	**SBR**	**SBR/EPS 85/15**
Compression set (%)	32.5	42.8	31.5	31.5
Abrasion loss (cc/hr)	2.38	3.35	3.07	4.02
Resilience(%)	56	51	51	47
Hardness (Shore A)	58	66	64	73

Rubber abrasion is complicated as it depends on a variety of intrinsic and extrinsic factors, such as physio-mechanical properties and working conditions [3]. Abrasion loss of gum compounds is in accordance with the tensile properties. Loading of EPS reduces the abrasion loss up to a maximum level because of effective interaction between the blend components. Further EPS loading results in the increase of rigid particles in the rubber. The rigid particles normally increase the abrasion loss of the rubbers due to the greater tendency to wear by at the ridges [23]. Abrasion resistance of filled rubber is basically determined by filler characteristics especially its morphology and surface reactivity [24]. SBR in filled systems possesses much lower abrasion than gum SBR, but the filled blends exhibit somewhat higher abrasion loss compared to the corresponding blend of gum systems. Because of effective interaction between silica and SBR, the silica filled system shows low value of abrasion loss compared to the black filled system.

The resilience values of the blends were found to be lower compared to the corresponding virgin compounds in all the three cases. A significant improvement in surface hardness was observed for all the blends compared to SBR. As expected, the addition of hard PS particles improves the hardness of the resulting blends. The hardness of filled compounds is higher than that of gum compounds because of increased rigidity. Greater hardness resulting from the presence of rigid particles in the host matrix reduces the elasticity of the polymer chains resulting in more rigid composites [25].

4.3.6 Swelling studies

Fig. 4.9 depicts the transport behaviour of toluene through gum SBR and its blends with varying weight percentages of EPS. The swelling index and crosslink density of the samples are given in Table 4.7. Initial toluene uptake was high and similar for all the compounds and after a certain time equilibrium is achieved resulting from slower sorption. The mol % uptake of toluene by the blends is found to be less compared to SBR, except at high loadings (20%) of EPS.

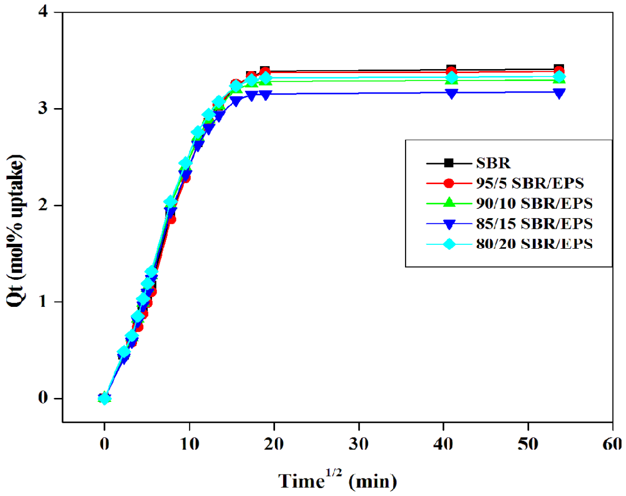


Fig. 4.9. Transport behaviour of toluene through gum SBR and its blend with varying weight percentages of EPS

The same trend is found in the case of swelling index. The presence of EPS in the blend restricts the penetration of nonpolar solvent because of the specific interaction between the phases and hence lowers the swelling index. But a higher loading of EPS disturbs the uniform dispersion and reduces the effective interaction. Due to the pi-pi adhesion between SBR and EPS the crosslink density has improved for the blend upto a certain level which is reflected in the tensile properties.

Table 4.7. Swelling index and crosslink density gum SBR and its blends with varying weight percentages of EPS

SBR/EPS blend ratio	Swelling index (%)	Crosslink density ($\times 10^{-5}$ mol/cc)
100/0	314.2	10.12
95/5	311.5	10.63
90/10	304.2	11.02
85/15	292.1	11.35
80/20	307.2	10.89

Fig. 4.10 illustrates the transport behaviour of toluene through filled (silica/black) SBR and 85/15 SBR/EPS blends. Swelling index and crosslink density values of the samples are given in Table 4.8. Filled compounds showed lower mol% uptake compared to gum compounds.

Black filled system (without EPS) is found to be of highest crosslink density. But for the blends a considerable improvement was observed for silica filled system whereas the blend of black filled system showed only a marginal decrease. Swelling index showed a reverse trend with crosslink density.

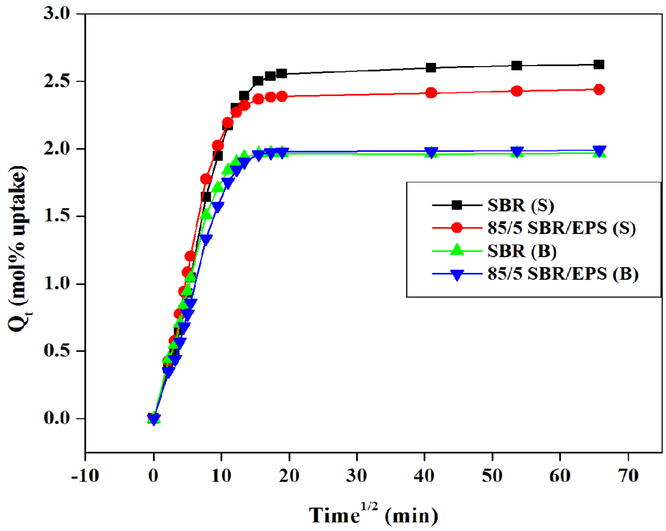


Fig. 4.10. Transport behaviour of toluene through filled (silica/black) SBR and 85/15 SBR/EPS blends

Table 4.8. Swelling index and crosslink density of filled (silica/black) SBR and 85/15 SBR/EPS blends

Filled compounds		**Swelling index (%)**	**Crosslink density ($\times 10^{-5}$ mol/cc)**
Silica	100/0	241.66	11.65
	85/15	224.65	11.96
Black	100/0	181.22	12.66
	85/15	183.34	12.05

4.3.7 Scanning electron microscopy

The scanning electron micrographs of the tensile fractured surfaces of (a) SBR and (b) 85/15 SBR/EPS blends of gum, silica and black systems are presented in Figs. 4.11, 4.12 and 4.13 respectively. Compared to gum (Fig. 4.11a), the filled SBRs (Fig. 4.12a and 4.13a) contain uniformly distributed dispersed particles (silica/black). But the silica filled SBR shows some agglomeration which is absent in the case of black filled SBR. This accounts for the better mechanical properties of black filled SBR. In the case of blends, the minor phase is always dispersed in the major phase [26-27]. Because of the presence of styrenic segments, interaction between the copolymer (SBR) and homopolymer (PS) is possible which induces partial miscibility in the blend [4]. This can be well evidenced from the SEM micrographs. From the SEM images it is clear that the interaction between the phases is more for gum SBR/EPS (Fig. 4.11b) blend followed by the silica filled system (Fig. 4.12b) and the least for the black filled system (Fig. 4.13b). Some extent of inter diffusion and co-continuity can be seen in the case of blend gum compound. Unidirectional stretching of both the phases also supports the existence of interaction.

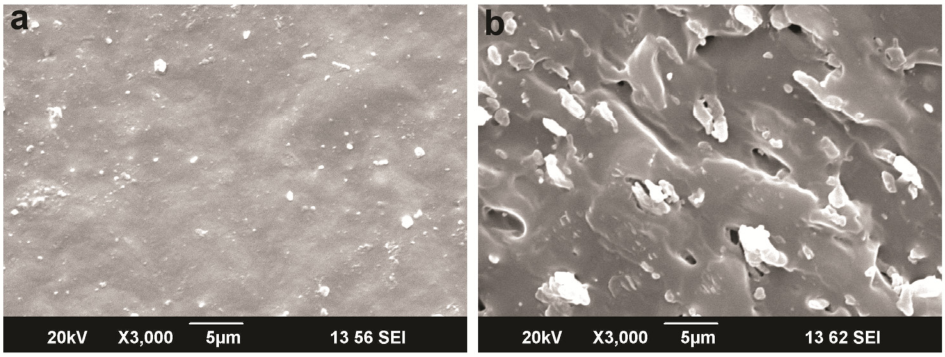


Fig. 4.11. SEM images of tensile fracture surfaces of unfilled samples (a) SBR and (b) 85/15 SBR/EPS blend

In the case of silica filled blend, interaction between the phases at certain regions and pull out of PS phase from the SBR indicate that the phase interaction is less compared to the gum compound. The roundness of dispersed phase as well as the non uniformity in size and shape reveals the possibility of lesser interaction.

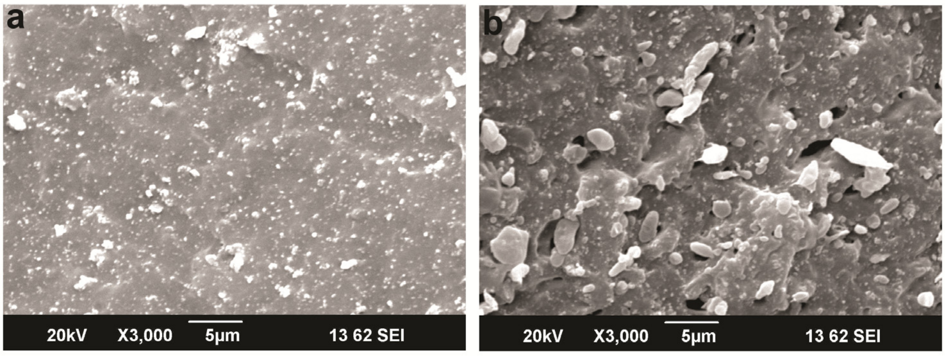


Fig. 4.12. SEM images of tensile fracture surfaces of silica filled samples (a) SBR and (b) 85/15 SBR/EPS blend

In the case of the black filled blend, the PS phase is simply dispersed in the SBR matrix without much interaction. The surface roughness is less compared to gum and silica systems. The non-uniform shape and size of the dispersed phase as a result of ineffective interaction lowers the tensile properties as discussed above in Section 4.3.2. The tensile properties of the gum blend showing greater improvement compared to gum SBR are in good agreement with the SEM of tensile fractured surfaces. The blend of silica system also shows some improvement in tensile properties as a result of limited interaction evident in the SEM.

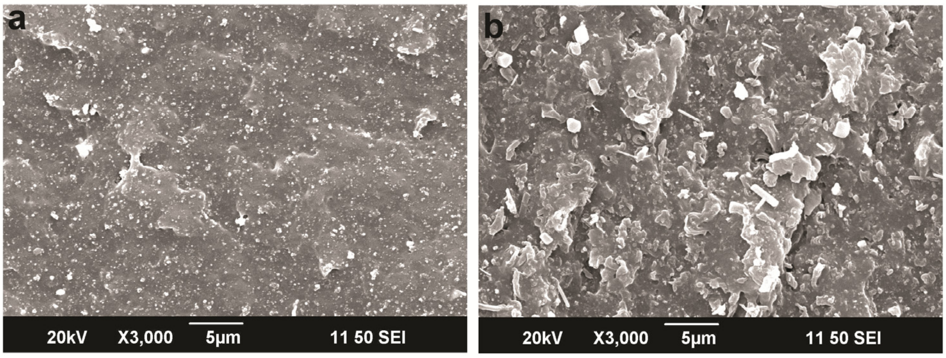


Fig. 4.13. SEM images of tensile fracture surfaces of carbon black filled samples (a) SBR and (b) 85/15 SBR/EPS blend

4.3.8 Thermogravimetric analysis

Fig. 4.14 represents DTG curves of gum SBR and SBR/EPS blends with varying EPS loadings and Fig. 4.15 is that of SBR and 85/15 SBR/EPS blends of gum, silica and black systems. The thermal data of SBR and SBR/EPS blends of gum, silica and black systems are tabulated in Table 4.9.

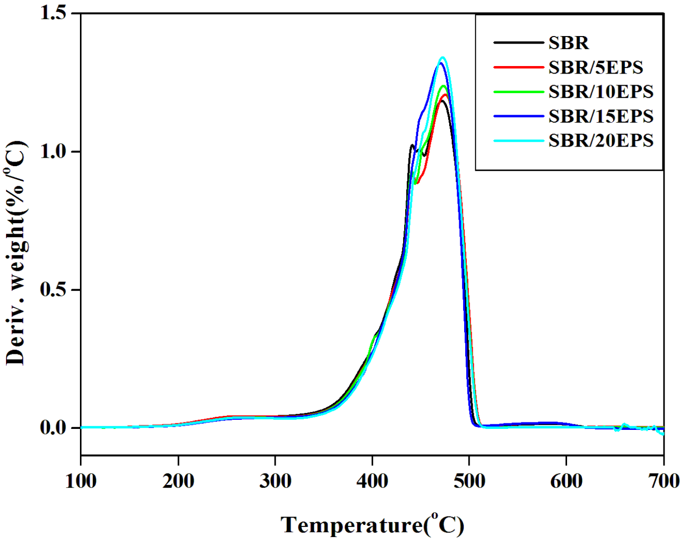


Fig. 4.14. DTG curves of SBR/EPS blends with varying EPS loading

The degradation temperature range of SBR is 345 °C -510 °C for all the systems with a marginal shift to higher temperature for the filled system. Also the filled systems show lower rates of degradation indicating somewhat better thermal stability than gum compounds.

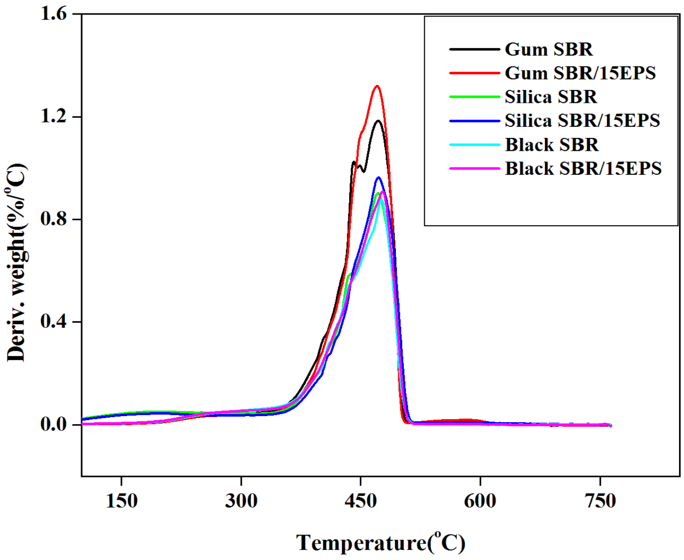


Fig. 4.15. DTG curves of SBR and 85/15 SBR/EPS blends of gum, silica and black systems

The onset of degradation temperatures (Ti) of SBR in gum, silica and black filled systems are 345 °C, 355 °C and 354 °C and the peak degradation temperatures (Tm) are 472 °C, 470 °C and 475 °C respectively. The 85/15 blends showed almost the same Ti, Tm, T_f and residue (%) values as that of SBR. From the data it is clear that the loading of EPS does not alter the thermal stability of SBR irrespective of whether the system is gum/silica/black.

Table 4.9. The thermal data of SBR and SBR/EPS blends of gum, silica and black systems

Thermal data	**Gum compounds**					**Silica filled compounds**		**Black filled compounds**	
	SBR	**SBR/EPS blends**				**SBR**	**SBR/EPS 95/15**	**SBR**	**SBR/EPS 95/15**
		95/5	**90/10**	**85/15**	**80/20**				
T_i (°C)	346.2	347.0	350.0	352.1	357.2	355.4	358.2	354.1	357.2
T_{max} (°C)	472.4	475.3	473.2	470.2	472.1	471.0	473.3	475.4	478.2
T_f (°C)	504.1	509.2	509.0	501.0	509.4	506.0	506.1	504.2	503.1
$T_{5\%}$ (°C)	322.0	318.4	332.2	334.2	337.3	198.0	212.2	308.4	303.0
$T_{50\%}$ (°C)	454.1	458.0	457.2	457.2	459.4	463.3	467.0	470.3	469.4
Residue (%) at 650 °C	4.2	4.8	4.6	4.2	3.9	21.4	21.2	29.2	27.3

4.3.9 Dynamic mechanical analysis

The storage modulus (Fig. 4.16) and loss modulus (Fig. 4.17) of SBR and 85/15 SBR/EPS blends of gum, silica and black filled systems are shown below. The glassy region (low temperature) of SBR as well as the blends exhibits the highest storage modulus. The storage modulus is found to decrease on temperature rise and finally levels off at high temperature. This decrease is due to the lowering of stiffness because of the enhanced segmental mobility at high temperature. Hence a drastic drop in modulus can be seen in the transition region. Only a slight difference in storage modulus was noticed among the compounds in the glassy region and the difference is pronounced at higher temperatures. Dynamic mechanical properties of SBR were affected by the content of EPS. Blends showed higher storage modulus than the corresponding SBR compounds which is more pronounced at high temperatures. The maximum storage modulus was observed with black filled blend and the lowest by gum SBR. Because of the interaction between EPS and SBR matrix, higher storage modulus values for the blends than that of neat SBR is observed. This confirms that EPS strongly restricts the movement of SBR macromolecular chains. The loss modulus also showed the same trend as the storage modulus and its peak represents the maximum heat dissipation per unit deformation.

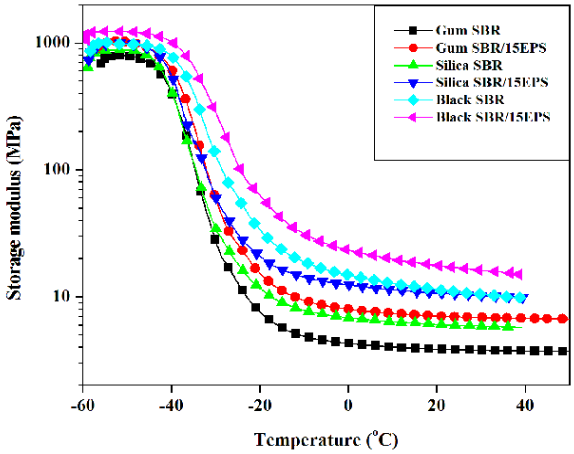


Fig. 4.16. Storage modulus variation of SBR and 85/15 SBR/EPS blends of gum, silica and black filled systems with temperature

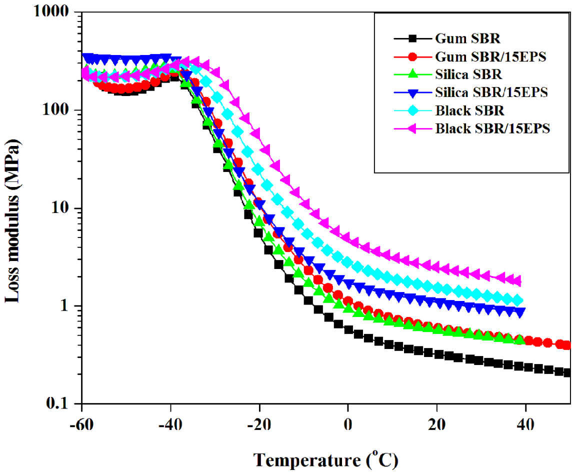


Fig. 4.17. Loss modulus variation of SBR and 85/15 SBR/EPS blends of gum, silica and black filled systems with temperature

Fig. 4.18 represents the tan δ curves of SBR and 85/15 SBR/EPS blends of gum, silica and black filled systems. Lower tan δ max values for the blends, indicate restricted segmental mobility through strong interaction between the blend components. This suggest that PS beads act as a crosslink points to tie molecular segments together through the specific interaction resulting in restricted segmental motion [28].

This behavior is more pronounced in black filled systems due to the further decrease in chain mobility on account of the higher reinforcement offered by carbon black.

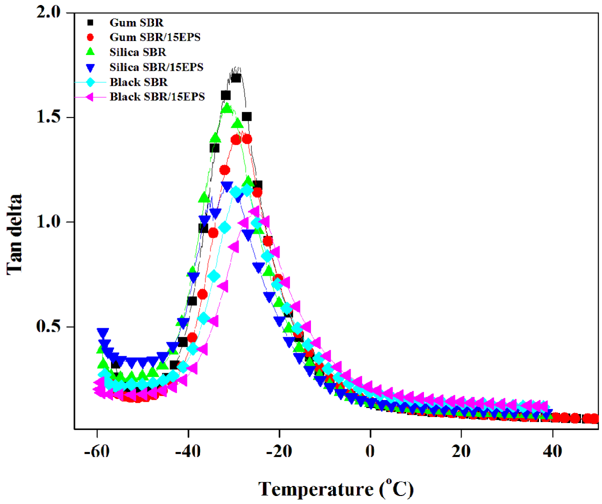


Fig. 4.18. Tan δ curves of SBR and 85/15 SBR/EPS blends of gum, silica and black filled systems

Fig. 4.19 is the tan δ curves of the blends in a wider range of temperature which covers glass transition temperatures (T_g) of both phases. The same figure in which the tan δ curve of EPS is also included, is shown in the inset. Table 4.10 gives the glass transition temperatures taken from the tan delta peak. Since PS and SBR are totally amorphous homopolymer and copolymer, the only transition traced in the curves is the glass transition temperature. As expected both PS (134 °C) and SBR (-29.2, -31.4 and -27.4 °C for gum, silica and black respectively) show single T_g. But the blends are characterised by two distinct T_gs, one each in both negative and positive temperature ranges. The thermomechanical behavior of the blends is somewhat similar to that of SBS which shows two T_gs around 100 °C and -67 °C [4]. In the case of all the blends it was observed that the glass transition temperature of SBR remains unchanged with EPS content, whereas that of the PS phase gets depressed. That is, the glass transition temperature of SBR is less affected by the presence of 15% EPS whereas that of PS was reduced by 6-7 degrees and the sharp peak of EPS has significantly changed to a broad peak. The broad peak as well as the shifting of the peak towards lower temperature can be an indication of phase interaction and interphase formation.

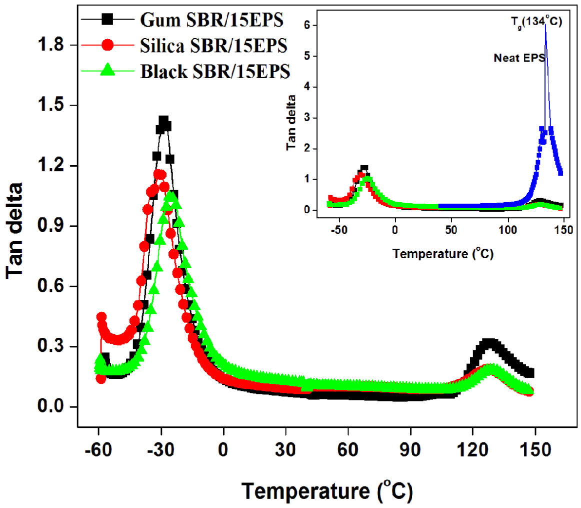


Fig. 4.19. Tan δ curves of the blends covering T_gs of both phases. Inset is the same figure in which the tan δ curve of EPS is also included

Table 4.10. Glass transition temperatures of the compounds

Compounds		Glass transition temperature, Tg (°C)
Pure EPS		134.0
Gum	SBR	-29.2
	85/15 SBR/EPS	-28.4, 128.0
Silica	SBR	-31.4
	85/15 SBR/EPS	-31.0, 127
Black	SBR	-27.4
	85/15 SBR/EPS	-25.0, 129.0

4.4 Conclusion

SBR/EPS blends show lower cure time and torque values compared to SBR compounds without EPS. A significant improvement in tensile strength (146%), modulus at 300% (180%) and tear strength (157%) is found for 85/15 SBR/EPS blend when compared with neat SBR for the gum systems. Silica filled blend showed an improvement of 54%, 123% and 76% for the above mentioned properties compared to silica filled SBR. For black filled blends modulus has improved by 85% and tear strength by 20% whereas tensile strength is comparable to black filled SBR. Because of the presence of brittle PS, elongation has reduced for all the blends.

An improvement in properties was found for the blends on aging for both unfilled and filled systems. But the blends showed some reduction in properties on aging compared to virgin SBR. Compression set, abrasion loss, hardness and resilience of unfilled 85/15 SBR/EPS blends are similar to filled SBR systems without EPS. The crosslink density values are in good agreement with the mechanical properties. Deformation of PS particles during tensile fracture and the interaction between the phases are well indicated in the morphology of both gum and silica filled system. This again justifies the improvement in mechanical properties.

Thermal stability of SBR was not affected by the incorporation of EPS. Higher storage modulus of the blends compared to neat SBR indicates better crosslink density for all the three systems. Glass transition temperature of SBR is less affected by the presence of 15% EPS whereas that of EPS was reduced by the blending.

Improvement in the mechanical and aging properties of the SBR/EPS blends compared to virgin SBR paves a way for the effective and economical utilization of waste EPS through value addition.

References

[1] Goyanes, S., Lopez, C. C., Rubiolo, G. H., Quasso, F. & Marzocca, A. J. Thermal properties in cured natural rubber/styrene butadiene rubber blends. *Eur. Polym. J.* **44,** 1525–1534 (2008).

[2] Radhakrishnan, C. K., Kumari, P., Sujith, a. & Unnikrishnan, G. Dynamic mechanical properties of styrene butadiene rubber and poly (ethylene-co-vinyl acetate) blends. *J. Polym. Res.* **15,** 161–171 (2008).

[3] Arayapranee, W. *Rubber Abrasion Resistance. In Abrasion Resistance of Materials*. Ed. Adamiak M. (InTech, 2012). doi:10.5772/1083

[4] Yousefi, A. A. Segmental mobility in the vicinity of T g in PS/SBR blends: Nanodomain size prediction of the dispersed phase. *J. Appl. Polym. Sci.* **127,** 659–665 (2013).

[5] Veilleux, J. & Rodrigue, D. Optimization of a Polymer Blend Based on Recycled Polystyrene And Styrene-Butadiene Rubber. in *Third US-Mexico Meeting 'Advances in Polymer Science' and XXVII SPM National Congress* (2014).

[6] Vo, L. T., Anastasiadis, S. H. & Giannelis, E. P. Dielectric study of Poly(styrene- co -butadiene) Composites with Carbon Black, Silica, and Nanoclay. *Macromolecules* **44,** 6162–6171 (2011).

[7] Amabilino, D. B. & Stoddart, J. F. Interlocked and Intertwined Structures and Superstructures. *Chem. Rev.* **95,** 2725–2828 (1995).

[8] Hirsch, K. A., Wilson, S. R. & Moore, J. S. A Packing Model for Interpenetrated Diamondoid Structures—an Interpretation Based on the Constructive Interference of Supramolecular Networks. *Chem. - A Eur. J.* **3,** 765–771 (1997).

[9] Chun, B. C. & Gibala, R. Mechanical and Morphological Behavior in Polystyrene Based Compatible Polymer Blends. *Polym. Eng. Sci.* **36,** 744–754 (1996).

[10] Hara, M. & Sauer, J. A. Synergism in Mechanical Properties of Polymer / Polymer Blends Synergism in Mechanical Properties of Polymer / Polymer Blends. *J. Macromol. Sci. Part C ISSN* **1797,** 327–362 (2015).

[11] Kambour, R. P., Bendler, J. T. & Bopp, R. C. Phase behavior of polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide), and their brominated derivatives. *Macromolecules* **16,** 753–757 (1983).

[12] Ten Brinke, G., Karasz, F. E. & MacKnight, W. J. Phase behavior in copolymer blends: poly(2,6-dimethyl-1,4-phenylene oxide) and halogen-substituted styrene copolymers. *Macromolecules* **16,** 1827–1832 (1983).

[13] Nunes, R. C. R. & Mano, E. B. Influence of cellulose as a filler in vulcanized rubber composites. *Polym. Compos.* **16,** 421–423 (1995).

[14] Robeson, L. M. & Faucher, J. A. Secondary loss transitions in antiplasticized polymers. *J. Polym. Sci. Part B Polym. Lett.* **7,** 35–40 (1969).

[15] W Jackson, W. J. & Caldwell, J. R. Antiplasticization. II. Characteristics of antiplasticizers. *J. Appl. Polym. Sci.* **11,** 211–226 (1967).

[16] Jiang, M., Huang, X. & Yu, T. Phase separation in blends of homopolymer and graft copolymer based on styrene and butadiene. *Polymer (Guildf).* **24,** 1259–1266 (1983).

[17] Munk, P. *In Introduction to Macromolecular Science*. Wiley Interscience: New York (1989)

[18] Vo, L. T. & Giannelis, E. P. Compatibilizing Poly(vinylidene fluoride)/ Nylon-6 Blends with Nanoclay. *Macromolecules* **40,** 8271–8276 (2007).

[19] Mathew, G., Singh, R., Nair, N. & Thomas, S. Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber. *Polymer (Guildf).* **42,** 2137–2165 (2001).

[20] Mostafa, a., Abouel-Kasem, a., Bayoumi, M. R. & El-Sebaie, M. G. Effect of carbon black loading on the swelling and compression set behavior of SBR and NBR rubber compounds. *Mater. Des.* **30,** 1561–1568 (2009).

[21] Nelson, P. A. & Kutty, S. K. N. Studies on Maleic anhydride grafted reclaimed rubber/acrylonitrile butadiene rubber blends. *Prog. rubber, Plast. Recycl. Technol.* **19,** 171–188 (2003).

[22] van der Schuur, M. & Gaymans, R. J. Influence of chemical crosslinks on the elastic behavior of segmented block copolymers. *Polymer (Guildf).* **46,** 6862–6868 (2005).

[23] Haghighat, M., Zadhoush, A. & Khorasani, S. N. Physicomechanical properties of α-cellulose-filled styrene-butadiene rubber composites. *J. Appl. Polym. Sci.* **96,** 2203–2211 (2005).

[24] Thavamani, P., Khastgir, D. & Bhowmick, A. K. Microscopic studies on the mechanisms of wear of NR, SBR and HNBR vulcanizates under different conditions. *J. Mater. Sci.* **28,** 6318–6322 (1993).

[25] Wang M, Zhang P, Mahmud K. Carbon–silica dual phase filler, A new generation reinforcing agent for rubber Part IX, application to truck tire trade compound. *Rubber Chem. Technol.* **74,** 124–37 (2001).

[26] Ibrahim, B. a & Kadum, K. M. Morphology Studies and Mechanical Properties for PS / SBS Blends. *Int. J. Eng. Technol.* **12,** 19–27 (2012).

[27] Joseph, S. & Thomas, S. Morphology, morphology development and mechanical properties of polystyrene/polybutadiene blends. *Eur. Polym. J.* **39,** 115–125 (2003).

[28] Cha, Y.-J. & Choe, S. Characterization of crosslinked polystyrene beads and their composite in SBR matrix. *J. Appl. Polym. Sci.* **58,** 147–157 (1995).

* * *

Chapter 5

UTILIZATION OF EPS AND MODIFIED EPS IN COMMERCIAL UNSATURATED POLYESTER RESIN (UPR)

Contents

5.1 Introduction

Waste generated by polymers cause a grave threat to the ecology of the planet as they remain practically without degradation even after a long period of exposure [1]. Among the common plastic wastes, expanded form of polystyrene (expanded polystyrene/EPS) is a major problem for the environment. The world wide consumption of EPS was 5.833 million t in 2011 [2]. Its nuisance value in the environment is high because of its large volume. Any reduction of the amount of waste EPS littering the environment can be considered an ecologically significant step. Due to economic reasons such as high transportation costs and small price difference between virgin polystyrene (PS) and recycled PS the recycling of EPS is less practical [3]. A promising strategy is to blend waste EPS with other polymers by cost effective methods. To enhance the miscibility of the blends modifications can also be done.

Many methods can be employed to increase the miscibility of polymer blends. One well known method is to modify the chemical structure of one component of the polymer blend by grafting. This functionalization of the blend components is often required [4, 5]. One of the most common methods adopted is grafting of maleic anhydride (MA) on to a polymer. Maleic anhydride grafting onto a polyolefin backbone by a radical process has been studied extensively [6-12]. However, similar grafting reactions of molten polystyrene with MA have been sparsely reported [13, 14].

In this part of the work, EPS has been utilized for blending with unsaturated polyester resin (UPR) formulations. Unsaturated polyester resins, due to their low manufacturing cost and high tensile strength, have been widely used as industrial thermosetting resins [15, 16]. Their extensive applications include glass fiber reinforced polyesters [17] and molding compounds [18]. Several articles have been published on blends of unsaturated polyester resin with different thermoplastics for controlling volume shrinkage as discussed in Chapter 1. Such thermoplastics are known a as low profile additives (LPA). However there are only a limited number of papers concerning the miscibility & mechanical properties of polymer blends where one component is crystallizable or amorphous and the other is highly crosslinkable UPR [15-16,19-22]. Techniques such as measurement of viscosity, ultrasonic velocity, density, and refractive index have been used to study the miscibility of the polymer blends of UPR with PS and polycarbonate (PC) as reported by Sun-Kuk Kim et al. [15]. N. Taheri Qazvini and N.

Mohammadi investigated the segmental dynamics of UPR/HIPS blends [23]. Polymer composite material based on unsaturated polyester resin/high impact polystyrene with waste dust as filler has been studied by Milena Koleva and co workers [24]. Studies on the flammability of UPR/EPS have been done by S. A. B. Syed Mustafa et al. [25].

The extent to which waste EPS must be incorporated to the UP resin in order to gain the best desirable properties of the finished product is the main focus of this study.

5.2 Experimental

5.2.1 Materials

The materials used are given in Section 2.1 of Chapter 2.

5.2.2 Methods

5.2.2.1 Preparation of EPS incorporated UPR

Preparation of EPS incorporated UPR is given in section 2.2.3 of Chapter 2. Varying quantities (2.5, 5, 7.5 & 10 phr) of expanded polystyrene were used and four mixes were prepared. To each of this 100 phr unsaturated polyester resin was added and stirring was done using a mechanical stirrer for 30min to get a homogeneous liquid. These blends were designated unmodified blends (UPR/EPS).

For the preparation of modified blends varying quantities (2.5,5, 7.5 & 10 phr) of grafted EPS were used in different mixes. These blends were designated modified blends (UPR/ modified EPS (UPR/EPS(m)).

5.2.2.2 Curing of EPS/polyester resin blends

Procedure for curing of resin samples is given in section 2.2.4.

5.2.2.3 Sample preparation for FTIR analysis

The MA grafted EPS (MA-g-EPS) prepared using Brabender Plasticorder was washed with water and acetone several times. Both the neat EPS and modified EPS samples were solution-cast using tetrahydrofuran as solvent. The solvent was evaporated before recording the IR spectra. FTIR analysis was also done for cured samples of neat UPR and both unmodified and modified blends.

5.2.3 Characterisation

Characterisation techniques were explained in detail in Section 2.3 of Chapter 2.

5.3 Results and discussion

5.3.1 Fourier Transform Infrared Spectroscopy

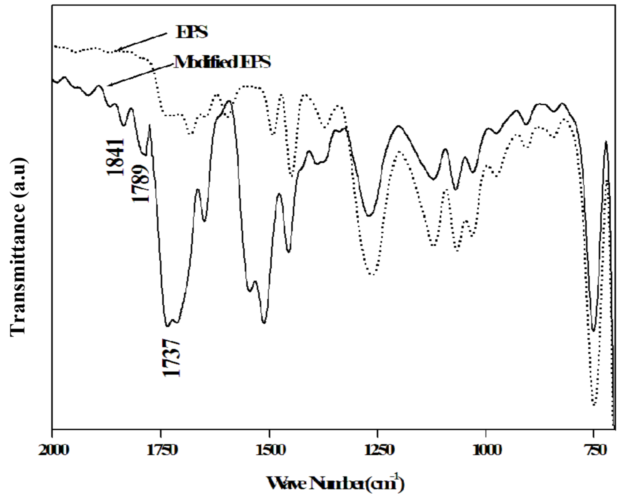


Fig. 5.1. Infrared spectrum of the unmodified EPS and MA grafted EPS

Representative infrared spectra of the unmodified EPS and MA grafted EPS are shown in Fig.5.1. The FTIR spectrum of modified EPS (EPS-g-MA) shows some additional absorption at 1737cm^{-1}, 1789cm^{-1} and 1841cm^{-1} which are not observed in the spectrum of unmodified EPS. From the literature, bands in the range 1870–1820 cm^{-1} and 1800–1775 cm^{-1} are due to five-membered anhydride rings [26, 27]. The characteristic bands at 1789 cm^{-1} and 1841 cm^{-1} in the above figure are assigned to a carbonyl stretching in MA grafted on EPS [13, 14, 28]. They are due to symmetric (strong) and asymetric (weak) carbonyl (C=O) stretching vibrations of succinic anhydride rings grafted on PS (polystyrene). This proves that MA units are introduced into the PS backbone because the unreacted MA was removed from the sample earlier. The absorption band around 1700-1740cm^{-1} is due to the presence of peroxide.

5.3.2 Gel time & peak exothermic temperature

Fig.5.2. shows the effect of EPS and modified EPS on the gel time (Fig.5.2a) and peak exothermic temperature (Fig. 5.2b) of UPR. Presence of LPA is found to initially delay the gelation marginally, upto 2.5 phr of EPS. It has been reported that the addition of low profile additive slows down the cure because of the dilution effect [29]. But higher loading of EPS leads to an earlier onset of viscosity rise which results in higher reaction rates and earlier gelation. This autoacceleration may be attributed to Trommsdorff effect or the gel effect [30].

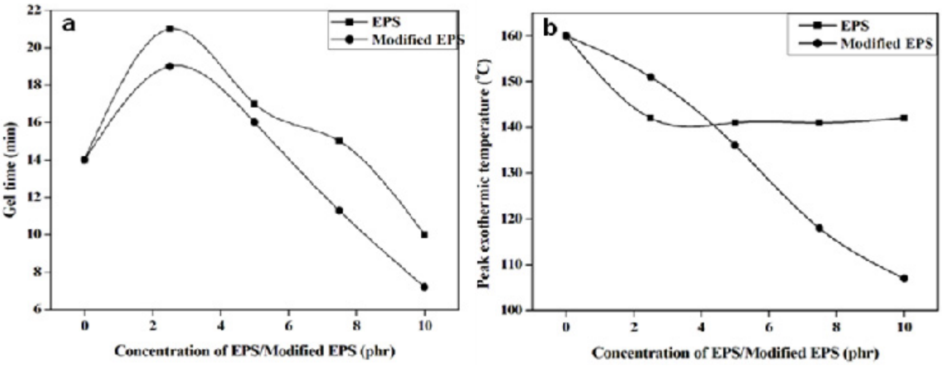


Fig.5.2. **Effect of EPS and modified EPS on the (a) gel time and (b) peak exothermic temperature of UPR.**

The localized increase in viscosity of the polymerizing system slows down the termination rate. The decreasing rate of termination causes a rapid increase in the overall rate of reaction. The higher molecular weight LPA contributes directly to the viscosity rise. Before autoacceleration sets in, the chain termination by combination of two free radical chains is very rapid occurring at very high frequency (about one in 10^4 collisions). However, when the growing polymer molecules with active free radical ends are surrounded by a highly viscous mixture consisting of a growing concentration of "dead" polymer, the rate of termination is limited only by diffusion [31, 32]. The Brownian motion of the larger molecules in the polymer is also restricted, therefore limiting the frequency of their effective (termination) collisions. In the context of LPAs, the increase in viscosity may also be related to chain entanglement of UPR with the high molecular weight EPS (M_n = 86054).

Presence of inert LPA has also the additional effect of lowering the peak exotherm [33]. Modified EPS also shows the same trend but the peak exotherm continuously falls with the addition of more and more EPS in this case. This may be due to the improved interaction between the two phases in the case of modified EPS which can give rise to side reactions involving the anhydride ring.

5.3.3 Specific gravity

Effect of loading of EPS/ modified EPS on specific gravity of UPR is shown in Fig. 5.3. Specific gravity of both the blends at lower EPS (2.5phr) loading is higher than that of pure UPR. In the case of the unmodified blend, on increasing the EPS loading, the specific gravity decreases to a level lower than that of pure UPR. This behaviour has been already reported [34]. This can be attributed to the lower density of LPA as well as generation of microvoids which is a part of the shrinkage compensation mechanism of the LPA. For the modified blend, the fall in specific gravity is only marginal due to enhanced phase interaction resulting from the presence of polar EPS (MA-g-EPS).

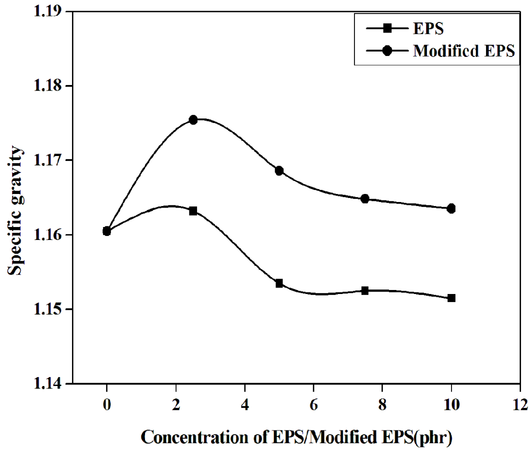


Fig. 5.3. Effect of loading of EPS/modified EPS on specific gravity of UPR

5.3.4 FTIR of cured polyester resin

Fig. 5.4 shows the FTIR spectra of cured neat UPR and its blends with EPS/modified EPS at 5 and 10phr loadings. All the characteristic peaks of cured resin are observed in the spectra of all the samples. There are no additional peaks in the spectra of blends as they contain similar components as the neat UPR. The presence of –C=O stretching are confirmed by the strong band at 1714 cm^{-1}. The peak at 1266 cm^{-1} confirms the presence of C-O-C- (ester linkage). Alkane, $–CH_2$, was confirmed by the presence of the band at 1457 cm^{-1}. The peak at 1513 cm^{-1} corresponds to the C=C stretching vibration in the aromatic ring. The absence of peaks at 1755cm^{-1}(C=O of anhydrides) and 1375cm^{-1} (-OH of phthalic anhydride) is an indication of resin formation and the peaks at 910 cm^{-1} (CH_2 out of plane of C=C vinyl styrene), 1645 cm^{-1}(C=C in polyester) support the crosslinking reaction. The band at 745 cm^{-1} is attributed to the o-disubstituted –C-H stretching in aromatic ring.

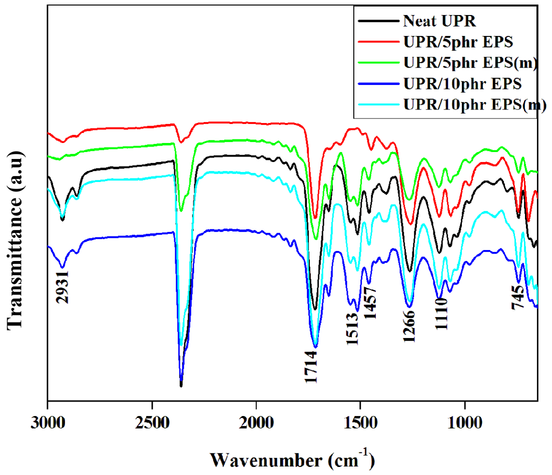


Fig. 5.4. FTIR spectra of cured neat UPR and its blends with EPS/modified EPS

5.3.5 Morphological studies

Scanning electron micrographs of (a) Pure UPR, (b) UPR/EPS$_{(5phr)}$, (c), UPR/modified EPS$_{(5phr)}$ (d) UPR/EPS$_{(10phr)}$ and (e) UPR/modified EPS$_{(10phr)}$ are shown in Fig. 5.5. The surface morphology of the neat UPR is found to be plane and flake-like [35]. For the unmodified blends (UPR/ EPS$_{(5phr)}$ and UPR/ EPS$_{(10phr)}$), the globular EPS phase is surrounded by the UPR network. Most PS particles have been ejected from the surfaces of polyester matrix, indicating poor adhesion. The microvoids between the two phases are the consequence of phase separation before curing. The small voids present in the EPS phase can also be due to the emission of monomer styrene entrapped in the EPS phase. In the case of modified blends, as the polarity and molecular weight of EPS increased, a thick interphase has formed between the UPR and EPS phases (by the disappearance of the microvoids between the two phases), as indicated by the thick arrow. It is believed that this phase is formed through gelation of microgel particles [16].

The presence of this interphase indicates better adhesion between the two phases which is responsible for the enhanced mechanical properties of modified blends. As the EPS content goes up, the domain size increases and the microvoids also become thicker due to the segregation of EPS from the UPR microgel. This helps to compensate volume shrinkage better.

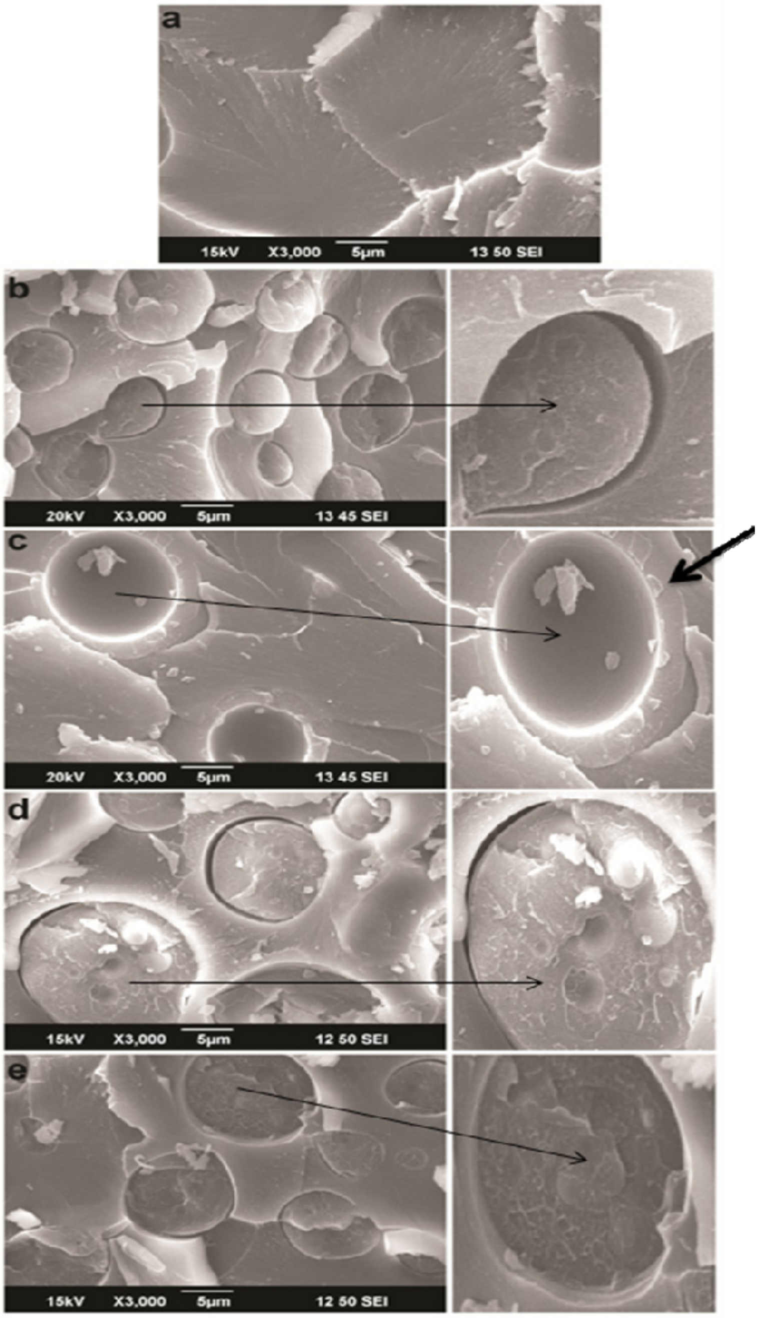


Fig. 5.5. Scanning electron micrographs of (a) Pure UPR, (b) UPR/EPS$_{(5phr)}$, (c), UPR/modified EPS$_{(5phr)}$ (d) UPR/EPS$_{(10phr)}$ and (e) UPR/modified EPS$_{(10phr)}$

5.3.6 Tensile Properties

Generally speaking, tensile properties show a decreasing trend with thermoplastic content when used as low profile additives [34]. With increasing content of these thermoplastics, the dispersed thermoplastic phase inevitably becomes more prominent and the tensile properties decline. As the volume fraction of microvoids would be generally lower for PS system (due to less phase separation between UPR and PS phases during curing) compared to other thermoplastic systems, PS systems should possess higher tensile properties than others.

Fig. 5.6 shows the variation of (a) tensile strength and (b) percentage of elongation of UPR with EPS/modified EPS loading. A reduction of tensile strength is observed on EPS loading for UPR/ EPS blends. This may be due to microvoids which may act as stress concentrators [19,29,34]. Another reason for inferior tensile strength of UPR/EPS blends compared to neat UPR, is the incompatibility of the two phases due to the non-polar nature of EPS. Also the plasticizing effect of EPS reduces the tensile strength. It is seen that the reduction in tensile strength is low with EPS due to the low volume fraction of the microvoids [34].

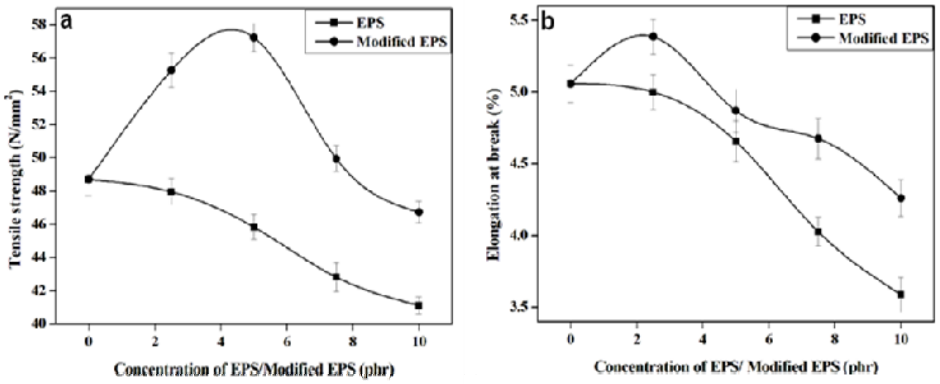


Fig. 5.6. The variation of (a) tensile strength and (b) elongation at break of UPR with EPS/modified EPS loading.

The decrease in tensile strength on EPS loading can be correlated to the morphology of tensile fractured surfaces, as discussed earlier. But modified EPS initially enhances the tensile strength due to improvement of compatibility between the phases [34]. Modified EPS is slightly polar, due to the presence of carboxylic group, which enhances the interaction/ adhesion between UPR and EPS. If good adheshion is achieved the dispersed particles internally cavitate more and their presence causes less mechanical property loss [36].

Elongation decreases with EPS/modified EPS loading. This is because poor compatibility of the system causes phase separation and the presence of a distinct brittle PS phase in the major continuous UPR phase reduces the strain at break. As the amount of EPS increases, the brittle phase dominates and the reduction in elongation will be severe [19]. For the modified blends the decrease in % of elongation is not so pronounced as in the case of unmodified blends.

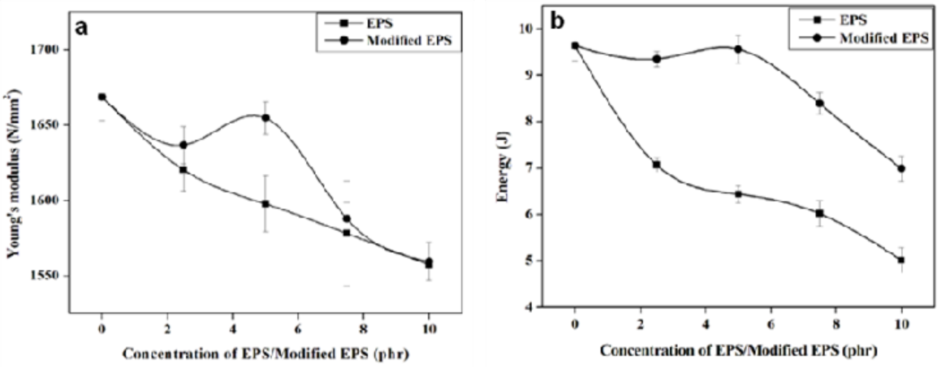


Fig. 5.7. The effect of EPS/modified EPS loading on (a)Young's modulus and (b) energy of UPR

Fig. 5.7 shows the variation of Young's modulus and energy absorbed that with loading of EPS/modified EPS into neat UPR. Young's moduli of all the blends are inferior to that of neat UPR. Since the degree of crosslinking is substantially unaffected by the presence of EPS, the fall in modulus can be attributed to a reduced degree of tightness of the network [20,29]. The plasticizing effect of EPS can also be responsible for this reduction.

The energy absorption capacity can be taken as a measure of fracture toughness. There is a decrease in toughness on EPS loading. In the case of modified blends, the toughness is largely unaffected up to 5phr EPS. The brittle nature of EPS lowers the tensile strength and elongation. The reduction in these properties can directly lead to a lowering of toughness which is, in this case, the area under the stress-strain curve. The presence of a thermoplastic additive can improve the toughness in principle. But this effect is largely neutralized by the loose encapsulation in the case of unmodified PS particles as shown by SEM (to be discussed later). Understandably, the toughness is better in the case of modified EPS.

5.3.7 Impact strength

Fig. 5.8 shows the effect of adding EPS/modified EPS on the impact strength of UPR. Impact strength shows a decreasing trend on addition of EPS/modified EPS to UPR. The addition of brittle thermoplastics such as PMMA or PS normally results in brittleness of the cured sample which lowers the impact strength [19]. This can also be due to the weak interfacial bonding between the component polymers. The impact strength is comparatively higher for modified blend systems where compatibility is enhanced [34] and the encapsulation of the PS particles is more effective.

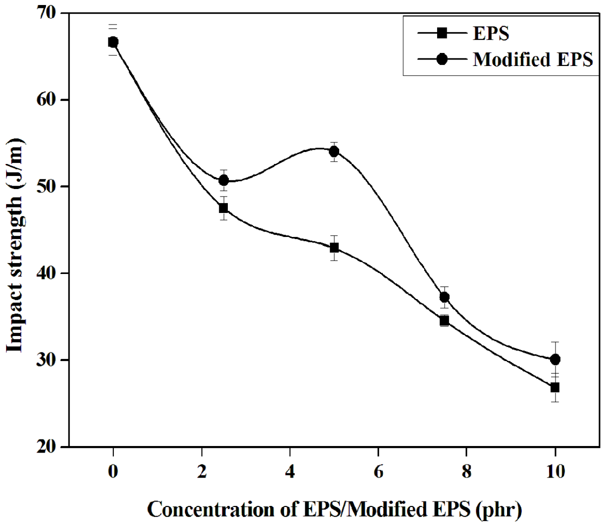


Fig. 5.8. The effect of loading EPS/Modified EPS on the impact strength of UPR

5.3.8 Flexural Properties

Fig. 5.9 is the flexural strength (a) and flexural modulus (b) curves of the neat UPR and its blends with varying content of EPS/modified EPS. A gradual decline of flexural strength is noticed on adding EPS. This behaviour is supported by the results which comply with past studies showing that tensile strength of polyester generally decline with addition of thermoplastics (LPA) [19-20,37 -39]. The reduction in flexural strength of the blends is associated with the heterogeneous nature of the blend system as obvious from SEM images. Because of the incompatibility and microvoids, the blend experiences poorer stress transfer resulting in low mechanical properties [40]. The modified blends show considerable improvement in flexural strength over unmodified blends and the strength at 5phr is very close to neat UPR.

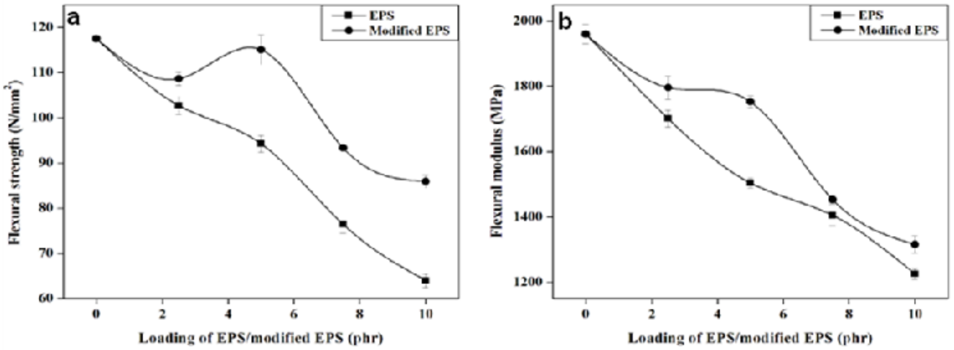


Fig. 5.9. Flexural strength (a) and flexural modulus (b) of the neat UPR and its blends with varying content of EPS/modified EPS

Flexural modulus showed a similar decreasing behaviour to flexural strength when thermoplastics were added to the resin. This result is similar to that of storage and Youngs' modulii. Here also modified blends showed better performance than unmodified blends.

5.3.9 Crosslink density

The crosslink density of the cured samples of neat UPR and its blends with EPS/modified EPS is shown below in Fig. 5.10. As expected, the crosslink density values of the blends show a decrease with increasing EPS content because of phase separation and less than perfect curing. At the same time, brittleness of the sample increases because of the brittle dispersed phases as well as the presence of voids in between phases as seen from SEM micrographs. The above factors, i.e., low crosslink density and brittleness together lower the mechanical properties of the unmodified blends. The modified blends show better crosslink density than unmodified blends. This is because of better chemical compatibility between the phases. The higher crosslink density and the absence of voids account for the better mechanical properties.

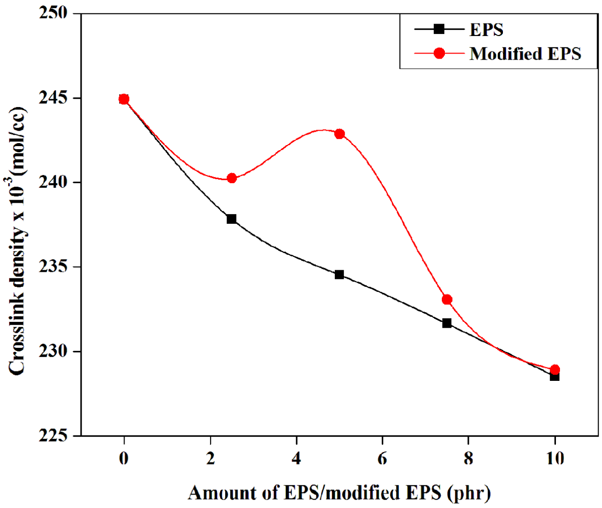


Fig.5.10. Crosslink density of the cured samples of neat UPR and its blends with EPS/modified EPS

5.3.10 Chemical resistance

Chemical resistance tests are done to estimate the ability of a composite to withstand exposure to acids, alkalis, solvents and other chemicals over specific periods of time. The weight gain for the neat unsaturated polyester and its blends with EPS/modified EPS in different solvents is shown in Table 5.1.

The results show that water absorption increases with increase of EPS content for both types of blends. The water absorption rate of a material is closely related to the open porosity (free volume) inside the material and hydrophilic functional groups [34, 41]. Higher water absorption rates imply that more voids are formed inside the composites as indicated by blend morphology and volume shrinkage data given in Chapter 7. At higher EPS concentrations the water uptake is lower because of its hydrophobic nature. The water absorption values for modified blends are lower than that of unmodified blends. This may be attributed to the better chemical compatibility and inter component adhesion of modified blends. Moreover, polymeric systems with higher crosslink density possess lower water uptake [42]. The water absorption at lower EPS concentration in the case of modified blends is comparable to neat UPR.

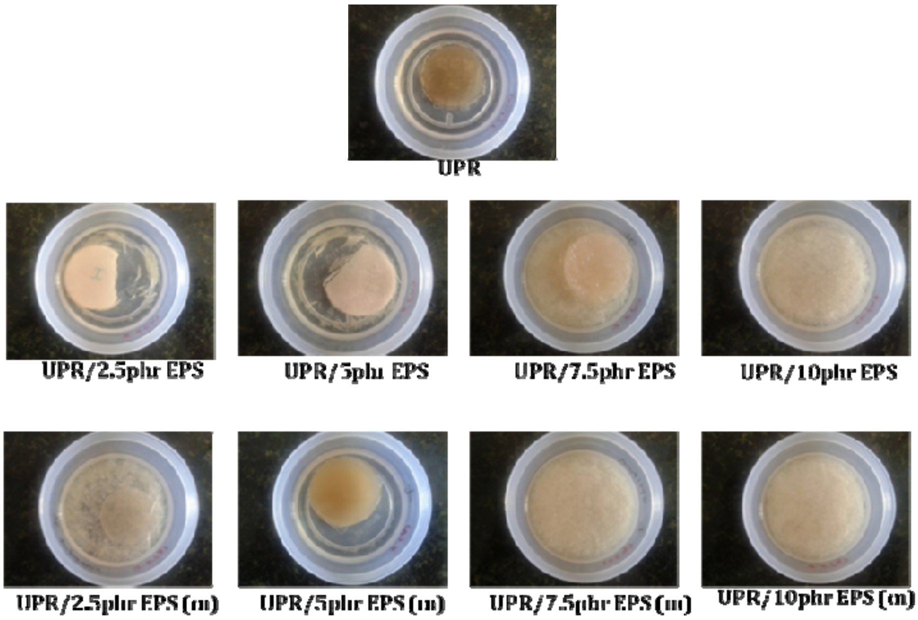
Table 5.1. The weight gain for the neat unsaturated polyester and its blends with EPS/modified EPS in solvents

	EPS Loading (phr)	**Weight gain (%) of samples immersed in solvents for specified period**					
		H_2O		**HCl (0.1N)**		**NaOH (0.1N)**	
		1 day	**5 day**	**1 day**	**5 day**	**1 day**	**5day**
Neat UPR	0	0.268	0.360	0.230	0.426	0.252	-
Unmodified UPR/EPS Blend	2.5	0.278	0.372	0.212	0.376	0.316	-
	5	0.286	0.395	0.214	0.391	0.302	-
	7.5	0.310	0.445	0.219	0.399	0.282	-
	10	0.293	0.436	0.244	0.413	0.278	-
Modified UPR/EPS Blend	2.5	0.273	0.385	0.175	0.360	0.260	-
	5	0.263	0.339	0.286	0.351	0.244	-
	7.5	0.302	0.421	0.205	0.367	0.275	-
	10	0.285	0.414	0.213	0.383	0.273	-

In the presence of acids and alkalies the hydrolysis of ester linkage in the main chain of polyester resin becomes faster [43-44]. In the acid medium hydrolysis is reversible. But in alkaline medium, resonance stabilized carboxylate anion is formed and the hydrolysis become irreversible. Therefore the resistance towards alkali is poorer than that towards acid. From the data it is clear that cured samples were not much affected by dilute HCl (0.1N) when compared with alkalies. The weight gain is higher for blends due to lower crosslink density. The modified blends showed better resistance towards acid attack. In dilute sodium hydroxide solution marginal weight loss is observed for the samples on immersion for one week due to erosion indicating poor resistance of the samples towards alkali.

The use of polar solvents such as ketone is often employed to assess the degree of crosslinking for solvent resistance and methyl ethyl ketone

(MEK) or acetone is recommended for the purpose. Initially, weight gain of samples is observed and an irregular trend is found upon EPS/modified EPS loading. After 24 h the weight change is difficult to measure because all samples, except neat UPR and UPR/5EPS(modified), start degrading. These samples possess higher crosslink density compared to others. The higher the degree of crosslinking, the less the free volume and segmental mobility (less dangling chains) available in the polymer so that solvent molecules can hardly penetrate the crosslinked network at all. In this respect, these two samples have good solvent resistance. The visual images of samples immersed in MEK for 1 week is shown in Fig. 5.11.



UPR

UPR/2.5phr EPS UPR/5phr EPS UPR/7.5phr EPS UPR/10phr EPS

UPR/2.5phr EPS (m) UPR/5phr EPS (m) UPR/7.5phr EPS (m) UPR/10phr EPS (m)

Fig. 5.11. The visual images of samples immersed in MEK for 1 week

5.3.11 Thermal studies

TGA provides reliable and quantitative estimation of relative thermal stabilities of materials. The thermal behaviour of UPR and its blend with EPS/modified EPS are shown as thermograms (Fig.5.12a) as well as derivative thermograms (Fig.5.12b). The corresponding thermal data are shown in Table 5.2. The thermal stability of all the samples were found to be similar. In all cases a minor weight loss before 300°C is observed, attributed to the loss of water, followed by a major weight loss in the temperature range of 320 °C to 475 °C attributed to the rupture of the polyester (-CO-C-) and polystyrene chains to form a primary char with the evolution of styrene, phthalic anhydride, CO and CO_2 [45,46]. In this area, large amounts of decomposition are observed. The final char oxidation stage is in the temperature range of 470–700 °C leaving the residue below 5%. The rate of degradation of blends is lower compared to neat UPR. From the thermograms it is clear that, at the initial stages of polymer decomposition, the extent of crosslinking is greater than the extent of bond rupture. However at middle stages of decomposition, the trend is reversed, and decomposition rate is high and at the last stage of decomposition the trend was found to be similar to that of initial stage.

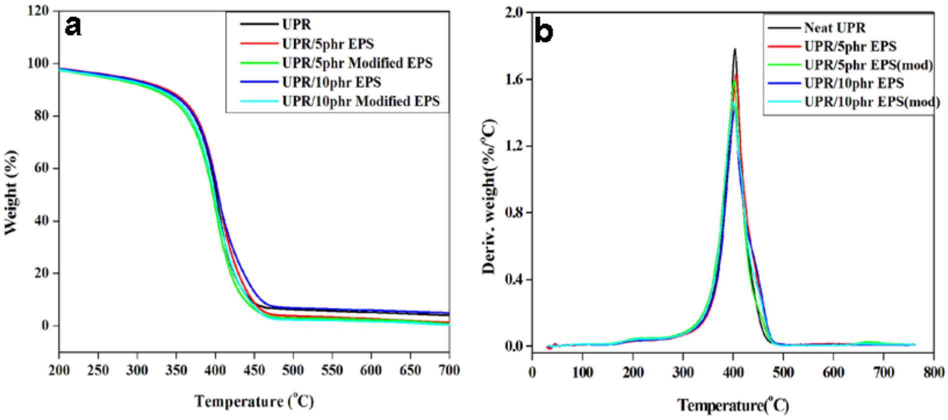


Fig.5.12. Thermal behaviour (a) thermograms and (b) derivative thermograms of UPR and its blend with EPS/modified EPS

The data show that UPR and its blends with EPS/modified EPS have comparable thermal stability. The presence of EPS did not affect the thermal stability of UPR. This can be probably due to the overlap of their decomposition temperatures. Again, thermal decomposition of UPR/EPS is almost independent of their morphology.

Table 5.2. Thermal data of UPR and its blend with EPS/modified EPS

Thermal data	**UPR**	**UPR/ 5EPS**	**UPR/ 5EPS (mod)**	**UPR/ 10EPS**	**UPR/ 10EPS (mod)**
T_i (^{0}C)	319.2	322.4	318.9	322.6	317.8
T_{max}(^{0}C)	403.6	406.4	401.6	403.2	400.8
T_f(^{0}C)	475.9	477.1	477.7	478.1	478.3
$T_{5\%}$ (^{0}C)	274.7	251.5	276.1	272.0	258.6
$T_{50\%}$ (^{0}C)	401.4	396.7	404.0	403.6	398.6
Residue (%) at 700 ^{o}C	4.1	0.7	1.4	4.9	0.4

5.3.12 Dynamic mechanical analysis

Fig. 5.13 represents the storage modulus of UPR and its blend with EPS/modified EPS. Dynamic mechanical analysis is effective in determining the thermo-mechanical properties, and phase miscibility of a cured system. The storage modulus of neat resin is higher compared to UPR/EPS blends. This is due to the lower crosslink density and void formation within the matrix. The modified blends showed an improvement in storage modulus compared to unmodified blends because of the compatibility. Thermoplastics such as polystyrene, which is immiscible with polyester resin before cure is dispersed as a separate distinguishable phase in the matrix with interphase voids and is well evidenced from SEM.

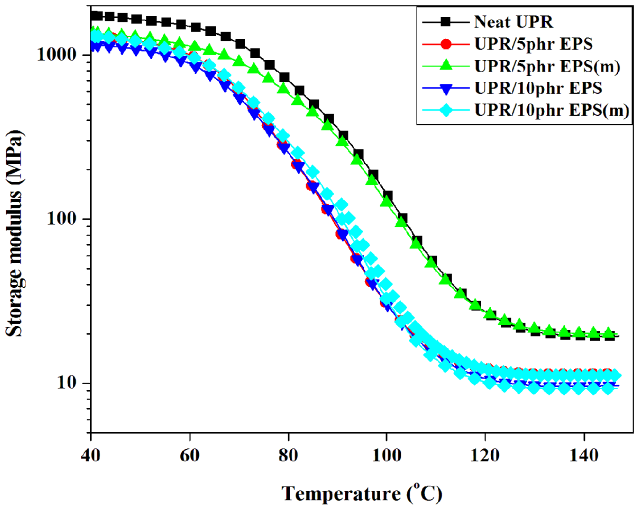


Fig. 5.13. Storage modulus of UPR and its blend with EPS/modified EPS.

This phase separation and poor adhesion creates severe incompatibility in the blends, resulting in the lowering of stiffness [47]. Therefore, the blends showed low storage modulii compared to neat UPR. But for modified blends with greater compatibility the modulus is enhanced to some extent.

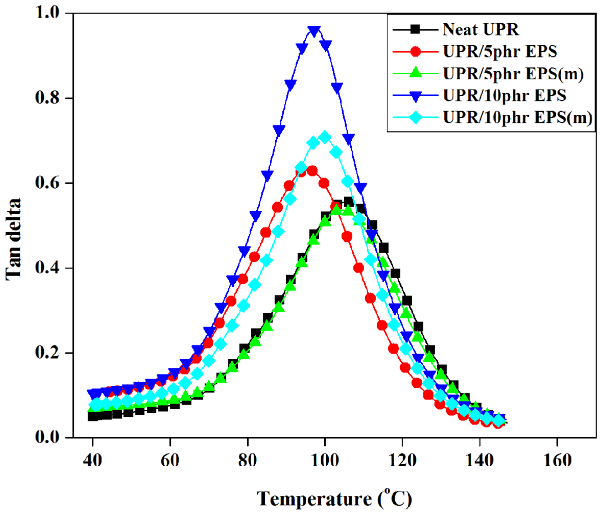


Fig. 5.14. Tan δ curves of UPR and its blend with EPS/modified EPS.

The tan δ curves of UPR and its blend with EPS/modified EPS is depicted in Fig. 5.14. The glass transition temperature as well as the loss factor of the neat UPR and its blends with EPS/modified EPS are determined from the tan delta curves and is tabulated in table.5.3. The neat UPR showed a glass transition temperature of 105°C. Though UPR and EPS are immiscible, a single transition temperature is exhibited by the blends, because T_g of polystyrene is close to UPR. Compared to neat UPR a lowering of T_g is observed, especially for the unmodified blends. This is the general trend in T_g when thermoplastics are incorporated into UPR [19]. The change in glass transition temperature for the blends is indicative of the extent of phase separation and the crosslinking of UPR [48-49]. Because of the non polarity, EPS is immiscible with UPR before curing, and exists as a separate phase in the UPR matrix. This causes some reduction in crosslinking of matrix chains. Consequently, the chain stiffness is reduced and chain flexibility is achieved at a lower temperature compared to neat UPR. This is the reason for lowering of T_g for the unmodified blends. Furthermore, the addition of the thermoplastic raises the viscosity of the system, resulting in an incomplete curing reaction [50-51]. But in the case of modified blends some partial miscibility (higher extent of molecular mixing between the chains) exists probably as a result of polarity as well as structural similarity between UPR and EPS. Here the phase separation during curing is negligible and crosslinking predominates. As a result T_g shifts to a higher temperature very close to neat UPR. Though some plasticization effect is present (which is unfavorable for increase of $T_{g)}$, the higher degree of crosslinking of the modified blend plays a dominant role leading to a higher T_g [37]. The transparency results discussed in Chapter 7 also supports the increase in T_g of modified blends [22]. The lowering of T_g for unmodified blends at 10phr EPS is less compared to that at 5phr EPS. This may be due to the presence of more EPS so that a shift of Tg towards the glass transition temperature of polystyrene takes place. The modified blend at 10 phr showed a slight increase of T_g.

Table 5.3. Glass transition temperature and loss factor of the neat UPR and its blends with EPS/modified EPS

Samples	Tan δ peak	Glass transition temperature (T_g)
Neat UPR	0.556	105.3
UPR/5EPS	0.631	95.7
UPR/5EPS(m)	0.539	104.2
UPR/10EPS	0.962	97.2
UPR/10EPS(m)	0.709	99.3

Loss tangent (tan δ peak value) of blends are slightly higher compared to neat UPR, except in the case of modified blend at 5phr EPS loading and is in agreement with the general behaviour for UPR/ thermoplastic blends. The higher damping factor for the blends is associated with the energy dissipation at the interphase [52] because of poor interfacial adhesion. The modified blends showed lower tan delta values compared to unmodified blends indicating an improvement in interfacial bonding. The restriction of chain mobility resulted in the reduction of sharpness and height of the tan δ peak.

5.4 Conclusion

Waste EPS has been successfully incorporated into unsaturated polyester resin by a solution blending process. Maleic anhydride grafting on EPS is confirmed by FTIR. Liquid resin properties such as gel time, peak exothermic temperature and specific gravity are reduced on EPS addition, but modified blends are better in this respect.

Formation of a thick interphase in the morphology of modified blends leads to better adhesion between the two phases and enhanced mechanical properties. Though a reduction in tensile strength is observed for unmodified blends, the tensile strength of modified blends has improved by 13.5% (at 2.5phr) and 17.5% (at 5phr) when compared with neat resin. Percentage elongation shows a decreasing tendency upon addition of EPS/modified EPS. Young's modulus of all the blends is inferior to neat UPR. Impact strength is found to be lowered on addition of EPS/modified EPS. Flexural strength and flexural modulus of the modified blends are superior to unmodified blends though both were lower than neat UPR. Crosslink density of modified blends is close to neat UPR.

Blends showed better resistance towards water, acid and alkali. Neat UPR and modified blend at 5phr EPS showed better resistance to MEK, but other samples undergo degradation. Incorporation of EPS does not alter the thermal stability of UPR. The dynamic mechanical measurements show that glass transition temperature and storage modulus of neat UPR and UPR/5EPS(m) are similar but superior to other samples. The results establish the viability of utilizing waste EPS in UPR.

References

[1] Batayneh, M., Marie, I. & Asi, I. Use of selected waste materials in concrete mixes. *Waste Manag.* **27,** 1870–1876 (2007).

[2] Winterling, H. & Sonntag, N. Rigid polystyrene foam (EPS, XPS). *Kunststoffe International* **10**, 18–21 (2011).

[3] John Scheirs. *Polymer Recycling*. John Wiley & Sons Ltd. (1998).

[4] Liu, N. C. & Baker, W. E. Reactive polymers for blend compatibilization. *Adv. Polym. Technol.* **11,** 249–262 (1992).

[5] Xanthos, M. Interfacial agents for multiphase polymer systems: Recent advances. *Polym. Eng. Sci.* **28,** 1392–1400 (1988).

[6] Yuan, H. & Hu, P. Study of a compatibilized ultra-high-molecular-weight polyethylene and polyurethane blend. *J. Appl. Polym. Sci.* **81,** 3290–3295 (2001).

[7] Khalf, A. I. & Ward, A. A. Use of rice husks as potential filler in styrene butadiene rubber/linear low density polyethylene blends in the presence of maleic anhydride. *Mater. Des.* **31,** 2414–2421 (2010).

[8] De Roover, B. *et al.* Molecular characterization of maleic anhydride-functionalized polypropylene. *J. Polym. Sci. Part A Polym. Chem.* **33,** 829–842 (1995).

[9] Liu, X., Wu, Q., Berglund, L. A., Fan, J. & Qi, Z. Polyamide 6-clay nanocomposites / polypropylene-grafted-maleic anhydride alloys. *Polymer (Guildf).* **42,** 8235–8239 (2001).

[10] Gaylord, N. G. Maleic anhydride-modified polymers and process for preparation thereof. USPat. 4506056, 1985.

[11] Gaylord, N. G. & Mehta, R. Peroxide-catalyzed grafting of maleic anhydride onto molten polyethylene in the presence of polar organic compounds. *J. Polym. Sci. Part A Polym. Chem.* **26,** 1189–1198 (1988).

[12] Ganzeveld, K. J. & Janssen, L. P. B. M. The grafting of maleic anhydride on high density polyethylene in an extruder. *Polym. Eng. Sci.* **32,** 467–474 (1992).

[13] Jo, W. H., Park, C. D. & Lee, M. S. Preparation of functionalized polystyrene by reactive extrusion and its blend with polyamide 6. *Polymer (Guildf).* **37,** 1709–1714 (1996).

[14] Chen, G., Yang, J. & Liu, J. J. Preparation of the HIPS/MA graft copolymer and its compatibilization in HIPS/PA1010 blends. *J. Appl. Polym. Sci.* **71,** 2017–2025 (1999).

[15] Kim, S.-K., Kim, J. T., Kim, H.-C., Rhee, K.-Y. & Kathi, J. Miscibility of Solution Blends of Unsaturated Polyester Resin with Polystyrene and Polycarbonate. *J. Macromol. Sci. Part B* **49,** 750–756 (2010).

[16] Ma, C. M., Hsieh, C., Kuan, H., Tsai, T. & Yu, S. Effects of molecular weight and molecular structure of low profile additives on the properties of bulk molding compound (BMC). *Polym. Eng. Sci.* **43,** 989–998 (2003).

[17] Lubin, G. *Handbook of fiberglass and advanced plastics composites : ed : G. Lubin.* (Van Nostrand Reinhold, 1969).

[18] Burns R. Polyester Molding Compounds. Marcel Dekker: New York; 1982.

[19] Huang, Y.-J. & Horng, J. C. Effects of thermoplastic additives on mechanical properties and glass transition temperatures for styrene-crosslinked low-shrink polyester matrices. *Polymer (Guildf).* **39,** 3683–3695 (1998).

[20] Huang, Y.-J. & Chen, L.-D. Effects of chemical composition and structure of unsaturated polyester resins on the miscibility, cured sample morphology and mechanical properties of styrene/unsaturated polyester/low-profile additive ternary systems: 2. Mechanical properties. *Polymer (Guildf).* **39,** 7049–7059 (1998).

[21] Ma, C. M., Hsieh, C., Kuan, H., Tsai, T. & Yu, S. Effects of molecular weight and molecular structure of low profile additives on the properties of bulk molding compound (BMC). *Polym. Eng. Sci.* **43,** 989–998 (2003).

[22] Teng, K. C. & Chang, F. C. Single-phase and multiple-phase thermoplastic/thermoset polyblends: 2. Morphologies and mechanical properties of phenoxy/epoxy blends. *Polymer (Guildf).* **37,** 2385–2394 (1996).

[23] Qazvini, N. T. & Mohammadi, N. Segmental dynamics of reactively prepared polystyrene blends: Unsaturated polyester resin versus high impact polystyrene. *J. Appl. Polym. Sci.* **106,** 498–504 (2007).

[24] Koleva, M., Vassilev, V. & Vassilev, G. Polymer composites containing waste dust from power production. II. Strength characteristics of composites based on UPR/HIPS polymer system. *Maced. J. Chem. Chem. Eng.* **27,** 47–52 (2008).

[25] Mustafa, S. A. B. S., Mohamed, R., Bahira, W. & Rasidan, K. Flame Retardancy of Polymeric Building Material with Recycled Expanded Polystyrene Filler. In *Proceedings of the International Conference on Global Sustainability and Chemical Engineering* (Hashim, M. A.) 403–409 (Springer Singapore, 2014).

[26] John Coates. Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry. R.A. Meyers (Ed.) 2000:10815–10837.

[27] Oromiehie A., Ebadi-Dehaghani H., and M. S. Chemical Modification of Polypropylene by Maleic Anhydride: Melt Grafting, Characterization and Mechanism. *Int. J. Chem. Eng. Appl.* **5,** 117–122 (2014).

[28] Li, H. M., Chen, H. B., Shen, Z. G. & Lin, S. Preparation and characterization of maleic anhydride-functionalized syndiotactic polystyrene. *Polymer (Guildf).* **43,** 5455–5461 (2002).

[29] Hayaty, M. & Beheshty, M. H. Shrinkage, Cure Characterization and Processing of Unsaturated Polyester Resin Containing PVAc Low-profile Additive. *Iran. Polym. J.* **13,** 389–396 (2004).

[30] Gooch, J. W. *Encyclopedic Dictionary of Polymers, Volume 1.* **8,** (Springer Science & Business Media, 2010).

[31] P., C. B. Understanding the Roles of Chemically-controlled and Diffusion-limited Processes in Determining the Severity of Autoacceleration Behavior in Free Radical Polymerization. (Northwestern University, 2002).

[32] Flory, P. J. *Principles of Polymer Chemistry*. (Cornell University Press, 1953).

[33] Liu, C. J., Kiasat, M. S., Nijhof, A. H. J., Blokland, H. & Marissen, R. The effect of the addition of a low profile additive on the curing shrinkage of an unsaturated polyester resin. *Polym. Eng. Sci.* **39,** 18–25 (1999).

[34] Chaudhuri, R. I. Effect of Low Profile Additives on Thermo-mechanical Properties of Fibre/UP Composites. (McGill University (Canada), 2007).

[35] Chan-Park, M. B. & McGarry, F. J. Tough low profile additives in sheet molding compound. *Polym. Compos.* **17,** 537–547 (1996).

[36] Kinkelaar, M., Muzumdar, S. & Lee, L. J. Dilatometric study of low profile unsaturated polyester resins. *Polym. Eng. Sci.* **35,** 823–836 (1995).

[37] Huang, Y.-J., Chen, T.-S., Huang, J.-G. & Lee, F.-H. Effects of poly(vinyl acetate) and poly(vinyl chloride-co-vinyl acetate) low-profile additives on properties of cured unsaturated polyester resins. II. glass-transition temperatures and mechanical properties. *J. Appl. Polym. Sci.* **89,** 3347–3357 (2003).

[38] Lucas, J. C., Borrajo, J. & Williams, R. J. J. Cure of unsaturated polyester resins: 2. Influence of low-profile additives and fillers on the polymerization reaction, mechanical properties and surface rugosities. *Polymer (Guildf).* **34,** 1886–1890 (1993).

[39] Dong, J.-P., Lee, J.-H., Lai, D.-H. & Huang, Y.-J. Effects of reactive low-profile additives on the properties of cured unsaturated polyester resins. II. Glass-transition temperature and mechanical properties. *J. Appl. Polym. Sci.* **100,** 867–878 (2006).

[40] Pereira, C. M. C., Herrero, M., Labajos, F. M., Marques, a. T. & Rives, V. Preparation and properties of new flame retardant unsaturated polyester nanocomposites based on layered double hydroxides. *Polym. Degrad. Stab.* **94,** 939–946 (2009).

[41] Tan, S. G. & Chow, W. S. Thermal properties, curing characteristics and water absorption of soybean oil-based thermoset. *Express Polym. Lett.* **5,** 480–492 (2011).

[42] Diew, S., Charoen, N., Azizon, K. & Pairote, K. Water absorption and mechanical properties of water-swellable natural rubber. *Songklanakarin J. Sci. Technol.* **31,** 561–565 (2009).

[43] Updegraff, I. H. in *Handbook of Composites* (ed. Lubin, G.) 17–37 (Springer US, 1982). doi:10.1007/978-1-4615-7139-1

[44] Balasubramanian, M. *Composite Materials and Processing.* (CRC Press, 2013). At https://books.google.com/books?id=6rDMBQAAQBAJ&pgis=1>

[45] K andola B, Nazare S, Horrocks A. In: Le Bras M, editor. Fire retardancy of polymers: the use of mineral fillers in micro- and nano-composites. Cambridge: Royal Chemical Society; 2005. p. 147.

[46] Troitzsch, J. *International Plastics Flammability Handbook: Principles, Regulations, Testing and Approaval.* (Hanser Publishers, 1990).

[47] Lam, P. W. K. A comparative study of structure-property relationships in low-profile polyester matrices. *Polym. Eng. Sci.* **29,** 690–698 (1989).

[48] Q Guo, in: G.O Shonaike, G Simon (Eds.), Polymer blends and alloys, vol. 6Marcel Dekker, New York (1999), pp. 155–187

[49] Inoue, T. Reaction-induced phase decomposition in polymer blends. *Prog. Polym. Sci.* **20,** 119–153 (1995).

[50] Bucknall, C. B. & Partridge, I. K. Phase separation in crosslinked resins containing polymeric modifiers. *Polym. Eng. Sci.* **26,** 54–62 (1986).

[51] Girase, R., Jaiswal, R., Chaudhari, L., Bhattacharya, S. & D'Melo, D. Studies on unsaturated polyester composites for high-temperature applications. *J. Vinyl Addit. Technol.* **18,** 46–51 (2012).

[52] Al-bahadly, E. A. O. The Mechanical Properties of Natural Fiber Composites. (2013).

……

Chapter 6

SYNTHESIS OF UPR AND MODIFICATION BY EPS

Contents

6.1 Introduction

Polyesters are polymers containing repeating ester linkages in their backbone chain. The unsaturated polyester has been synthesized by the condensation reaction of an unsaturated dibasic acid or anhydrides, a saturated dibasic acid or anhydride, and a polyfunctional alcohol [1]. The crosslinking site is provided by unsaturated acid/anhydride whereas the saturated acid/anhydride gives the degree of spacing. Crosslinking/grafting is carried out through unsaturated monomers such as styrene. For a general purpose polyester resin, the reactants usually consists of phthalic anhydride (PA), maleic anhydride (MA), propylene glycol (PG) and the diluent styrene [2]. Use of phthalic anhydride (which has enhanced compatibility with styrene) results in a resin with lowest cost, flexibility, high HDT, water resistance, rigidity (due to frequent ester linkages as a result of short spacing between acid groups), high flexural and tensile strength. Though fumaric acid (FA) is more reactive and gives a resin with better properties compared to MA, the latter is the commonly used unsaturated acid as it is inexpensive. Also during condensation MA isomerizes to FA. Among glycols, propylene glycol is the most widely used diol because of good styrene compatibility, less tackiness after curing and good mechanical properties. Due to better compatibility, low viscosity, ease of cure, low cost, moderate HDT and high reactivity, styrene replaces other crosslinking monomers, though it has got disadvantages such as volatility and toxicity. Since phthalic anhydride and propylene glycol are of low cost and their combination with MA results in a high quality UPR, PA/MA/PG system can be considered as a desirable composition.

This polyesterification reaction is carried out in oxygen free atmosphere (N_2, CO_2, etc.) and the reaction kinetics is dependent upon the structure and stoichiometry of the reactants [3]. Two main reactions are involved in the synthesis of UPR; (1) monoester formation and (2) poly condensation. The first reaction takes place in the temperature range 60-130 °C whereas a higher temperature (above 160 °C) is required for the second one. The conversion extent of the reaction was 90-95%. The water of condensation coming out of the reaction has to be removed in view of the reversibility of the reaction. Normally, the molecular weight of UP resins is around 3000 g/mol or less at equilibrium. Though higher molecular weight UP resins show better toughness and mechanical properties [4], higher level of polycondensation leads to gel formation in the resin. So the extent of reaction is controlled during synthesis.

Many side reactions can also occur during polycondensation reaction. One is the Ordlet saturation. The maleate double bond in UPR is highly electron deficient and the addition of glycol across the double bond (Michale addition) leads to branching and reduction of unsaturation instead of condensation and results in change of functionality. Higher MA concentration result in the reduction of around 15% unsaturation in the final product. Second is the isomerisation of MA to FA, occurs mainly in the presence of branched secondary glycols such as propylene glycol [5]. The isomerisation is enhanced for linear glycols with even-numbered carbon atoms compared to odd-numbered carbon atoms. It has been reported that propylene glycol imparts 95% isomerisation. Another possible side reaction is transesterification, that is alcoholysis or acidolysis of the polyester chains by hydroxyl or carboxyl groups of monomers.

The present study is an attempt to utilize waste expanded polystyrene in UPR during the final stage of synthesis. The desired quantities of EPS/modified EPS were dissolved in styrene and this mixture was added to the resin instead of styrene when the temperature reaches 100 °C. Here UPR/EPS (unmodified/modified EPS) blend with two different styrene contents (35 and 40 wt %) were prepared and the results were compared with their pure forms.

6.2 Experimental

6.2.1 Materials

The materials used are given in section 2.1 of Chapter 2.

6.2.2 Methods

6.2.2.1 Synthesis of UP resin and blend preparation

A one stage polycondensation reaction was used for the synthesis of polyester resin. Propylene glycol, maleic anhydride and phthalic anhydride were taken in a three necked R. B. flask equipped with a mechanical stirrer, a CO_2 inlet for inert atmosphere and a reflux condenser. The molar ratio of PG, MA, and PA was 1: 0.4: 0.6 respectively. A slight excess (10%) of PG was also used to compensate its loss by evaporation. Triphenyl phosphate (0.05%) was added to this mixture for getting colour. The reaction mixture was heated to 210 °C and the heating was continued for several hours. At this temperature maleic anhydride is isomerised to the less strained fumaric acid (cis-trans isomerisation) [5]. FA is more reactive in UP resin synthesis compared to MA and the product obtained will have superior properties [6]. About 10 ml of xylene was also used for the azeotropic removal of water. The acid value was determined at regular time interval. When the acid value became 40 vacuum was applied for removing the unreacted reactants and residual water, in order to reduce the acid value to less than 30. At this step heating was cut off and 0.02 wt% hydroquinone and 0.25 wt% paraffin wax (to prevent the crosslinking reaction by the oxygen in the air [7]) were added. When the reaction mixture was cooled down to 100 °C, required wt% of styrene was added. For the preparation of UPR and

UPR/EPS blends with 40 weight % styrene, initially only 30% styrene was added to the reaction mixture at 100 °C with stirring. This was divided into three equal portions and to each an additional 10 weight % styrene (with and without EPS/modified EPS) were added followed by thorough mixing. For the synthesis of UPR and UPR/EPS blend with 35% styrene, the amount of styrene added initially would be 25%. The UPR/ styrene/EPS composition is given below in Table 6.1. The dissolution of EPS/modified EPS in styrene and curing of UPR as well as its blends are described in Chapter 2.

Table 6.1. The formulation used for UPR/EPS/styrene composition

Mixes	Components			
	UPR(%)	Styrene (%)	EPS (phr)	
			Modified	Unmodified
60/40	60	40	0	0
60/40/5	60	40	0	5
60/40/5(m)	60	40	5	0
65/35	65	35	0	0
65/35/5	65	35	0	5
65/35/5(m)	65	35	5	0

6.2.2.2 Curing of resin

Procedure for curing of resin is given in section 2.2.4 of Chapter 2.

6.2.3 Characterisations

A detailed explanation of characterisation techniques are given in Section 2.3 of Chapter 2.

6.3 Results and Discussion

6.3.1 The acid value and number average molecular weight ($\overline{Mn}$)

Fig. 6.1 shows the variation of acid value with reaction time for two cases of UPR synthesis with 40% and 35% styrene concentration. To get a desired molecular weight of around 1900 ($\overline{Mn}$) the reaction was stopped on reaching an acid value less than 30. A reaction time of 16-17 h was required for completion of syntheses.

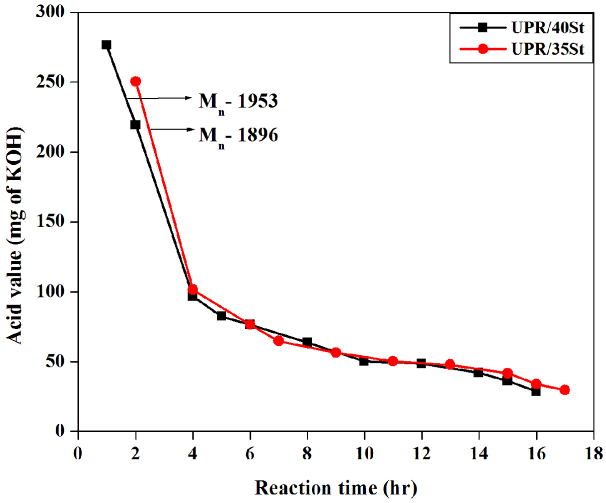


Fig. 6.1. Variation of acid value with reaction time for two different synthesis of UPR

6.3.2 Specific gravity

The specific gravity of UPR/40St and UPR/35St blended with EPS/modified EPS is tabulated below (Table 6.2). The addition of EPS to UPR lowers the specific gravity to a level lower than that of neat UPR at both styrene concentrations. This can be attributed to the lower density of EPS as well as generation of micro voids due to phase separation. For the modified blend, the fall in specific gravity is only marginal due to enhanced phase interaction resulting from the presence of polar EPS (MA-g-EPS). The styrene ratio controls the reactivity of the unsaturated polyester and also the crosslinking density of the final network [8]. With Increase in the styrene ratio, specific gravity of the matrix decreases.

Table 6.2. Effect of EPS/modified EPS on specific gravity of UPR/40St and UPR/35St

Composition of resins	Specific gravity
UPR/40St	1.133
UPR/40St/5EPS	1.130
UPR/40St/5EPS(m)	1.131
UPR/35St	1.135
UPR/35St/5EPS	1.132
UPR/35St/5EPS(m)	1.134

6.3.3 Viscosity

The viscosity of the uncured resin with different styrene ratios on addition of EPS and modified EPS is shown in Fig. 6.2. At both styrene concentrations a significant increase in viscosity was observed for UPR due to the presence of EPS. It was reported that at fixed molar ratio of styrene to polyester C=C bond the viscosity is increased on addition of thermoplastics because of the higher molecular weight of thermoplastics in comparison to the liquid UP resin [9].

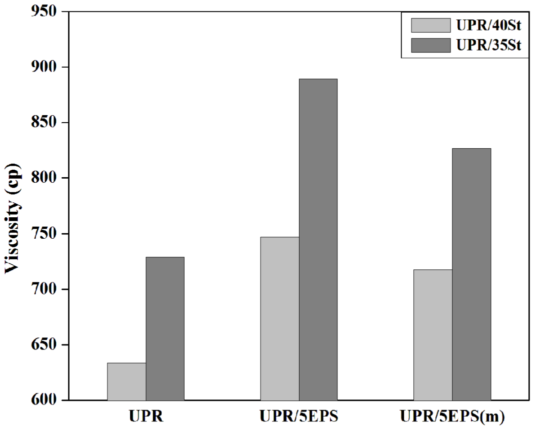


Fig. 6.2. The viscosity of the uncured resin with EPS/modified EPS in two different styrene ratios

Therefore addition of EPS/modified EPS increases the viscosity of the neat UPR. Due to phase interaction the increase in viscosity of UPR/EPS (m) with both styrene concentrations are low compared to corresponding UPR/EPS. The change in styrene percentage also affects the viscosity and UPR/35St showed higher viscosity compared to UPR/40St. This is because of styrene serving as a diluent for UPR.

6.3.4 Gel time and peak exothermic temperature

The effect of EPS and modified EPS on the gel time (Fig. 6.3) and peak exothermic temperature (Fig. 6.4) of UPR with two different styrene ratios are shown below. Presence of thermoplastics causes a reduction in gel time. It has been reported that though low profile additive slows down the cure due to dilution of the resin, higher loading leads to an earlier onset of viscosity rise resulting in a higher reaction rate and earlier gelation [9]. This latter effect is Trommsdorff effect or gel effect [10] and is the reason for above observation. A detailed explanation is given in section 5.3.2 of Chapter 5. Changing the ratio of styrene in neat UPR as well as its blends with EPS/modified EPS, has affected the gel time. UPR/35St is cured faster than UPR/40St. Thus the increase in gel time of UPR/40St is considered as a clear indication of dilution effect of styrene monomer.

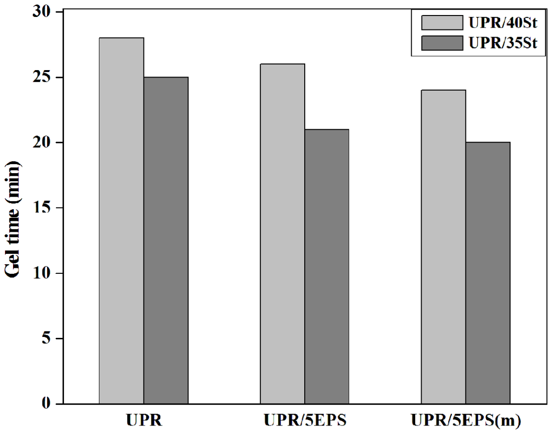


Fig. 6.3. Effect of EPS and modified EPS on the gel time of UPR at two different styrene ratios

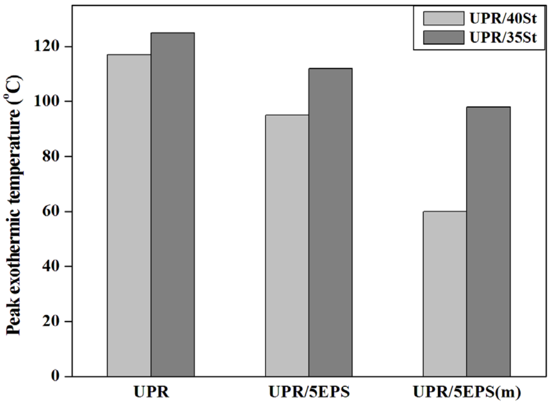


Fig. 6.4. Effect of EPS and modified EPS on the peak exothermic temperature of UPR at two different styrene ratios

The peak exothermic temperature is very important in the processing of unsaturated polyester into a composite product. The crosslinking reaction is a highly exothermic one, and the temperature can increase up to 100-200 ºC. Presence of thermoplastics generally lowers peak exothermic temperature for a specific styrene ratio [11]. Modified EPS also shows the same trend but the lowering of peak exotherm is more than UPR/5EPS. This may be due to the improved interaction between the two phases in the case of modified EPS which can give rise to side reactions involving the anhydride ring. At low styrene ratio neat UPR and its blends with EPS/modified EPS showed higher peak exothermic temperature compared to the corresponding compounds with high styrene ratio.

6.3.5 FTIR spectral analysis of cured polyester resin

Fig. 6.5 represents the FTIR spectra of cured UPR and their blends with EPS/modified EPS at two styrene ratios. All the basic characteristic peaks of cured polyester resin according to the literature [12-18] are present and detectable in the spectra of UPR as well as its blends with EPS/modified EPS at both the styrene ratios. The presence of >C=O stretching were confirmed by the strong band at 1726 cm^{-1}. The peak at 1260 cm^{-1} confirms the presence of -C-O-C- (ester linkage). Alkane $–CH_2$ was confirmed by the presence of a band at 1449 cm^{-1}. The absence of peaks at 1755cm^{-1}(C=O of anhydrides) and 1375cm^{-1} (-OH of phthalic anhydride) is an indication of resin formation. The absence of peaks at 910 cm^{-1} (CH_2 out of plane of C=C vinyl styrene), 1645 cm^{-1} (C=C in polyester) supports the crosslinking reaction. The band at 744 cm^{-1} is attributed to the (o-disubstituted –C-H stretching in aromatic ring).

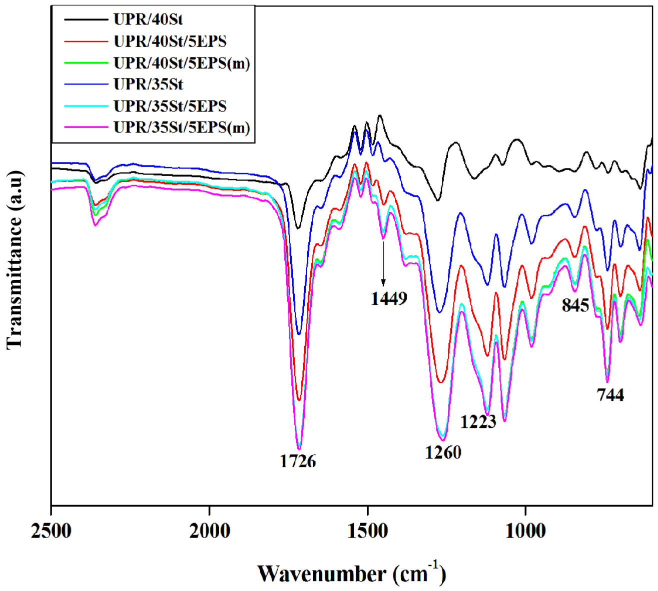


Fig. 6.5. FTIR spectra of cured UPR at two styrene ratios and their blends with EPS/modified EPS.

6.3.6 Morphological studies

Morphological studies were done on the tensile fractured surfaces of the cured samples of neat UPR, UPR/5EPS blend and UPR/5EPS(m) blend at 40% styrene. The SEM images are shown in Fig. 6.6. In the case of neat UPR at 40% styrene the surface morphology is found to be flake-like [11]. For the unmodified blend (UPR/5EPS) the globular EPS phase is embedded in the continuous UPR phase.

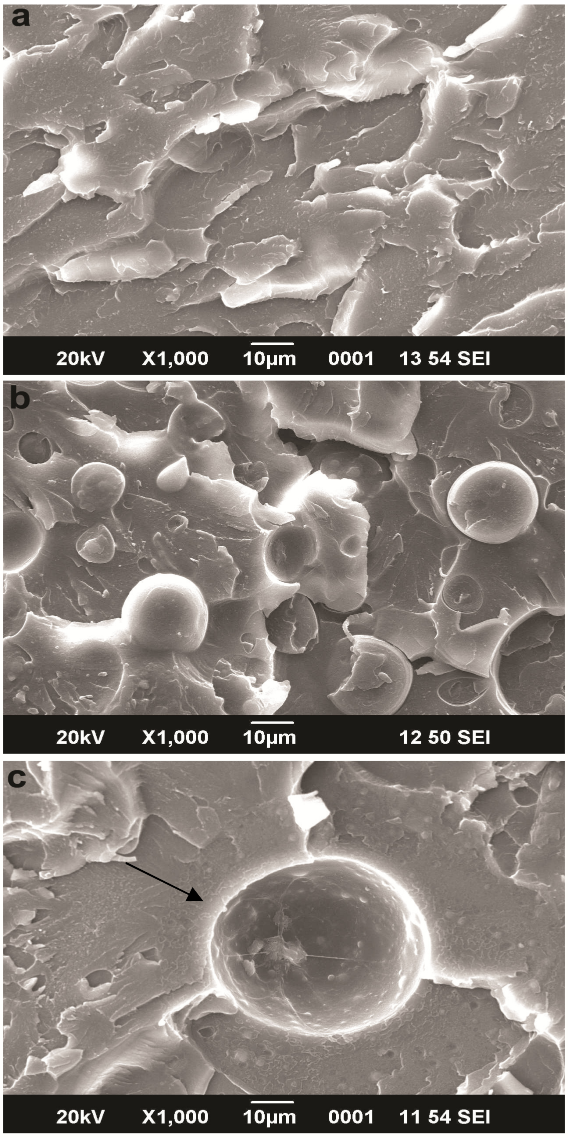


Fig. 6.6. Scanning electron micrographs of the fractured surfaces of cured samples of (a) neat UPR, (b) UPR/5EPS blend and (c) UPR/5EPS(m) blend at 40% styrene

Many EPS globules have been pulled out from the fractured surfaces of polyester matrix, indicating poor adhesion. The microvoids between the two phases are the consequence of phase separation before curing. The air bubbles present in the EPS phase can be due the styrene monomer getting entrapped in the EPS phase. In the case of modified blends, as the polarity and molecular weight of EPS increased, an interphase has been formed between the UPR and EPS phases as indicated by the arrow. The presence of this interphase indicates better adhesion between the two phases which is responsible for the enhanced mechanical properties of modified blends. It is believed that this phase is formed through gelation of microgel particles [19].

Fig. 6.7 shows scanning electron micrographs of the fractured surfaces of cured (a) neat UPR (b) UPR/5EPS blend and (c) UPR/5EPS (m) blend at 35% styrene. The right side shows the magnified images of the circled portion of each SEM. In the case of neat UPR the fractured surface appears to be having a fish-scale type morphology. The blends exhibited a two phase morphology in which the EPS phase is dispersed in the UPR matrix as spherical domains. The unmodified blend exhibits poor interfacial interaction which is clearly indicated by the spherical particle pull out. A combination of crack pinning and crack path deflection mechanisms is evident in the SEM of modified blend. The presence of tail like structures near the particles on the fracture surface is an evidence of crack pinning in which the thermoplastic particles behave as impenetrable objects that cause the crack to bow out. The rigid thermoplastic particles can also cause deviation of the crack from its main plane, resulting in increased surface area. Both these mechanisms necessitate more energy for the propagation of the crack [20]. The modified blend is characterized by better interfacial interaction as indicated by the presence of interphase [21-22].

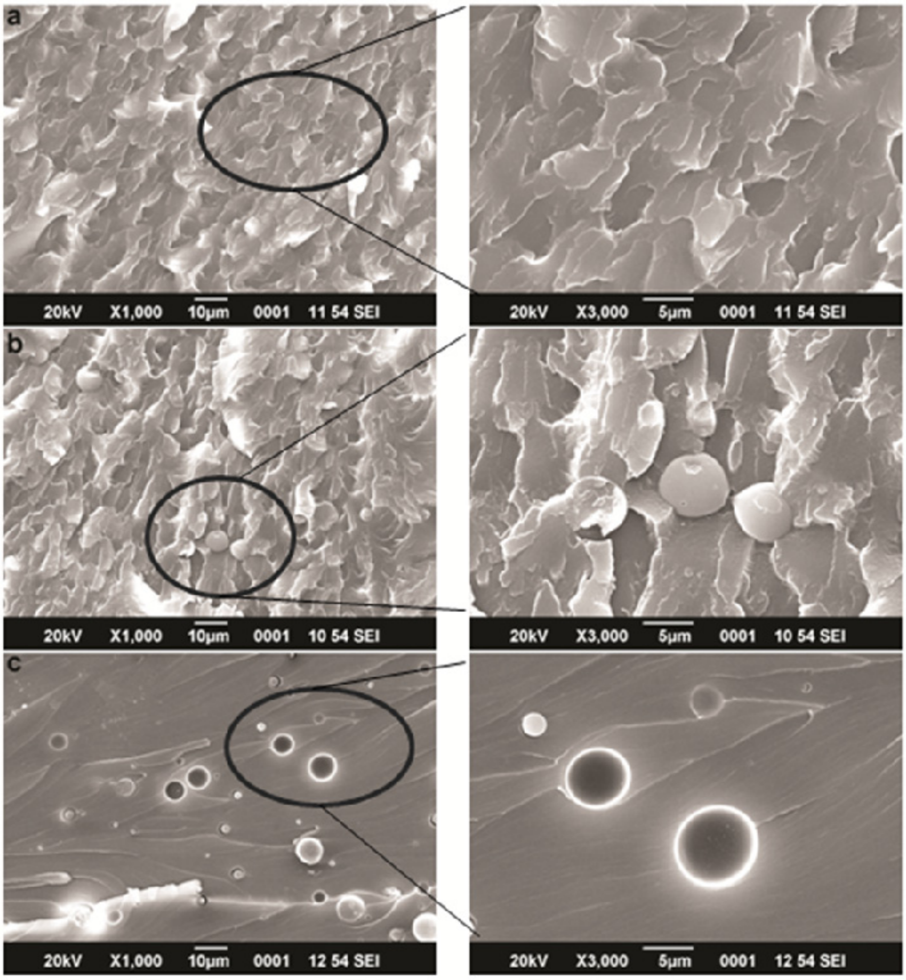


Fig. 6.7. Scanning electron micrographs of the fractured surfaces of cured (a)neat UPR, (b)UPR/5EPS blend and (c) UPR/5EPS (m) blend at 35% styrene

6.3.7 Tensile Properties

Fig. 6.8 represents the effect of EPS and modified EPS on the tensile strength of UPR at two different styrene ratios. The tensile strength of UPR is found to be decreased in the presence of unmodified EPS. On modification of EPS, an improvement of 10% and 14.3% over neat UPR was achieved for the blends at 40% styrene and 35% styrene respectively. The lower tensile strength of unmodified blends is a combined outcome of phase incompatibility, plasticizing effect of EPS and the presence of microvoids as explained in the previous chapter [9,23-24].

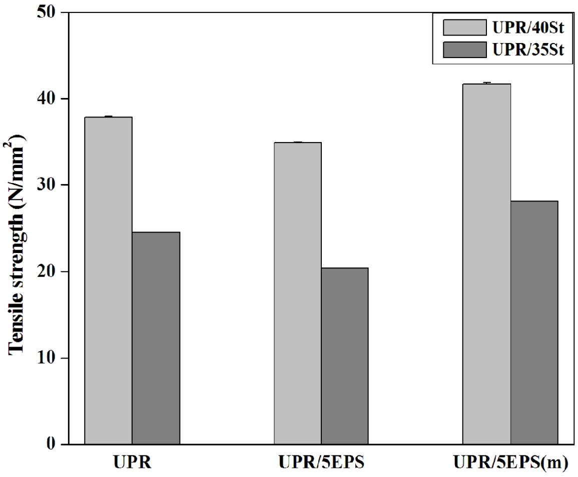


Fig. 6.8. Effect of EPS and modified EPS on the tensile strength of UPR at two different styrene ratios

The better performance of modified blends is due to the compatibility between UPR and MA-g-EPS which is well evidenced in the SEM of modified blends. On comparing the tensile strength values of samples at two different styrene ratios, we can notice that UPR at 40% styrene showed higher tensile strength than that at 35% styrene. In the curing of resin, styrene worked as a crosslinking agent; the free radical could react with the styrene to form a bridge to another polyester chain. If the crosslinking is optimum the mechanical properties would be highest. At 40% styrene the crosslinking is sufficient to achieve better properties while at 35% styrene there may not be enough number of crosslinks [8].

The effect of EPS and modified EPS on the elongation at break of UPR at two different styrene ratios is presented in Fig. 6.9. The incorporation of EPS decreases the elongation at break. This is because of the presence of distinct brittle PS phase in the major continuous UPR phase that reduces the strain at break. For the modified blends the percentage of elongation is improved than even neat UPR. Specimens at 35% styrene showed comparatively better elongation than that at 40% styrene. This is because styrene normally adds brittleness to the specimen through increased crosslinking and causes loss of elongation. Comparatively higher elongation for modified blend at 35% styrene is evident from the SEM which shows ductile fracture surface instead of a brittle fracture.

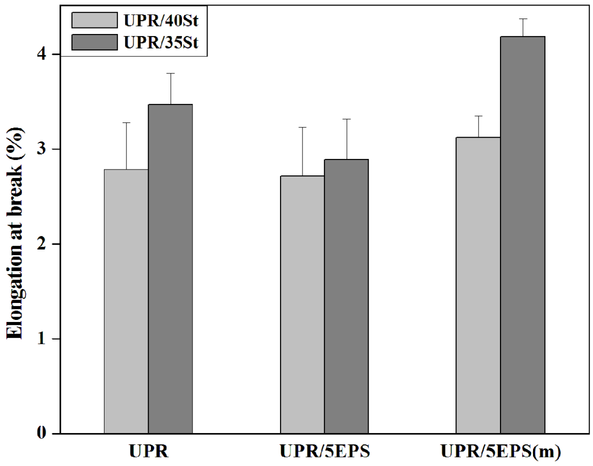


Fig. 6.9. Effect of EPS and modified EPS on the elongation at break of UPR at two different styrene ratios

Fig. 6.10 shows the effect of EPS and modified EPS on the (a) elastic modulus and (b) energy absorbed of UPR at two different styrene ratios. Elastic modulii of all the blends are inferior to that of neat UPR. The fall in modulus can be attributed to a reduced degree of tightness of the network [9,25]. The plasticizing effect of EPS can also be responsible for this reduction. In the case of modified blends, a marginal improvement compared to unmodified blends is noticed as a result of enhanced crosslinking. The change in styrene ratio has significant effect on the elastic modulus. The modulus follows the same trend as tensile strength; both of them being superior at high styrene content. When styrene ratio is low the modulus is less because styrene ratio controls the reactivity of the unsaturated polyester and also the crosslink density of the final network [26].

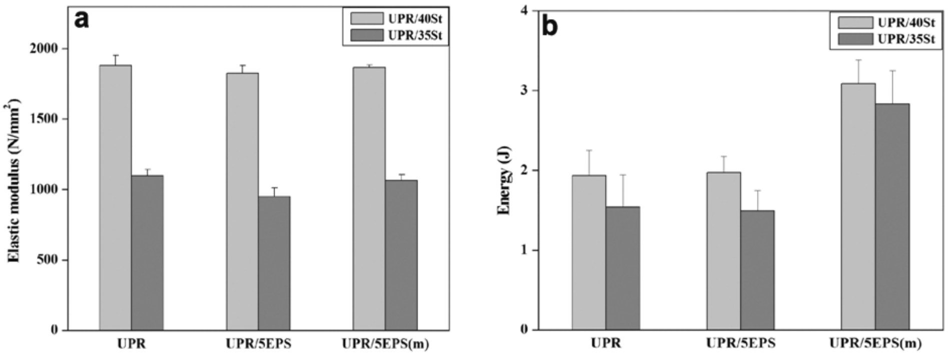


Fig. 6.10. Effect of EPS and modified EPS on the (a) elastic modulus and (b) energy absorbed of UPR at two different styrene ratios

The energy absorption capacity can be taken as a measure of fracture toughness and is unaffected by the presence of 5phr EPS in the case of unmodified blends. Though thermoplastic additives can improve the toughness of UPR in principle, the brittle nature of EPS lowers the tensile strength and elongation, directly leading to the reduction of toughness which is calculated from the area under the stress-strain curve. Though globular morphology is more effective in improving the fracture toughness compared to co-continuous morphology, high volume fraction of localized microvoids can have an adverse effect due to crack propagation through the voids. The combined effect of above factors leads to the marginal variation of energy for unmodified blends [27]. There is a substantial improvement in toughness in the case of modified blends due to the less brittle and rigid nature of modified EPS phase. The presence of thick interphase in the SEM of UPR/40st/5EPS(m) and the crack pinning/crack path deflection in the SEM of UPR/35st/5EPS(m) are indications of energy absorption capacity [23,33]. UPR and its blends at higher styrene ratio showed slightly better energy absorption compared to those at lower styrene ratio. This is because of the higher crosslink density of UPR at high styrene ratio. Insufficient crosslinking may cause deterioration of properties. Also it has been reported that if the styrene ratio is too high, the material become more brittle due to high crosslink density as well as immiscibility between styrene and UPR and the toughness decreases [28].

6.3.8 Impact strength

Fig. 6.11 shows the effect of EPS and modified EPS on the impact strength of UPR at two different styrene ratios. A drop in impact strength is observed on addition of 5phr EPS to UPR for both styrene ratios. This is due to the fact that the addition of brittle thermoplastics such as PMMA or PS normally imparts brittleness of the cured sample, especially when they are dispersed as separate brittle phase without any interaction with the matrix [26]. However the impact strength is comparatively higher for modified blend systems and is even better than neat UPR.

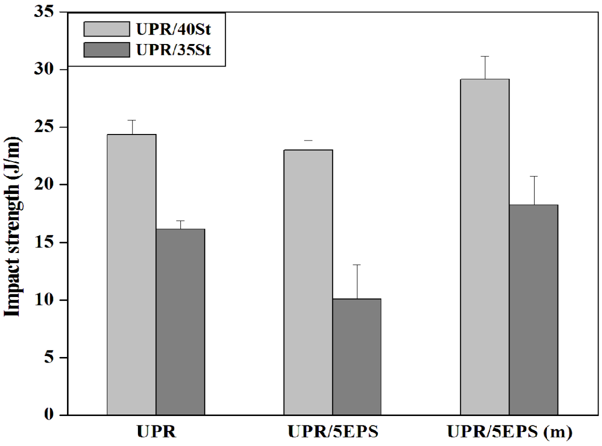


Fig. 6.11. Effect of EPS and modified EPS on the impact strength of UPR at two different styrene ratios

This can be explained by the compatibility enhancement confirmed by the SEM images of modified blends. In the case of modified blend at 40% styrene, due to better interfacial interaction the EPS phase is bound tightly to the matrix causing the crack path to deviate from the main plain. Therefore the energy required to propagate the crack increases. The SEM image of modified blend at 35% styrene exhibits a combination of toughening mechanisms; crack pinning and crack path deflection. The pinning of crack path by rigid particles causes the crack front to bow out between the particles resulting in a reduction in the rate of propagation. Crack path deflection occurs when rigid particles force the propagating crack to tilt out of the plane normal to the applied stress forming a non-planar crack front, resulting in an increase in fracture surface area. Both of these required higher energy for fracture and increase in impact strength [23,33]. Lower impact strength of samples at 35% styrene is due to insufficient crosslink density.

6.3.9 Flexural Properties

The effect of EPS and modified EPS on flexural strength (Fig. 6.12) and flexural modulus (Fig. 6.13) of UPR at two different styrene ratios are given below. Flexural strength is found to decrease upon 5 phr EPS addition. This is due to the heterogeneous nature of the material as evidenced in the SEM image. This behaviour is supported by the previous studies in which these properties decline with addition of thermoplastics [29-31]. Because of the incompatibility and the presence of microvoids, the blend experiences poorer stress transfer resulting in a reduction of mechanical properties [32]. The modified blends showed considerable improvement in flexural strength over unmodified blends and is very close to that of neat UPR. This is because of the greater compatibility between the phases and consequent large interfacial area [33]. At higher styrene content, the UP resins become stiffer and more stress can be supported by the resin. Therefore resin at 40% styrene content performs better than that at 35% styrene content.

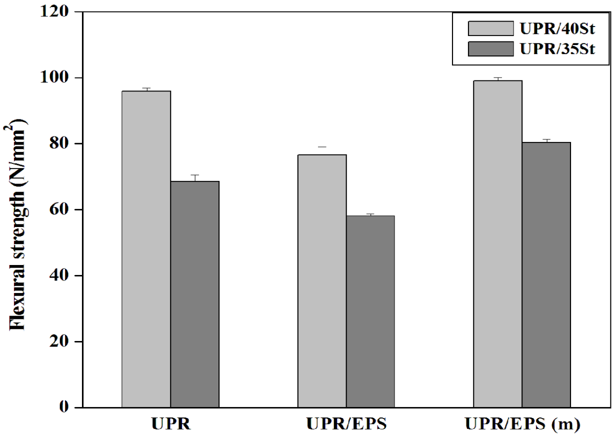


Fig. 6.12. Effect of EPS and modified EPS on flexural strength of UPR at two different styrene ratios

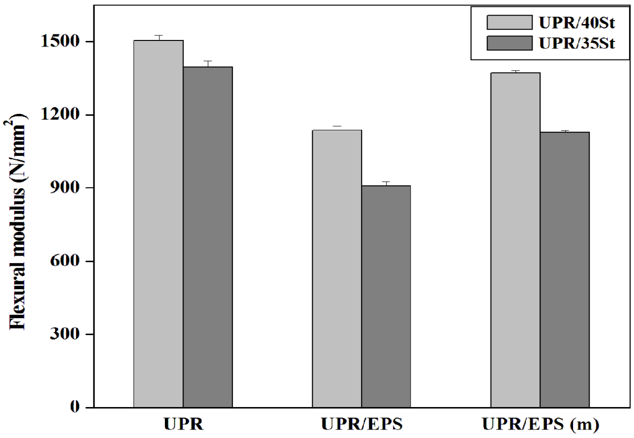


Fig. 6.13. Effect of EPS and modified EPS on flexural modulus of UPR at two different styrene ratios

Flexural modulus showed a similar behaviour to flexural strength when EPS and modified EPS were added to the resin. The trend is repeated in the case of storage and elastic modulii. Here also modified blends showed better performance than unmodified blends.

6.3.10 Crosslink density

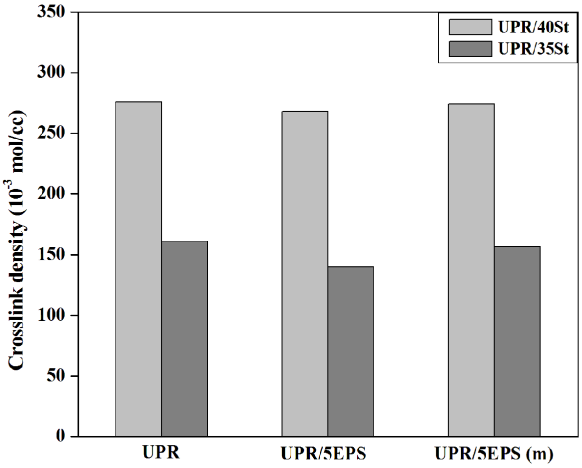


Fig. 6.14. Effect of EPS and modified EPS on crosslink density of UPR at two different styrene ratios

The crosslink density of the cured samples of neat UPR and its blends with 5phr EPS and modified EPS at two different styrene ratios is shown in Fig. 6.14. As expected, the crosslink density shows a reduction on EPS addition whereas modification of EPS increases the crosslink density at both styrene ratios. This is because of enhanced chemical compatibility between the phases. Consequently better interfacial interaction and formation of a thick interface occurs, favouring a higher stiffness in the material. Here, since the crosslink density is calculated from the modulus of the materials, the reduction in stiffness of the material associated with phase separation and formation of interphase voids influences the results. The crosslink density is greater at 40% styrene ratio.

6.3.11 Solvent resistance

Chemical resistance tests are done to estimate the ability of a composite to withstand exposure to acids, alkalis, solvents and other chemicals over specific periods of time. The weight gain/loss for the neat unsaturated polyester and its blends with EPS/modified EPS in solvents such as water, 0.1N HCl, 0.1N NaOH and MEK is shown in Table 6.3.

Table 6.3. Weight gain/loss for the neat unsaturated polyester and its blends with EPS/modified EPS in different solvents

Samples	Quantity of solvent absorbed (%)		
	H_2O	HCl	NaOH
UPR/40St	0.24	0.23	0.35
UPR/40St/5EPS	0.27	0.28	0.38
UPR/40St/5EPS(m)	0.24	0.26	0.33
UPR/35St	0.36	0.27	0.37
UPR/35St/5EPS	0.38	0.29	0.39
UPR/35St/5EPS(m)	0.37	0.27	0.36

The results show that water absorption increases with increase of EPS content for both types of blends. The water absorption rate of a material is closely related to the open porosity (free volume) inside the material and hydrophilic functional groups [33,34]. Higher water absorption rates imply that more voids are formed inside the composites as indicated by blend morphology and volume shrinkage data given in Chapter 7. At higher EPS concentrations the water uptake is lower because of its hydrophobic nature. The water absorption values for modified blends are lower than that of unmodified blends. This may be attributed to the better chemical compatibility and inter component adhesion of modified blends. Moreover, polymeric systems with higher crosslink density possess lower water uptake [34]. The water absorption at lower EPS concentration in the case of modified blends is comparable to neat UPR. Modified lends showed that resistance towards alkali and acid compared to unmodified ones. Samples at 40% shows better performance than that at 30% styrene. The resistance towards acid is better than alkali. The detailed discussion is given in Chapter 5.

6.3.12 Thermal studies

Thermal behaviour of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio is shown as derivative thermograms in Fig. 6.15. Corresponding thermal data is given in Table 6.4. The thermal stabilities of all the samples were found to be similar with a marginal variation in the maximum degradation temperature. In all cases a minor weight loss before 300 °C due to the loss of water, followed by a major weight loss in the temperature range of 315 °C to 475 °C, attributed to the main chain rupture of the polyester with the evolution of styrene, phthalic anhydride, CO and CO_2 is noticed [35,36]. The small shoulder observed at 461 °C for the blends shows the degradation of EPS and is less pronounced in the case of modified blends due to better compatibility. The degradation leaves a residue around 2% in all the cases. The rate of degradation of blends is lower compared to neat UPR.

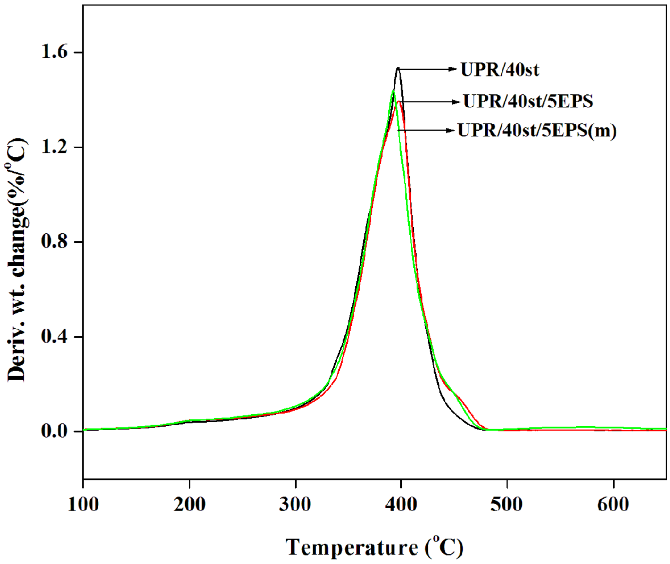


Fig. 6.15. Derivative thermograms of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio

Table 6.4. Thermal data of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio

Thermal data	**UPR/40st**	**UPR/40st/5EPS**	**UPR/40st/5EPS(m)**
T_i (°C)	317.4	318.8	317.2
T_{max} (°C)	396.8	396.0	393.2
T_f (°C)	468.8	477.4	468.8
$T_{5\%}$ (°C)	259.4	245.8	243.0
$T_{50\%}$ (°C)	386.3	387.9	385.7
Residue (%) at 700 °C	2.2	2.5	2.2

6.3.13 Dynamic mechanical analysis

Fig. 6.16 represents the storage modulus of UPR at 40% styrene ratio and its blends with 5phr EPS/modified EPS. The storage modulus of neat resin is higher compared to the blends. This is due to the lower number of crosslinks and void formation within the matrix in the case of blends. The modified blends showed an improvement in storage modulus compared to unmodified blends. Since polystyrene is immiscible with polyester resin before cure, it is dispersed as a separate distinguishable phase in the matrix with clear phase edges and interphase voids as seen in the SEM images. This phase separation and poor adhesion causes severe incompatibility resulting in lowering of stiffness in the blends [37]. The modified blend with greater compatibility between the phases showed higher storage modulus than unmodified blend and is almost comparable with neat resin beyond the transition region.

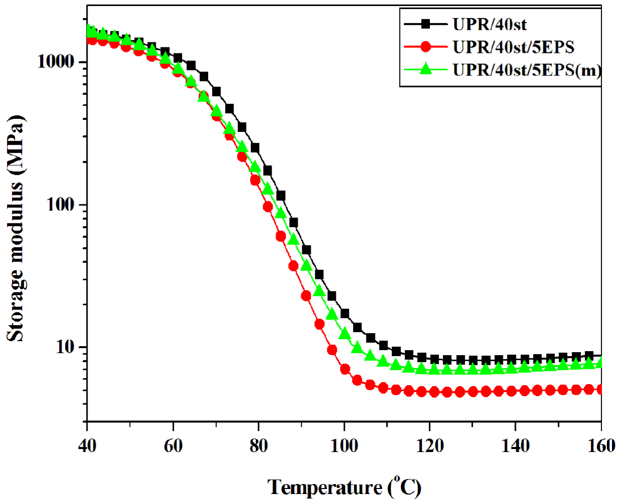


Fig. 6.16. Storage modulus of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio

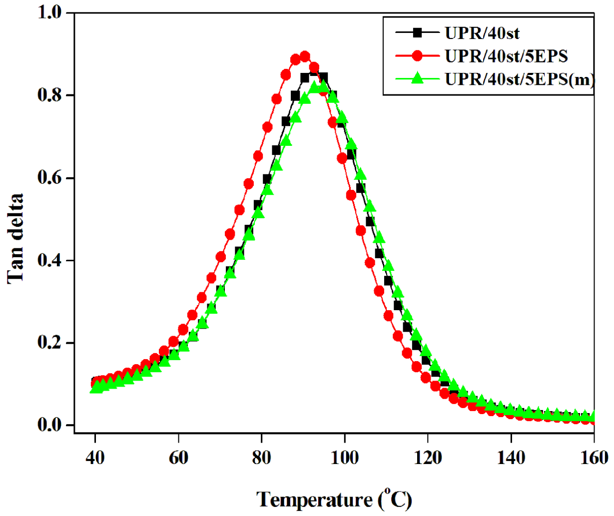


Fig. 6.17. Tan delta curves of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio

The tan δ curves of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio is depicted in Fig. 6.17. The glass transition temperatures as well as the loss tangent determined from the tan δ curves are given in Table 6.4. The UPR/40st showed a glass transition temperature of 92.9 °C. The blends also showed a single T_g notwithstanding the immiscibility between UPR and EPS. This is because the T_g of polystyrene lies close to that of UPR. A slight lowering of T_g is observed in the case of unmodified blends and is the general trend in T_g when thermoplastics are incorporated into UPR [19]. This indicates the extent of phase separation and crosslinking of UPR [38,39]. The incorporation of EPS reduces the chain stiffness introducing chain flexibility at a lower temperature compared to neat UPR. But in the case of modified blends due interfacial interaction between the phases as a result of polarity, the phase separation during curing is negligible and crosslinking predominates. Therefore T_g shift closer to that of UPR/40st. Though some plasticization effect is present (which is unfavorable for increase of $T_{g)}$, the higher degree of crosslinking of the modified blend plays a dominant role leading to a higher T_g [37]. The transparency results discussed in Chapter 7 are also in support of the increase in T_g of modified blends [22]. Tan δ peak value of UPR/40st/5EPS is slightly higher compared to UPR/40st. This higher damping factor for the unmodified blend is associated with the energy dissipation at the interphase [40] resulting from the poor interfacial adhesion between phases. The UPR/40st/5EPS(m) showed lower tan δ values indicating an improvement in interfacial bonding.

Table 6.5. Glass transition temperature and loss factor of UPR and its blends with 5phr EPS/modified EPS at 40% styrene ratio

Samples	Tan delta peak	Glass transition temperature, T_g (°C)
UPR/40st	0.857	92.9
UPR/40st/5EPS	0.896	90.0
UPR/40st/5EPS(m)	0.820	93.9

6.4 Conclusion

Synthesis of unsaturated polyester resin has been successfully done at two different styrene ratios and waste EPS/modified EPS has incorporated into it at the final stage of synthesis. Liquid resin properties such as gel time, peak exothermic temperature and specific gravity are reduced on EPS addition , the unmodified blend showed much higher viscosity than others. The above properties, except gel time are higher for samples at 35% styrene ratio when compared with those at 40% styrene. Formation of a thick interphase observed in the modified blend at 40% styrene ratio and the crack pinning and crack path deflection mechanisms observed in the modified blend at 35% styrene ratio lead to better adhesion between the two phases and enhanced mechanical properties. The tensile strength of the modified blends at both styrene ratios were higher than the corresponding neat resins and samples at 40% styrene ratio showed better properties compared to samples at 35% styrene ratio. UPR/EPS blends shows lower percentage of elongation compared to neat UPR. Samples at 35% styrene showed better elongation. Modified blends showed a slight improvement in elastic modulii compared to unmodified blends and are almost comparable to neat UPR. Higher styrene content blends showed greater modulus. The impact strength is comparatively higher for both modified blend systems and is even better than that of neat UPR. The modified blends showed a considerable improvement in flexural properties over unmodified blends. Crosslink densities of modified blends at both the styrene concentrations were comparable to the corresponding neat resin. Better crosslink density is shown by the modified blend at high styrene content. Modified blends showed better resistance towards water, acid, alkali and MEK. Incorporation of EPS does not alter the thermal stability of UPR. The dynamic mechanical measurements showed that storage modulus and glass transition temperature are slightly improved and the tan delta peak was lowered for modified blend and are close to neat UPR. The results provide evidence that utilization of waste EPS in UPR is feasible and may also provide some improvement in mechanical properties.

References

[1] Partton, T. C. *Alkyd resin technology*, (Interscience Publishers, 1962).

[2] Cherian, B. A Studies on toughening of unsaturated polyester resins. Ph.D. Thesis. Cochin University of Science & Technology (2004).

[3] Gott, S. L., Suggs, J. L. & Blount, W. W. *Mod. Plast.* **50,** 98 (1973).

[4] Tanikoshi, T., Arai, M., Niikura, I. & Takiyara, E. *J. Adv. Comp. Mat. Japan Soc. Comp. Mat.* **5,** 345 (1996).

[5] Curtice, L. G. et. al. *Ind. Eng. Chem. Prod. Res. Dev.* **3,** 218 (1964).

[6] Parker, E. E. & Muffett, E. W. *Ind. Eng. Chem.* **46,** 1615 (1954).

[7] Wilks, E. S. (Ed.), *Industrial Polymer Handbook Vol. 2.* (Wiley-VCH, New York, 2001).

[8] Osman, E. A. Curing Behaviour and Tensile Properties of Unsaturated Polyester Containing Various Styrene Concentrations. *Malaysian Polym. J.* **7,** 46–55 (2012).

[9] Hayaty, M. & Beheshty, M. H. Shrinkage, Cure Characterization and Processing of Unsaturated Polyester Resin Containing PVAc Low-profile Additive. *Iran. Polym. J.* **13,** 389–396 (2004).

[10] Gooch, J. W. *Encyclopedic Dictionary of Polymers, Vol. 1.* (Springer Science & Business Media, 2010).

[11] Chan-Park, M. B. & McGarry, F. J. Tough low profile additives in sheet molding compound. *Polym. Compos.* **17,** 537–547 (1996).

[12] Simitzis, J., Zoumpoulakis, L. & Soulis, S. Effect of composition and polyesterification catalysts on the optical properties of cured polyesters. *Polym. Int.* **51,** 297–307 (2002).

[13] Simitzis, J., Zoumpoulakis, L. & Soulis, S. DSC curing study of catalytically synthesized maleic-acid-based unsaturated polyesters. *Polym. Int.* **51,** 308–318 (2002).

[14] S. Soulis, J.Simitzis, L. Z. Review of the research results concerning the synthesis, curing, structure and properties of unsaturated polyesters. *Curr. Trends Polym. Sci.* **8,** 107 – 125 (2003).

[15] Skoog, D. A., Holler, F. J. & Nieman, T. A. *Principles in instrumental analysis*. (Kostarakis, Athens, 2005).

[16] Valavanides T. *Basic principles in molecular spectroscopy and applications in organic chemistriy.* (Sichrona Themata, Athens, 2008).

[17] McMurry, J. *Organic chemistry.* (Crete University Publications, Herakleion, 2007).

[18] Atta, A. M., Nassar, I. F. & Bedawy, H. M. Unsaturated polyester resins based on rosin maleic anhydride adduct as corrosion protections of steel. *React. Funct. Polym.* **67,** 617–626 (2007).

[19] Ma, C. M., Hsieh, C., Kuan, H., Tsai, T. & Yu, S. Effects of molecular weight and molecular structure of low profile additives on the properties of bulk molding compound (BMC). *Polym. Eng. Sci.* **43,** 989–998 (2003).

[20] Pearson, R. A. & Yee, A. F. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide). *Polymer (Guildf).* **34,** 3658–3670 (1993).

[21] Pascault, J.-P., Sautereau, H., Verdu, J. & Williams, R. J. J. *Thermosetting Polymers*. (CRC Press, 2002). Kim, D. S., Cho, K., An, J. H. & Park, C. E. Toughening Mechanisms of Modified Unsaturated Polyester with Novel Liquid Polyurethane Rubber. *J. Mat. Sci.* **29,** 1854-1866 (1994).

[22] Huang, Y.-J. & Horng, J. C. Effects of thermoplastic additives on mechanical properties and glass transition temperatures for styrene-crosslinked low-shrink polyester matrices. *Polymer.* **39,** 3683–3695 (1998).

[23] Chaudhuri, R. I. Effect of Low Profile Additives on Thermo-mechanical Properties of Fibre/UP Composites. PhD Thesis. McGill University, Canada. (2007).

[24] Huang, Y.-J. & Chen, L.-D. Effects of chemical composition and structure of unsaturated polyester resins on the miscibility, cured sample morphology and mechanical properties of styrene/unsaturated polyester/low-profile additive ternary systems: 2. Mechanical properties. *Polymer (Guildf).* **39,** 7049–7059 (1998).

[25] Sanchez, E. M. S., Zavaglia, C. a C. & Felisberti, M. I. Unsaturated polyester resins: Influence of the styrene concentration on the miscibility and mechanical properties. *Polymer.* **41,** 765–769 (2000).

[26] Sina, C. A novel thermoplastic / clay / thermoset hybrid system for toughening of unsaturated polyesters. PhD Thesis. Concordia University Montreal, Quebec, Canada. (2013).

[27] Jacob, M., Thomas, S. & Varughese, K. T. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. *Compos. Sci. Technol.* **64,** 955–965 (2004).

[28] Huang, Y.-J., Chen, T.-S., Huang, J.-G. & Lee, F.-H. Effects of poly(vinyl acetate) and poly(vinyl chloride-co-vinyl acetate) low-profile additives on properties of cured unsaturated polyester resins. II. glass-transition temperatures and mechanical properties. *J. Appl. Polym. Sci.* **89,** 3347–3357 (2003).

[29] Lucas, J. C., Borrajo, J. & Williams, R. J. J. Cure of unsaturated polyester resins: 2. Influence of low-profile additives and fillers on the polymerization reaction, mechanical properties and surface rugosities. *Polymer (Guildf).* **34,** 1886–1890 (1993).

[30] Dong, J.-P., Lee, J.-H., Lai, D.-H. & Huang, Y.-J. Effects of reactive low-profile additives on the properties of cured unsaturated polyester resins. II. Glass-transition temperature and mechanical properties. *J. Appl. Polym. Sci.* **100,** 867–878 (2006).

[31] Pereira, C. M. C., Herrero, M., Labajos, F. M., Marques, a. T. & Rives, V. Preparation and properties of new flame retardant unsaturated polyester nanocomposites based on layered double hydroxides. *Polym. Degrad. Stab.* **94,** 939–946 (2009).

[32] Tan, S. G. & Chow, W. S. Thermal properties, curing characteristics and water absorption of soybean oil-based thermoset. *Express Polym. Lett.* **5,** 480–492 (2011).

[33] Diew, S., Charoen, N., Azizon, K. & Pairote, K. Water absorption and mechanical properties of water-swellable natural rubber. *Songklanakarin J. Sci. Technol.* **31,** 561–565 (2009).

[34] Kandola, B., Nazare, S., Horrocks, A. In: Le Bras, M. (Ed.), *Fire retardancy of polymers: the use of mineral fillers in micro- and nano-composites.* (Cambridge: Royal Chemical Society, 2005).

[35] Troitzsch, J. *International Plastics Flammability Handbook: Principles, Regulations, Testing and Approaval.* (Hanser Publishers, 1990).

[36] Lam, P. W. K. A comparative study of structure-property relationships in low-profile polyester matrices. *Polym. Eng. Sci.* **29,** 690–698 (1989).

[37] Guo, Q., In: Shonaike, G. O., Simon, G. (Eds.), *Polymer blends and alloys*. **6,** 155–187 (Marcel Dekker, New York, 1999),

[38] Inoue, T. Reaction-induced phase decomposition in polymer blends. *Prog. Polym. Sci.* **20,** 119–153 (1995).

[39] Al-bahadly, E. A. O. The Mechanical Properties of Natural Fiber Composites. (2013).

……

Chapter 7

EFFECT OF EPS/MODIFIED EPS ON VOLUME SHRINKAGE AND TRANSPARENCY OF UNSATURATED POLYESTER RESIN

Contents

7. 1 Introduction

Even with the many significant advantages of UPR, their applications in certain areas are limited due to a number of problems. The free radical copolymerisation of UPR and styrene ends up in diffusion controlled process. During curing the degrees of freedom of molecules get restricted due to polymerization. Also, branching leads to further reduction of the degrees of freedom. The free monomers become constrained to a tight network of polymer units so that the weak Van der Waals bonds get converted into strong but shorter covalent bonds. This results in a significant increase in the stiffness (chemical hardening) and reduction in specific volume (chemical shrinkage) of the system. Furthermore, if the system is cured at some elevated temperature an extra shrinkage (thermal shrinkage) may also be observed when cooled to ambient condition [1-2]. The overall effect results in a high degree of polymerization shrinkage, about 7-10%. This creates problems such as low quality surface, less dimensional stability for the material, warpage of moulded parts, internal cracks and voids [3-5].

To overcome the problems associated with volume shrinkage many researchers have attempted to modify UPR. There are different techniques to address shrinkage related problems. They are inclusion of low profile additives (LPA) in the formulation, in-mold coating (IMC), secondary and finishing operations, appropriate part and tool design and modification of the molding process, such as vacuum molding and multiple pressurization. Excepting the first one, other methods are expensive because they are equipment/labour intensive. Therefore, using a low profile additive is the most desired method for minimising the volume shrinkage in UPR [6]. The function of LPA is to compensate for the thermal and chemical shrinkage of UPR economically [7-8]. The LPA acts as a non reactive component in the system so that its effect may be considered as "diluting" the resin shrinkage. However, it is known to have an effect on compound viscosity and thickening. The type of LPA, its molecular weight and concentration, UP resin structure, processing conditions etc. have a significant effect on resin shrinkage, surface quality and dimensional control of moulded polymer composites as reported by many researchers [8-11]. Several thermoplastics such as polyethylene (PE), polystyrene (PS), polyvinyl acetate (PVAc), polymethyl methacrylate (PMMA), polyurethane (PU) etc. have been used as LPAs. Among these PVAc, PMMA and PU are widely used. The effectiveness of volume shrinkage control is ranked as PU>PVAc>PMMA>PS.

The mechanism of volume shrinkage control by LPA has not been fully understood yet. The necessary criterion for the LPA action is that the UPR and LPA should be phase separated at the very beginning of the curing. This phase separation during curing depends on the chemical structure, molecular weight and dipole moment of LPAs [8]. Subsequent microvoid and/or microcrack formation at the interface between the LPA and crosslinked UP phases as well as inside the LPA phase due to microstress cracking could then lead to volume shrinkage compensation. Phase separation, void formation, and thermal expansion due to the low profile additives are three predominant mechanisms controlling the shrinkage of polyester matrices.The more the microvoids, the better the shrinkage compensation and the higher the loading of LPA, greater the microvoid volume fraction. But this will affect the mechanical properties similar to polymeric foams with negative shrinkage. Therefore shrinkage reduction should be balanced against the mechanical properties of UPA when a LPA is used.

There are two types of phase separation: binodal decomposition (nucleation and growth, NG) and spinodal decomposition (SD). Nucleation and growth results in dispersed domain size increasing with time, and the shape of the domains is spheroidal in nature. SD mechanism occurs with phase separation by interconnected cylinder-like structure. This tends to grow, coalesce and form larger spheroidal structure eventually. Initially miscible polymer blends follow the SD mechanism with high interconnectivity. The co-continuity is also observed with initially immiscible blends, without SD mechanism. Here nucleation, growth, and droplet coalescence are the determining factors for co-continuity [12].

The LPAs form homogenous solutions with UPR irrespective of whether they are compatible or incompatible. This is because LPAs can be dissolved in styrene to form one phase mixture, so that LPAs are at least partly soluble in the uncured poly-ester/styrene solution. The compatible LPAs like PVAc in UPR is stable before polymerization, whereas polymethylmethacrylate (PMMA), PS etc. form metastable/ unstable mixture and phase separation occurs before the reaction [13].

The transparent UPRs have received much attention in the field of fancy goods and button making. Such UPRs should be resistant to yellowing and discolouration. It has been reported that the LPAs, though effective in reducing the volume shrinkage, may turn the material opaque. The sample with good shrinkage control has a high internal surface area, and is always opaque [9]. This is because of the formation of microvoids during curing due to thermal expansion. The cured samples with shrinkage compensation are stark white (opaque) in appearance and the one without is translucent. Good low-profile performance is associated with stark white appearance with reduced transparency. The effect of LPA on the transparency of UPR has also been studied by Wai-Mang L. Kan and L. James Lee [14].

This chapter examines the effect of EPS and modified EPS as low shrinking additives in UPR and correlates this with the optical properties.

7.2 Experimental

7.2.1 Volume shrinkage ($\Delta V/V_o$)

Specific gravity method was used for the determination of volume shrinkage. Density measurements were employed for obtaining volume shrinkage data. The uncured sample was taken in a 25ml density bottle, and its density at 25 °C prior to reaction, $\rho_{1,}$ was measured. The density of the cured sample at 25 °C, ρ_2, was determined by an immersion method using distilled water. The volume shrinkage was then calculated by the relationship,

$$\Delta V/V_o = (1/\rho_2 - 1/\rho_1)/(1/\rho_1)$$

7.2.2 Transparency tests

Transparency of the samples was determined by visual checking as well as from optical properties. The optical properties were quantified according to the total light transmittance by UV-Visible spectroscopy mentioned in Chapter 2.

7.3 Results and Discussion

7.3.1 Volume shrinkage

The predominant mechanisms determining LPA action have been identified as phase separation, void formation, and thermal expansion [15]. It is generally agreed that during curing reaction the LPA and crosslinked UPR phases must phase separate first [8,14-16]. Phase separation is recognized as the precondition for the shrinkage compensation to take place. Micro stress cracking initiated at the interface due to phase separation leads to microvoid and/or micro crack formation between the LPA and crosslinked UPR phases.

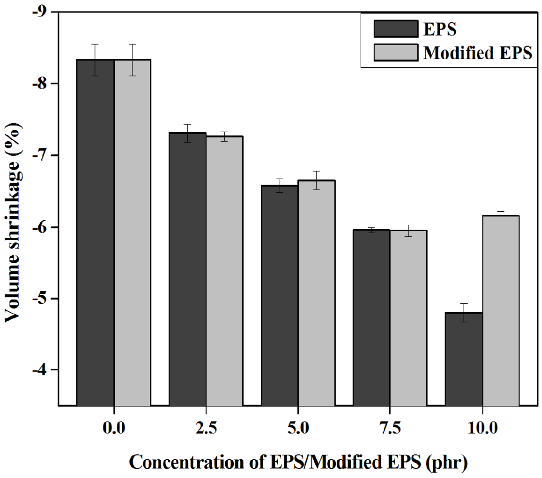


Fig. 7.1. Effect of loading of EPS and modified EPS on volume shrinkage of commercial UPR

Fig. 9 shows the effect of loading of EPS and modified EPS on volume shrinkage of commercial UPR. The volume shrinkage decreases with increasing additive percentage. The decrease in volume shrinkage is observed with EPS content. In the case of modified EPS the shrinkage compensation is maximum at medium concentrations. The shrinkage control is dependent on the compatibility of LPA and UPR and the compatibility depends on the difference in polarity between LPA and unreacted UPR [6-7]. The less polar PS (dipole moment, 0.3) is incompatible with UPR (dipole moment, 2.0 to 2.5) and phase separated before curing. But during curing polarity of UPR decreases (becomes 0.2 to 0.8 when fully cured) demanding a greater driving force for phase separation so that LPA performance should decline [8]. However, a higher content of PS is effective in volume shrinkage compensation. This is because both the occupied volume of the dispersed phase after cure and the segregation effect of PS in micro gel particles generated would also increase with increasing PS concentration, resulting in favourable effects on micro void formation and volume shrinkage control. Also the thermal expansion is higher for polystyrene compared to other thermoplastics. In the case of UPR/modified EPS blends, due to the enhanced compatibility before curing, an interphase is generated (evident in the morphology) and this may contain only less micro cracks and micro gels resulting in a decrease in shrinkage control efficiency. Hence the volume shrinkage compensation in this case is reduced compared to unmodified blends [17]. Owing to high microvoid formation, UPR/EPS blend displays better shrinkage control, over the modified blend at 10phr loading and this can be verified through the water absorption rate and morphology. Unmodified blend at 10phr loading showed 42% reduction in shrinkage compared to neat UPR.

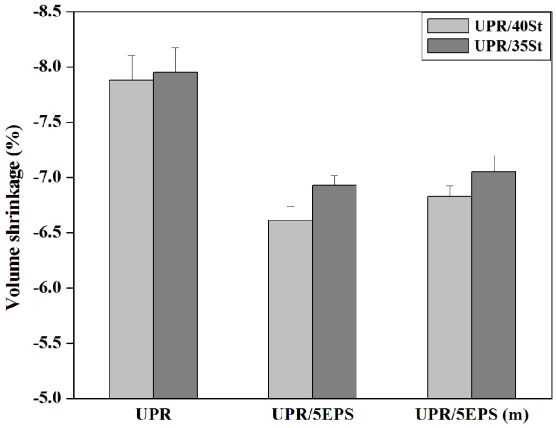


Fig. 7.2. Effect of loading of EPS and modified EPS on volume shrinkage of synthesised UPR at two styrene ratios

Fig. 7.2 shows the effect of EPS and modified EPS on volume shrinkage of synthesised UPR at two styrene ratios. Here also the unmodified blends showed better performance compared to modified blends because of higher microvoid formation. Comparing the styrene ratios, UPR with 40% styrene showed lower volume shrinkage than that of UPR with 35% styrene in the case of neat as well as blends. A schematic representation of the compatibility between UPR phase and EPS/modified EPS is shown below in Fig. 7.3 which supports the effect of EPS/modified EPS on volume shrinkage.

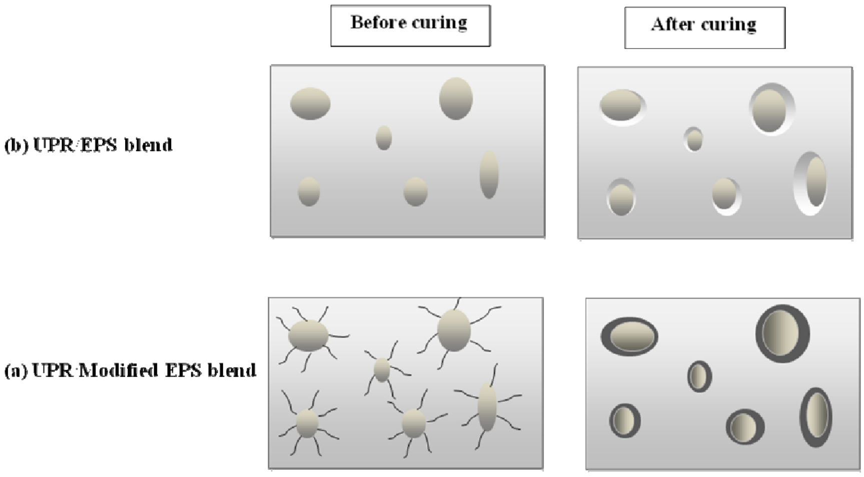


Fig. 7.3. Compatibility between UPR phase and EPS/modified EPS

7.3.2 Transparency studies

Fig. 7.4 and Fig. 7.5 are the photographic images of the cured samples of commercial and synthesized resins respectively. A visual study of transparency of the samples is possible using the photographic images. The change in transparency is clear from the photographs of both commercial as well as synthesized samples. The neat UPRs are transparent in appearance. For unmodified blends the components are phase separated initially, but due to the gradual development of compatibility of polystyrene and UPR during curing, it is believed that internal pigmentation (light scattering is high) occurs yielding uniform colours. Here a change of transparency of the blend system from fully transparent (for neat UPRs) to cloudy for all EPS containing samples is observed. The opaque nature of unmodified blends confirms heterogeneous morphology and macroscopic phase separation. But for modified blends, polar MA-g-EPS is compatible with UPR before curing and therefore little light scattering occurs inside the material, causing poor pigmentability. This results in translucent cured samples [17].

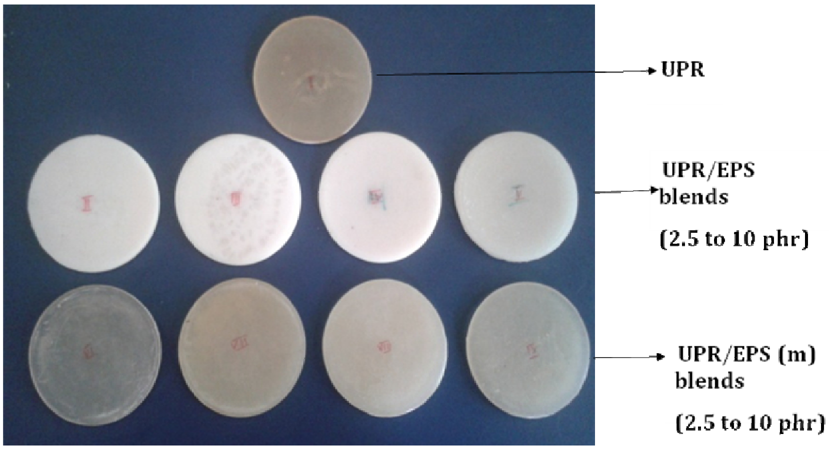


Fig. 7.4. Photographic images of the cured samples of commercial resins samples

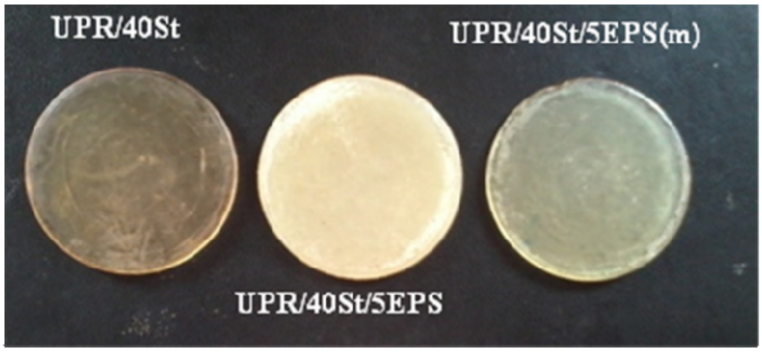


Fig. 7.5. Photographic images of the cured samples of synthesized resin samples at 40% styrene ratio

It was noted that UPRs usually showed good optical properties. To investigate the effect of the EPS on the optical properties of the UPRs, the transmittance of cured neat UPR, and its blends with EPS/modified EPS were measured. Fig. 7.6 is the UV-Visible spectra, (a) transmittance, (b) absorbance and (c) reflectance of commercial UPR and its blends with EPS/modified EPS at loadings of 5 and 10 phrs.

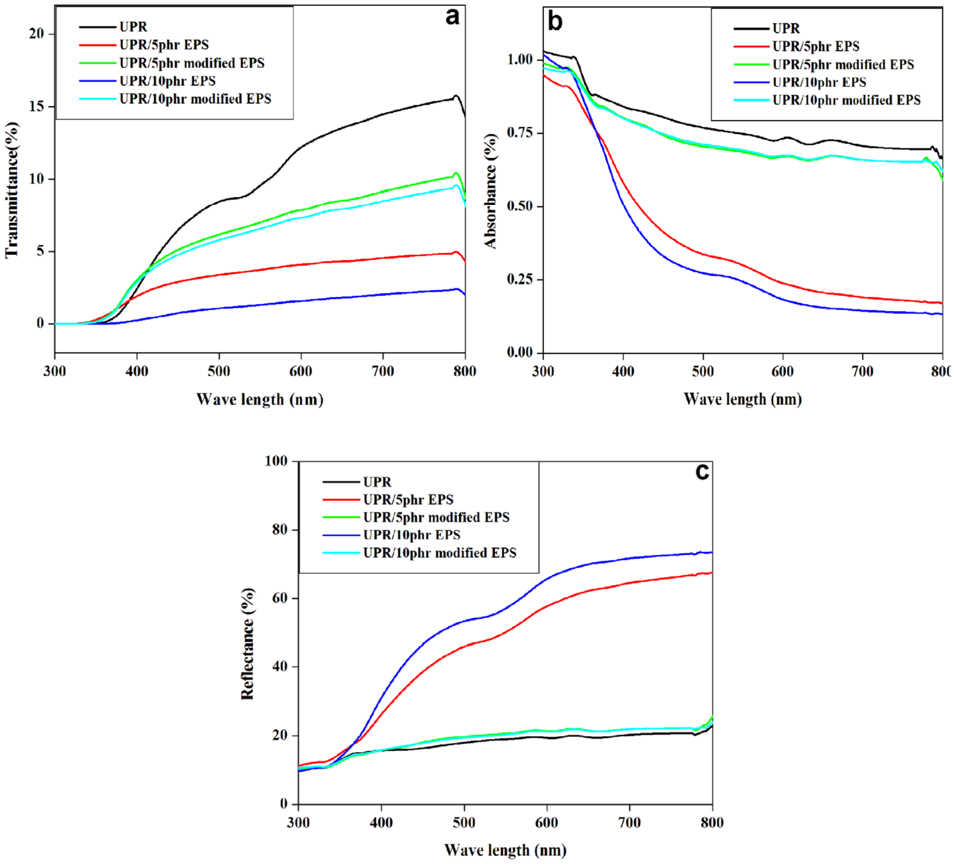


Fig. 7.6. UV-Visible spectra, (a) transmittance, (b) absorbance and (c) reflectance of commercial UPR and its blends with EPS/modified EPS at loadings of 5 and 10 phrs.

In the case of commercial UPR, the % transmittance of cured neat UPR is higher compared to the blends. The neat UPR showed a transmittance of 16% at a wavelength of 789 nm. The incorporation of EPS into UPR lowers the transmittance to 5% at 5phr loading and 2.4% at 10phr loading. This shows the change in transparency upon EPS loading and as loading increases transparency decreases and the sample become opaque [18], which is supported by the photographic images shown above. In unmodified blends, because of the phase separation the transmittance is lowered. But a better % transmittance for modified blends compared to unmodified blends is an indication of compatibility [19]. Here modified blends showed transmittance of 10.4% and 9.5% at 5phr and 10phr modified EPS respectively. All the resins indicated very low transmittance in the UV region (below 400 nm) due to the presence of of aryl units on the backbones of the resins, which often showed absorption at 250–400 nm [20]. The absorbance value of neat UPR is higher and the % reflectance is lower compared to those of the blends for the entire range of wavelength (200-800 nm). The modified blend showed higher absorbance than unmodified blends and the reflectance showed a reverse trend. The absorbance and % reflectance of modified blends are very close to neat UPR.

The transmittance (a), absorbance (b) and reflectance (c) of synthesized UPR (40% St) and its blends with EPS/modified EPS at 5phr loading based on UV-Visible spectra are shown in Fig.7.7. About 40% transmittance was observed for synthesized neat UPR. Compared to commercial UPR a significant improvement of 60% was shown by synthesized UPR. The UPR/5EPS blend showed transmittance of 3%. The modified blend showed transmittance of 14%. The absorbance of neat UPR and modified blends were higher and the % reflectance for the same was lower compared to the unmodified blends for the entire range of wavelength (200-800 nm).

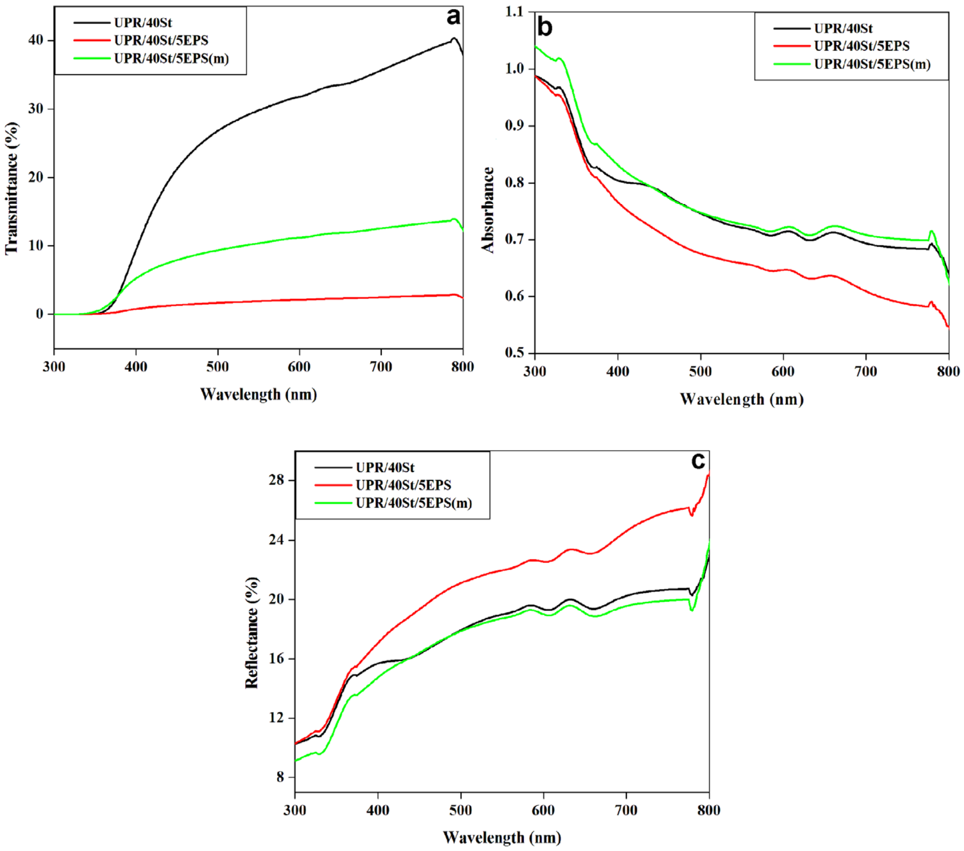


Fig.7.7. Transmittance (a), absorbance (b) and reflectance (c) of synthesized UPR (40% St) and its blends with EPS/modified EPS at 5phr loading

7.3.3 Conclusion

Volume shrinkage is a major drawback of UPR. The incorporation of EPS has reduced the volume shrinkage to a great extent. For unmodified blends of commercial UPR, volume shrinkage shows a gradual reduction with EPS content and at 10phr there is an impressive 42.3% reduction in shrinkage. In the case of commercial resin, for modified blends the shrinkage compensation is maximum at medium loadings (20% improvement at 5phr) and at higher% the performance is poorer. Synthesised UPR with 40% styrene showed lower volume shrinkage than UPR with 35% styrene either alone or as blends with EPS/modified EPS. Synthesised resins showed better transparency than commercial resin. Transparency is higher for the modified blends than unmodified blends. Though the shrinkage compensation is higher at higher EPS loadings the best compromise between volume shrinkage, transparency and desirable properties (discussed in Chapter 5) was found at medium loadings. EPS hence acts as an effective LPA in UPR and this is yet another advantage when EPS is incorporated into UPR as a pollution control method.

References

[1] Pang, K. P. & Gillham, J. K. Anomalous behavior of cured epoxy resins: Density at room temperature versus time and temperature of cure. *J. Appl. Polym. Sci.* **37,** 1969–1991 (1989).

[2] Shah, D. U. & Schubel, P. J. Evaluation of cure shrinkage measurement techniques for thermosetting resins. *Polym. Test.* **29,** 629–639 (2010).

[3] Xu, L. & Lee, L. J. Effect of nanoclay on shrinkage control of low profile unsaturated polyester (UP) resin cured at room temperature. *Polymer (Guildf).* **45,** 7325–7334 (2004).

[4] Schoch, K. F., Panackal, P. A. & Frank, P. P. Real-time measurement of resin shrinkage during cure. *Thermochim. Acta* **417,** 115–118 (2004).

[5] Haider, M., Hubert, P. & Lessard, L. Cure shrinkage characterization and modeling of a polyester resin containing low profile additives. *Compos. Part A Appl. Sci. Manuf.* **38,** 994–1009 (2007).

[6] Kinkelaar, M., Muzumdar, S. & Lee, L. J. Dilatometric study of low profile unsaturated polyester resins. *Polym. Eng. Sci.* **35,** 823–836 (1995).

[7] Kinkelaar, M., Wang, B. & Lee, L. J. Shrinkage behaviour of low-profile unsaturated polyester resins. *Polymer (Guildf).* **35,** 3011–3022 (1994).

[8] Huang, Y.-J. & Liang, C.-M. Volume shrinkage characteristics in the cure of low-shrink unsaturated polyester resins. *Polymer (Guildf).* **37,** 401–412 (1996).

[9] Li, W. & Lee, L. J. Shrinkage control of low-profile unsaturated polyester resins cured at low temperature. *Polymer (Guildf).* **39,** 5677–5687 (1998).

[10] Beheshty, M. H., Vafayan, M. & Poorabdollah, M. Shrinkage Control and Kinetics Behaviour of Clay-Unsaturated Polyester Nanocomposites. *Iran. Polym. J.* **15,** 841–849 (2006).

[11] Li, W. & Lee, L. J. Low temperature cure of unsaturated polyester resins with thermoplastic additives. II. Structure formation and shrinkage control mechanism. *Polymer (Guildf).* **41,** 697–710 (2000).

[12] McMaster L. P. Aspects of Liquid-Liquid Phase Transition Phenomena in Multicomponent Polymeric Systems. In *Copolymers, Polyblends, and Composites* (ed. Platzer, N. A. J.) *Adv. Chem. Ser.* **142,** 43–65 (American Chemical Society, 1975).

[13] Beheshty, M. H., Hayat, M. & Vafayan, M. Evaluation of Low-profile Additives in the Curing of Unsaturated Polyester Resins at Low Temperatures. *Iran. Polym. J.* **15,** 143–153 (2006).

[14] Kan, W. M. J. & Lee, L. J. LPA performance in low temperature SMC/BMC molding. (1996).

[15] Chaudhuri, R. I. *Effect of Low Profile Additives on Thermo-mechanical Properties of Fibre/UP Composites*. (McGill University (Canada), 2007).

[16] Huang, Y.-J. & Horng, J. C. Effects of thermoplastic additives on mechanical properties and glass transition temperatures for styrene-crosslinked low-shrink polyester matrices. *Polymer (Guildf).* **39,** 3683–3695 (1998).

[17] Ma, C. M., Hsieh, C., Kuan, H., Tsai, T. & Yu, S. Effects of molecular weight and molecular structure of low profile additives on the properties of bulk molding compound (BMC). *Polym. Eng. Sci.* **43,** 989–998 (2003).

[18] Gu, H. *et al.* Transparent anhydride–cured epoxy nanocomposites reinforced with polyaniline stabilized nanosilica. *J. Mater. Chem. C* **3,** 8152–8165 (2015).

[19] Im, H., Kim, H. & Kim, J. Novel Miscible Blends Composed of Poly (Methyl Methacrylate) and 2,2-Bis(3,4-Carboxyphenyl)Hexafluoropropane Dianhydride- Based Polyimides with Optical Grade Clarity. *Mater. Trans.* **50,** 1730–1736 (2009).

[20] Chen, X., Li, K., Zheng, S. & Fang, Q. A new type of unsaturated polyester resin with low dielectric constant and high thermostability: preparation and properties. *RSC Adv.* **2,** 6504 (2012).

* * *

Chapter 8

SUMMARY AND CONCLUSIONS

Many industries use expanded polystyrene (EPS) because of its versatile applications, dimensional stability, cleanliness, and low cost. After use, EPS usually ends up in landfills or is incinerated. But the low bulk density (15–50 kg/m^3) and voluminous nature make it as a major source of environmental littering. Neither of these are environment-friendly solutions and are becoming less practical due to increasing land cost and public opposition. Hence, any reduction in the amount of waste EPS littering the environment can be considered an ecologically significant step. In response to the high cost of disposal and growing public opposition to land filling, a number of recycling strategies for EPS have been devised. Still, the recycling of EPS has not attained the same status as that of other polymers because of the high transportation cost as well as the small price difference between virgin and recycled products. Therefore, a cost effective method for the utilization of this waste material is a necessity in the present scenario. If the waste EPS could be used in the processing of other polymers the economics of recycling may be more favourable. This work aims to investigate economically significant techniques for the utilization of this material in various polymers without compromising the polymer properties.

In this study, an attempt has been made to utilize waste EPS by blending it with other polymers. Elastomers used were natural rubber and styrene butadiene rubber. The blending of EPS was also done with an unsaturated polyester resin, a thermosetting plastic. Blends of both commercial as well as synthesized resins were prepared. The properties of the above blends were evaluated. In order to retain the inherent properties of the polymers, modification was also done using a grafting technique. The study establishes the potential of this method for utilizing waste EPS.

Mechanical, thermal and morphological properties of unfilled and filled (carbon black and silica) NR/EPS blends were studied and compared with the corresponding unfilled and filled NR without EPS in order to select the best filler for the blend. The effect of compatibilization on the properties of silica filled NR/EPS blends using maleic anhydride was investigated. Grafted blends were prepared for compatibility enhancement at varying MA content, initiator (DCP) content and blend ratios. The final cured blends were obtained after adding required quantity of NR and compounding ingredients. Cure characteristics, physico-mechanical properties, dynamic-mechanical, solvent sorption, thermal stability, phase morphology etc. of the final cured blends were analysed and compared with that of NR.

The effect of EPS in SBR compounding was also studied. Blends of SBR and EPS were first prepared initially in a Brabender Plasticorder. These were subsequently blended with more of SBR and compounding and curing done. Different blend ratios of unfilled compounds were prepared and the properties were compared with the corresponding samples without EPS. Similarly, silica/black filled SBR/EPS blends were also prepared at optimum blend composition and cure characteristics, physico-mechanical properties, dynamic-mechanical, solvent sorption, thermal analysis and phase morphology of the blends were studied and compared with corresponding SBR samples.

Another study was done to investigate the utilization of EPS in commercial unsaturated polyester resin (UPR). Blends of UPR/EPS were prepared by dissolving EPS (varying concentrations, 2.5 – 10 phr) in styrene and this was mixed with UPR by mechanical stirring (called unmodified blends). Maleic grafting was done on EPS and the modified blends were also prepared. Curing was done using methyl ethyl ketone peroxide (catalyst) and cobalt naphthenate (accelerator) combination for 24 h, followed by post curing at 80 °C for 3 h. Neat resin samples without EPS were also prepared for comparison.

Synthesis of UPR with two different styrene concentrations with incorporation of EPS in the final stage of synthesis was done. UPR/5EPS (unmodified/modified EPS) blend with two different styrene contents (35 and 40 wt %) were prepared and the results were compared with their pure forms. 5phr EPS was used here because in the previous chapter the blends showed the best compromise of all properties at this particular concentration. Curing was done for the neat, UPR/5EPS(unmodified) and UPR/5EPS(modified) resins for both styrene concentrations.

A significant aspect of this work is the study on the effect of EPS and modified EPS as low profile additive (LPA) on the volume shrinkage and transparency of both commercial as well as synthesised UPR samples. Density method was used for the determination of volume shrinkage and transparency was measured by UV-Visible spectroscopy.

Conclusions

The following major conclusions can be drawn from the investigation.

NR

- The cure properties of silica filled blends of NR/EPS are comparable to those of the neat compound.
- The reduction in tensile strength for silica filled NR/EPS blend is very small compared to other systems.
- The modulus at 300% elongation and tear strength for the blends were improved compared to NR irrespective of the filler.
- The TGA data suggest that blends have thermal stability comparable to
- Greater extent of roughness in the fractured surface morphology of silica filled NR/EPS blend indicates better reinforcement.
- From the overall performance, it can be concluded that silica is best suited for NR/EPS blends as a filler.
- Most properties of the silica filled 95/5 NR/EPS blend showed remarkable improvement on compatibilization.
- Tensile strength, tear strength and modulus at 300% elongation for the optimum blend were enhanced and elongation was decreased compared to that of silica filled NR.

- The optimum blend showed a better abrasion resistance and hardness.
- The crosslink density, glass transition temperature and thermal stability of the optimum blend is comparable with silica filled NR without EPS.
- Greater interfacial interaction and better dispersion is evidenced in the morphology of silica filled NR/EPS blends
- The overall data suggest that 5% waste expanded polystyrene can be incorporated into silica filled NR compounds without deteriorating the properties of NR.

SBR

- A significant improvement in tensile strength (146%), modulus at 300% (180%) and tear strength (157%) is found for unfilled 85/15 SBR/EPS blend when compared with neat SBR, followed by silica filled blends and finally black filled system.
- Tensile strength is increased on thermal aging for the unfilled blends.
- Compression set, abrasion loss, hardness and resilience of unfilled 85/15 SBR/EPS blends are similar to filled SBR systems without EPS.
- The crosslink density values are in good agreement with the mechanical properties.
- Better interfacial interaction is evidenced in the morphology of both gum and silica filled systems.

- Thermal stability of SBR was not affected by the incorporation of EPS.
- Glass transition temperature of SBR is less affected by the presence of 15% EPS whereas that of EPS was reduced by the blending.
- Improvement in the mechanical and aging properties of the SBR/EPS blends compared to virgin SBR paves the way for the effective and economical utilization of 15% waste EPS.

UPR

- Cure characteristics and specific gravity of resin were reduced on EPS addition, but modified blends are better in this respect.
- Morphology of modified blends showed a better adhesion between the two phases.
- Tensile strength of modified blends has improved by 17.5% (at 5phr) when compared with neat resin whereas impact strength is lowered.
- Flexural strength and flexural modulus of the modified blends are superior to unmodified blends.
- Crosslink density of modified blends is close to neat UPR.
- Modified blends showed better resistance towards water, acid and alkali.
- Incorporation of EPS does not alter the thermal stability of UPR.

- Glass transition temperature and storage modulus of neat UPR and UPR/5EPS(m) are similar.
- The results establish the viability of utilizing waste EPS in UPR.
- Specific gravity, viscosity and peak exothermic temperature are higher for samples at 35% styrene ratio compared to samples at 40% styrene ratio.
- Morphology of modified blends at both 35% and 40% styrene ratios indicate a better adhesion between the two phases.
- The tensile strength, elongation, and energy of the modified blends at both styrene ratios were improved. and are higher for samples at 40% styrene ratio showed better performance, except in elongation.
- Modified blends at 40% styrene showed a better impact strength and flexural properties over unmodified blends.
- Crosslink densities of modified blends at both the styrene concentrations were comparable to the corresponding neat resin.
- Modified blends showed better resistance towards water, acid and alkali.
- Incorporation of EPS does not alter the thermal stability of UPR.
- Storage modulus, glass transition temperature and the loss tangent were improved for modified blend and are close to neat UPR.
- The results provide ample proof for effective utilization of waste EPS in UPR synthesis.

- The volume shrinkage of commercial UPR is reduced in the presence of EPS (42.3% reduction in shrinkage at 10phr), hence it acts as an effective LPA.
- The loss of transparency due to EPS is reduced by modified EPS in both commercial as well as synthesized samples. Synthesized resins showed better transparency than commercial resin.
- Utilization of 5phr EPS in UPR is the best compromise between volume shrinkage, transparency and desirable mechanical properties.

Future work

There is ample scope of continuation of the studies on the utilization of waste expanded polystyrene. Some of possibilities are listed below.

- Preparation of blends of EPS with thermoplastics like polystyrene, polyethylene, polypropylene, etc.
- Preparation and characterisation of blends of EPS with polar elastomers like NBR.
- Blending EPS/modified EPS with other thermosetting resins such as epoxy, phenol formaldehyde, etc.
- Experimenting with different compatibilizers for improving the interaction between EPS and other components.

…..…..

List of Abbreviations and Symbols

ABS	Acrylonitrile-butadiene-styrene terpolymer
ASTM	American Standard for testing and materials
BMC	Bulk moulding compound
CBS	N-cyclo hexyl 2-benzothiazole sulphenamide
CoNp	Cobalt naphthenate
CoOc	Cobalt octoate
CRI	Cure rate index
DEG	Diethylene glycol
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetry
EPDM	Ethylene-propylene-diene-terpolymer
EPS	Expanded polystyrene
ESR	Electron spin resonance
FA	Fumaric acid
FTIR	Fourier Transform Infrared Spectroscopy
GMA	Glycidyl methacrylate monomer
GP	General purpose
HDPE	High density poly ethylene
HIPS	High impact polystyrene
IR	Infra red
ISNR	Indian Standard Natural Rubber
ISO	International organizations for standardization
IUPR	Isophthalic polyester resin
LDPE	Low density poly ethylene
LPA	Low profile additive
LPA	Low profile additive

MA	Maleic anhydride
MA-g-EPS	Maleic anhydride grafted expanded polystyrene
MEK	Methyl ethyl ketone
MEKP	Methyl ethyl ketone peroxide
NBR	Acrylonitrile butadiene-rubber
NR	Natural rubber
NR-g-PS	Natural rubber grafted polystyrene
PA	Phthalic anhydride
PB	Polybutadiene
PBT	Poly(butylenes terephthalate)
PC	Polycarbonate
PET	Poly (ethylene terphthalate)
PP	Poly propylene
PS	Polystyrene
PVA	Polyvinyl chloride
PVC	Poly vinyl chloride
RHP	Rice husk powder
RPA	Rubber Process Analyzer
SAN	Poly(styrene-co-acrylonitrile)
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscope
SMC	Sheet moulding compound
SP	Styrenated phenol
St	Styrene
TGA	Thermogravimetric analysis
TMTD	Tetramethyl thiuram disulphide
TPE	Thermoplastic elastomer
TPU	Thermoplastic polyurethane
TQ	1,2-dihydro-2,2,4-trimethyl quinoline
UPR	Unsaturated polyester resin

UTM	Universal testing machine
UV	Ultra violet
G'	Storage modulus
G"	Loss modulus
G*	Ccomplex modulus
J	Joule
M_H	Maximum torque
M_L	Minimum torque
MPa	Mega Pascal
Mt	Torque at time
N	Newton
R	Universal gas constant
rpm	Revolutions per minute
T	Temperature
t_{10}	Scorch time
t_{90}	Cure time
Tan δ	Loss tangent
Tg	Glass transition temperature
ρ	Density
χ	Interaction parameter

.....⁂.....

List of Publication

Journal Papers

[1] **Renju V. S.**, Eby Thomas Thachil Utilization of waste expanded polystyrene: Blends with silica-filled natural rubber. *Materials and Design.* 40 (2012) 221–228.

[2] **Renju V. S.**, Eby Thomas Thachil. Waste expanded polystyrene- An ingredient in natural rubber compound, *Recycle Now*, vol I (2010) issue 7.

[3] Ayswarya E. P., Vidya Fransis, **Renju V. S.**, Eby Thomas Thachil. Rice husk ash –A valuable reinforcement for high density polyethylene. *Materials design* 41(2012) 1-7.

[4] Teena Abraham, Gean A Varghese, **Renju V. S.**, Eby Thomas Thachil. Preparation of nano alumina through gel combustion method. *Pauline Journal of Research Studies1* (1) 2013.

[5] **Renju V. S**, Ayswarya E. P, and Eby Thomas Thachil, Waste expanded polystyrene as Low Profile Additive (LPA) in unsaturated Polyester Resin. *Journal of Applied Polymer Science.* (Communicated).

[6] **Renju V. S**, Bipinpal P. K. Julie C. S., Teena Abraham and Eby Thomas Thachil, Utilization of Waste Expanded Polystyrene in Styrene butadiene Rubber Compounding. *European Polymer Journal.* (Communicated).

[7] **Renju V. S**, Bipinpal P. K. Sona Narayanan, and Eby Thomas Thachil, Synthesis of Unsaturated polyester resin and Modification by EPS. Polymer. (Communicated).

Conference Papers

[1] Effect of Maleic anhydride and Dicumyl peroxide on the Cure Characteristics of Silica Filled Natural Rubber/Expanded Polystyrene Blend. Renju V. S. and Eby Thomas Thachil. National Seminar on Frontiers in Chemistry, St. Aloysius College, Thrissur, 29, 30 October 2015.

[2] Natural rubber compounding- a possible route to combat environmental littering due to waste EPS. Renju V. S. and Eby Thomas Thachil. IRC 2012, International rubber conference, Kovalam, 28-31, October 2012.

[3] Effect of DCP on the mechanical properties of Natural rubber/Expanded polystyrene blend". Renju V, S. and Eby Thomas Thachil. National conference on Advances in Materials Science: Macro to Nano Scales at Department of chemistry, Union Christian College, March 2012.

[4] Effect of compatibiliser on the mechanical properties of natural rubber/expanded polystyrene blend. Renju V. S. and Eby Thomas Thachil. Polymer Science and Engineering: Emerging Dimensions, PSE-2010, International conference, Chandigarh, November 26-27, 2010.

[5] Studies on the use of waste expanded polystyrene in natural rubber compounding. Renju V. S. and Eby Thomas Thachil. National Seminar on Chemistry and Environment, Dept. of Chemistry, St. Pauls College, Kalamassery. September, 2010.

……

Curriculum Vitae

RENJU V. S.
Vaikathusseril
Kidangoor South P.O.
Kottayam
Pin: 686583
Kerala, India

Ph: +91-974536450
E-mail:renjusnath@gmail.com

Nationality : Indian

Language Proficiency : Malayalam, English, Hindi

Qualifications : M.Sc. Chemistry (Mahatma Gandhi University, Kerala, India)

B. Ed. (Mahatma Gandhi University, Kerala, India),

SET (Directorate of HSE, Kerala)

Post Graduate Diploma offered by Indian Rubber Institute & Indian Institute of Technology (IIT), Kharagpur

Research experience : Seven years in Polymer Science and Rubber Technology

Teaching experience : Three Years

……

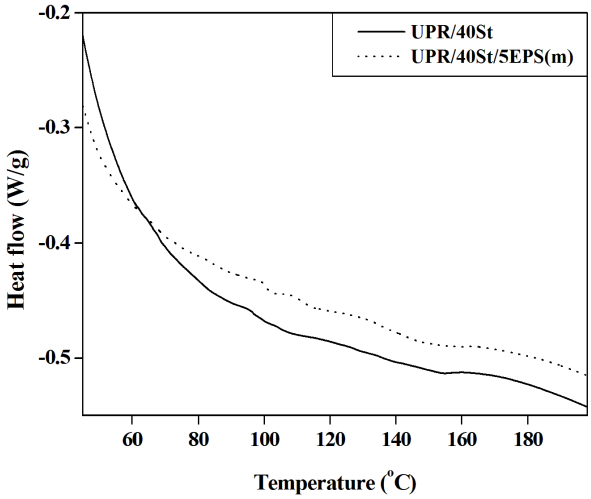
Supplementary information based on reviewers’ comments

(i) Qn: What is the percentage of grafting (PG) and grafting efficiency (GE) of MA in NR/EPS

Ans: The percentage of grafting (PG) and grafting efficiency (GE) of MA in NR/EPS blend at optimum MA and DCP are determined as, 0.33% and 32.52% respectively.

(ii) Qn: In chapter six, Incorporate the synthesized polyester resin IR and DSC thermogram in the thesis.

Ans: IR spectrum had been incorporated in chapter six (Fig. 6.5). The DSC thermogram of synthesized resin is given below.



DSC thermogram of UPR/40St and UPR/40St/5EPS(m)

DSC provides information concerning the glass transition, as a shift in baseline corresponding to the glass transition temperature of unsaturated polyester resin. From the DSC curves the Tg values of UPR/40St and UPR/40St/5EPS(m) were found to be 98.8 °C and 101.2 °C respectively.