OPTIMISATION OF THE MECHANICAL PROPERTIES OF HDPE/PP BLENDS AND THEIR RECYCLABLE COMPOSITES

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by

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Optimisation of the Mechanical Properties of HDPE/PP Blends and Their Recyclable Composites

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The earth was formless and desolate, the raging ocean that covered everything was engulfed in total darkness and the power of God was moving over the water.

God commanded "Let there be light" and light appeared.

[Gen: 1, 2-3]

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CERTIFICATE

This is to certify that the thesis entitled "***Optimisation of the Mechanical Properties of HDPE/PP Blends and Their Recyclable Composites***" which is being submitted by Mr. Jude Martin Mendez, in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22, is a record of the bonafide research work carried out by him under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Kochi-682022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

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DECLARATION

I hereby declare that the work presented in this thesis entitled "***Optimisation of the Mechanical Properties of HDPE/PP Blends and Their Recyclable Composites***" is based on the original research work carried out by me under the guidance and supervision of **Dr. K.E.George,** Professor, 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.

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PREFACE

About half of the total polymers produced in the world is composed of polyolefins. They are the cheapest plastics and are widely used for packaging applications. Due to their extensive usage in domestic as well as industrial areas, the waste dumps contain a large amount of these polymers. Because of the low density and hollow shape of the items, they emerge both in waters and landfills. They cause environmental pollution since they are non-biodegradable. Recycling of such commingled plastics is the best option of dealing with such wastes particularly for a country like India. However, melt mixing of two or more polymers most often gives blends which are inferior in properties to either of the polymers mixed. The properties vary with concentration and the type of polymers used for preparing the blend. The main goal of combining two or more polymers is to obtain a material with appropriate features and conditions for processing. Post – use polymers are mixed in order to recycle such materials and to reduce the environmental impact generated by these solid materials.

Studies claim that reduction of rheological mismatch for a blend containing polyolefins can enhance dispersive mixing. This can be achieved by modification of these polymers with peroxides. Such low molecular weight compounds used as modifiers are usually added in relatively low concentrations. They offer considerable economic advantages compared to polymeric compatabilizers that are more expensive and usually only effective at higher concentrations.

This study was undertaken in order to upgrade blends of HDPE and PP, two of the most widely used standard plastics so as to widen their application spectrum. Dicumyl peroxide was used as the modifier for the upgradation. Optimum concentration of dicumyl peroxide required for modification was determined by measurement of mechanical, rheological, thermal and morphological properties. Selected blends were used to prepare recyclable composites with nylon clothes by compression moulding. The composites were characterized by measurement of mechanical and thermal properties. The composites were recycled and the mechanical properties of the recycled material were determined.

A brief summary of the thesis is as follows –

Chapter 1 is an introduction and a review of the earlier studies in this field. Scope and objectives of the present work are also discussed.

The specifications of the materials used and the experimental procedures for the preparation and characterization of unmodified and modified HDPE/PP blends and nylon mat reinforced composites are presented in **Chapter 2**.

The preparation of HDPE/PP blends, their modification with varying concentrations of DCP and measurement of their mechanical properties – tensile properties, flexural properties and impact strength are presented in **Chapter 3**. The blends were subjected to reactive extrusion at 170^0C & 180^0C as well as injection moulding at the same temperatures. Their tensile properties were measured and compared in order to find the relative merit of these two processing routes and the effect of the concentration of the modifier. The morphological investigation was done using scanning electron microscope.

The melt viscosity of unmodified and modified HDPE/PP blends was determined using a capillary rheometer. The results are presented in **Part A** of **Chapter 4.** The thermal studies are described in **Part B** as thermogravimetric analysis, dynamic mechanical analysis and differential scanning calorimetry. The thermal stability, the load bearing capacity and crystallization characteristics of the blends and their modifications are described.

Chapter 5 describes the preparation of composites with three grades of nylon mat reinforcements using unmodified and modified HDPE, PP and their blends matrix material. The characterization of composites by their tensile, flexural and impact strength studies are presented. The composites were recycled by injection moulding and the mechanical properties of the recycled materials were measured. The morphological investigation was done using scanning electron microscope.

In **chapter 6**, the thermal studies of the composites are described using thermogravimetric analysis and dynamic mechanical analysis.

The summary and conclusions of the study are given in **Chapter 7.**

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CHAPTER 1

INTRODUCTION

1.1 POLYMERS AND POLYMER BLENDS

About half of the total polymers produced and used in the world is composed of polyolefins. These are the cheapest plastics and are largely used for short-term packaging. Because of the low density and hollow shape of the items, they emerge both in waters and landfills, provoking considerable environmental impact [1, 2].

The simple processing of mixed polyolefin waste usually leads to products with low mechanical properties because these polymer mixtures are frequently incompatible and contaminated by impurities [3]. Polypropylene due to its favourable price, density and versatility is gradually replacing many materials in commercial applications. Even though this polymer is highly susceptible to photo-degradation, it is commonly used in producing many materials that are exposed to atmosphere like packaging materials and automobile bumpers. The radiations absorbed by the polymer causes removal of hydrogen atoms attached to tertiary carbon atoms leading to the reduction of molecular weight with modification of the chemical structure [4]

The incompatibility of PP with both LDPE and HDPE causes loss of the mechanical properties of the blend. Recycled LDPE and HDPE are difficult to completely separate from the other polyolefins because of their close densities and similarity of physical properties. So the recycled product may contain fragments of PP as contaminant [5, 6].

The main goal of combining two or more polymers is to obtain a material with appropriate features and conditions for processing. Post – use polymers are mixed in order to recycle such materials and to reduce the environmental impact generated by these solid materials. It is important to determine the behaviour of these materials in order to optimize the non – used polymer / recycled polymer relation and to obtain suitable properties that do not result in a deterioration of the finished product [7].

In recent decades the total consumption of plastics and their applications have increased manifold due to the properties of these materials, their adaptability and use of economic manufacturing methods. Due to large scale usage, a great amount of plastic waste is generated which is causing environmental problems [8].

Due to the immiscible nature of the components, both in the melt as well as solid state, resulting blends show deterioration in impact performance and tensile properties [9]

In many industrial applications of polymeric materials, several criteria play important roles in the selection or resins. In terms of overall performance, these generally include (1) The bulk properties, (2) The surface properties and (3) The processability of the resin. Bulk properties are critical in determining the thermal behaviour and mechanical strength of polymers [10,11]. On the other hand surface properties play important roles in determining the wettability and adhesion, friction and wear, gloss and scratch resistance, paintability and printability, biocompatibility and antistatic properties [12]

The majority of polymers found in waste plastic streams form phase separated morphology. Properties like ductility and impact strength should be improved by compatibilization. Compatibilization is done by the addition of block or graft copolymers with segments capable of interacting with blend constituents. These copolymers lower the interfacial tension and improve adhesion between the matrix and dispersed phase [13, 14]. According to Xanthos (1992) chemical modification of a blend by reactive extrusion can improve the properties of the polymer blend [15]

Hettema *et al.* claim that reduction of rheological mismatch for a blend containing low viscosity PE and high viscosity. PP can enhance dispersive mixing. This is caused by preferred reaction of these polymers with peroxides. They have also claimed that the low molecular weight compounds used in reactive extrusion are usually added in relatively low concentrations. They offer considerable economic advantages versus polymeric compatabilizers that are more expensive and usually only effective at higher concentrations [16].

Randall *et al.* describe the preparation of impact modified PP blends by treating a reactor blend of PP and LLDPE with peroxide. Various fragments will be present and they recombine to form block or graft copolymers. This method increased the Gardner impact strength [17].

Gongde Liu *et al.* also showed that addition of PP to UHMWPE improved the processability of the blend compared to UHMWPE or its blend with HDPE [18].

According to Deanin and Chung the poor impact resistance at low temperature and poor environmental stress cracking resistance has set limitations to the use of polypropylene. These properties of polypropylene can be improved by incorporation of ethylene during polymerization or mechanical blending with polyethylene. Propylene – ethylene copolymers give better performance than PP at low temperature but these copolymers require controlled, specialized polymerization during manufacture and so are more expensive. Thus blending of PP and PE is an economic alternative [19].

According to Nolly *et al.* and Bartlett *et al.* samples prepared by compression moulding were less ductile and less strong than those prepared by injection moulding [20, 21].

An increase in the mixing time as well as intensity improved the degree of dispersion but prolonged or intensive mixing also increased the thermal and mechanical degradation. There is an optimum mixing procedure that should be sought [22].

Polyolefin are the most important plastics. Polyethylene and polypropylene have the most products and lies in the first position of plastics. Polyolefin blends are frequently used to get the balanced mechanical and processing properties. The properties of individual polyolefin can be changed in a significant way by mixing with other components. For this reason polyolefin blends have attained widespread commercial applications. Many studies have been conducted to study the relationship between morphology and properties of polyolefin blends and to control the micro-phase separation, morphology and orientation of studied blends in order to get excellent properties [23 – 25].

Study of properties and morphology of polyolefin blends is of great interest importantly because of their rich and fascinated morphology depending on molecular structure, thermal history and external stress field. The work of Prof. Bevis, oscillating shear stress field has been very important in controlling polymer morphology and mechanical properties.

It was found that HDPE and PP were phase separated in the melt state and form separated crystallites during cooling. However a study of PP/HDPE blends by Inoue and coworkers proposed a single phase mixture of PP/HDPE = 60/40 obtained in high shear fields in an injection moulding machine based on the regularly phase-separated structure [26].

Macosko *et.al.* observed the average diameter of particles of the blend with and without compatibilizer. They noted that less than 10 minutes of mixing even at very low shear rate was enough to reach the final particle size. Most of the size reduction occurred very rapidly during the softening of the pellets or powder. The particle size was slightly smaller with the block copolymer present [27].

It is interesting to check the miscibility, morphology and mechanical properties of polymer blends in a high shear rate combined with oscillating shear field during cooling. Experiments were carried out for HDPE/PP blends via oscillating packing injection moulding after subjecting a high shear rate at the nozzle. A great enhancement of tensile strength was achieved for the blends with PP content less than 10 weight percentage [28].

1.2 POLYMER BLENDING

The practice of polymer blending is as old as the polymer industry itself. During the first half of the twentieth century, the greatest progress in polymer industry was the development of a wide range of new polymers. This was based on the new understanding of polymer synthesis and the development of commercialization of economical manufacturing methods for a range of monomers. Most of the major commodity and engineering plastics in current use were being manufactured in 1950's. By 1970 most of the common monomers had been exploited and then only a few new developments have been taken place in synthesis, generally reserved for specialized polymers and to low volume applications.

During the same period polymer blending began to flourish. It was gradually accepted that new economical monomers were less likely but a range of new materials could be developed by combining different existing polymers. While most monomers available cannot be copolymerized to a product of intermediate properties, their polymers could be melt blended economically. Now polymer blends in one form or another dominate much of polymer practice. This rapid development can be attributed to the following points –

1. The opportunity to develop new properties or improve on properties to meet specific customer needs.
2. The capacity to reduce material costs with little sacrifice in properties.

3. The ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products.
4. Permit the much more rapid development of modified polymeric materials to meet emerging needs by by-passing the polymerization steps.

1.3 IMPORTANT BLENDING PRINCIPLES

Polymer blends may be broadly classified into two – miscible and immiscible blends. Miscible blends are characterized by the presence of a single phase and a single glass transition temperature. They involve thermodynamic solubility. Their properties can be predicted as composition weighed average of the properties of individual components. Immiscible blends are phase separated, exhibiting the glass transition temperature and/or melting temperature of both components. The overall performance of the blend depends on the properties of the individual components as well as the morphology of the blends and the interfacial properties between the blend phases. For a polymer blend to be miscible, the free energy of mixing should be negative which means that the blend should have an exothermic heat of mixing. An exothermic heat of mixing can be achieved by the introduction of specific interactions between blend components. These interactions range from strong covalent and ionic bonding to weak non-bonding interactions like ion – dipole, dipole – dipole, donor – acceptor interactions etc.

During blending of two polymers we have to take care of a few possibilities. Simply adding a polymer to another brings out both good and bad properties of the later. The adverse effects are so pronounced that the resultant material is most likely unusable. The main reason is that most polymer pairs are immiscible and blending leads to a phase separated material. This material has three inherent problems.

a) Poor dispersion of one polymer phase in the other

For most polymer pairs, the interfacial tension is high of the order of 1.5 x 10^{-3} to 1.5 x 10^{-2} J m^{-2}. This high value makes dispersion of one phase in the other by melt blending difficult. When the dispersed phase has large surface area, the interfacial contact between the two phases is small. When this material is subjected to mechanical load, it does not respond efficiently.

b) Weak interfacial adhesion between the two phases

For most polymer pairs, the Flory parameter 'χ' is large (0.05 – 0.5) and the interfacial width 'h' is narrow (1 – 5 nm). This means that there is little penetration of polymer chains from one phase into the other and vice versa, and consequently few entanglements are formed across the interfaces [29]. The failure of the interface between two glassy polymers thus requires only the breaking of weak van der Waal's bonds. For most incompatibilized blends, the interfaces are probably the most vulnerable locations. When they are subjected to an external stress, the interfaces will most likely fail well before the base polymer components.

c) Instability of immiscible polymer blends

An immiscible polymer blend is thermodynamically unstable. The state of dispersion of one phase in another is governed by both thermodynamics (interfacial tension) and thermo-mechanics (agitation). It is a result of the competition between the interfacial energy of the system which encourages maximum separation of components, and the external mechanical agitation imposed on it, which is to induce mixing. Agitation produces flow stresses which tend to deform and break domains. Interfacial tension opposes the deformation and break-up of domains and encourages coalescence of the dispersed phase domains when they come in close proximity. When agitation ceases the interfacial tension becomes the driving force for the system to evolve. Each phase will coalesce; minimize the total interfacial area as well as the total interfacial energy of the system. Coalescence is slow in an immiscible polymer blend but is still too fast for most practical applications. Due to the instability of the blends, the morphology of the blend depends on the conditions to which it is subjected. The morphology of an immiscible polymer blend obtained from a screw extruder may not be the same as that when the blend is injection moulded.

Immiscible polymer blends are much more interesting for commercial development since immiscibility allows to preserve the good features of each of the base polymer components of the blend. Some properties can be achieved only through immiscible polymer blends. For example the impact strength of a polymer cannot be improved significantly by adding an elastomer miscible with it. Our challenge is to develop processes or techniques that allow control of both the morphology and the interfaces of a phase separated blend. Such processes or techniques are called compatibilization. Polymer blends with intentionally modified morphology and interfaces are called compatibilized blends.

Compatibilization techniques have been inspired by colloidal science. Addition of a graft or block copolymer to an immiscible polymer blend plays the role of an emulsifier or surfactant in a water – oil emulsion. The compatibilizer has an additional role of enhancing interfacial adhesion between the two phases. Such a compatibilizer is also known as interfacial agent, emulsifier or adhesion promoter.

There are three distinct strategies for compatibilizing immiscible polymer blends.

1. Non – reactive compatibilization – by adding non – reactive block or graft copolymers.
2. Specific compatibilization – groups having specific non – bonding specific interactions are attached to polymer chains.
3. Reactive compatibilization – introducing reactive molecules capable of forming the desired co-polymer *insitu*, directly during blending.

The classical approach to compatibilizing immiscible polymer blends is the non – reactive compatibilization. A well selected copolymer having two distinct segments when introduced into an immiscible polymer blend will be located at the interphases. Each segment will penetrate to the phase with which it has specific affinity. This will reduce the interfacial tension, enhance interfacial adhesion, promote dispersion of the dispersed phase in the matrix and stabilize the morphology of the blend [30 - 34].

But this approach bears two major limitations.

1. Each immiscible polymer blend needs a specific block or graft copolymer as compatibilizer. A particular synthetic procedure is required to prepare each of them which are often tedious and costly. For a large number of immiscible polymer blends, synthetic procedures are unavailable for the preparation of block or graft copolymer.

2. The amount of block or graft copolymer to be added to a polymer blend is much higher than the required to saturate the interfaces. Due to thermodynamic and thermo mechanical reasons some of the compatibilizer added may not reach the interfaces. For the copolymers to reach the interfaces, it has to undergo melting / plasticization, dispersion, solubilisation and molecular diffusion. The copolymer has to be dispersed first in sufficiently small domains so as to be solubilised by chain entanglement and distributed as single macromolecular chains and / or micelles in the base polymer components. These solubilised macromolecular chains reach the interfaces by molecular diffusion. But the time required for this process is much higher compared to the residence time of a blend in the extruder / mixer. Therefore major problems facing non-reactive compatibilization are how to reach the compatibilizer to the interface [35].

The effectiveness of block and graft copolymers as compatibilizers have led to a revolution to devise new approaches to produce new block and graft copolymers for the purpose. The most important is the *in-situ* preparation of compatibilizer during melt blending by the use of reactive polymers. During reactive compatibilization of immiscible polymer blends three main scenarios are observed.

1. The base polymer components are mutually reactive. The reaction between components leads to the formation of a copolymer and compatibilization is straightforward. Most polycondensates are of this type with functional groups at the ends.

2. One polymer (A) bears potentially reactive groups and the other (B) is chemically inert. The non-reactive polymer is functionalized with a functional group that can react with reactive groups that can react with reactive groups on (A). This leads to a reactive copolymer (C) which reacts with the polymer (A). The compatibilizer will be of A-C type, segment A miscible with polymer A and segment C in polymer B.

3. Neither component contains reactive groups. In such cases different compatibilization methods are employed. We may add two reactive polymers C and D which are mutually reactive and are miscible with A and B respectively. The resulting copolymer will be of the type C-D. Or else we can functionalize the polymers A and B with different functional groups which react to form the copolymer [36].

The basic principle involved in non-reactive as well as reactive compatibilization is the same except that in reactive compatibilization, chemical reactions are involved in the blending process. This makes reactive compatibilization very attractive and cost effective.

1. Compatibilizers are generated directly at the interfaces during melt blending without separate synthetic and purification steps.

2. The problem of getting the compatibilizer to the interface is avoided as the compatibilizer is formed at the interface during melt blending. Thus reactive compatibilization is also called *in-situ* compatibilization or reactive blending.

3. When the desired compatibilizer cannot be synthesized directly, reactive compatibilization is the best method available.

4. The product cannot be de-engineered easily by analysis which provides an element of secrecy to the manufacturer. It is very difficult to extract and characterize the compatibilizer formed. The process can be conducted in different ways with different property outcomes for the product.

The study of reactive polymer blending involves many aspects. Polymer Chemistry and Organic Reaction Chemistry are important in the study of thermodynamics and kinetics of reactions at the interface. The flow regimes in the processing devices need to be studied. The melting and mixing processes control the formation of interfaces as well as control the resulting morphology.

Reactive polymer blending has become a very important contributor in development of new polymer materials. A wide range of commercial processing equipment is used for reactive blending. They are twin screw extruders, Farrel continuous mixers, Buss kneaders and single screw extruders. The machines should be configured to give adequate residence time so that both requisite mixing and reaction can occur. Each blend system has a unique set of processing requirements and we cannot make generalizations on equipment preferences. At present screw extruders play a dominant role in the preparation of reactively compatibilized blends.

1.4 METHODS FOR BLEND COMPATIBILIZATION

1. Addition of Block and Graft Copolymers

A compatibilization strategy used in polymer blending is the addition of a pre made block copolymer composed of blocks that are each miscible with one of the homopolymers [37]. These segments need not be identical with the blend components. According to Noolandi and Hong as well as Leibler, the block copolymers prefer to span the interface [38, 39]. The copolymer locates at the interface between immiscible polymer blend components, reducing the interfacial tension between blend components, reducing the resistance to minor phase breakup during melt mixing which reduces the size of the dispersed phase and stabilizing the dispersion against coalescence. This finer morphology and the increased interfacial adhesion result in improved physical properties.

2. Utilization of Non-Bonding Specific Interactions

Non-Bonding specific interactions like Hydrogen bonding, ion-dipole, dipole-dipole, donor-acceptor and π-electron interactions can be employed for the compatibilization of polymer blends. A large number of such interactions are available in the literature. These specific interactions are weak and high concentrations (one interacting group per repeating unit) are often required for compatibilization. Polymers capable of such interactions cannot be added only in small quantities for compatibilization of blends. The addition of large quantities of the compatibilizer may change the properties of the desired phase constituents and/or be uneconomical.

3. Reactive Compatibilization

Here the compatibilizers are formed in-situ through ionic or covalent bonding during the melt blending of suitably functionalized polymers [40 – 44].

In this type of reactive compatibilization one phase contains reactive groups inherent in the polymer, while the other has no inherent functionality. Reactive groups can be incorporated into the second phase by adding to it a functionalized polymer miscible. In some cases both phases will have to be functionalized. The *in-situ* formed copolymer compatibilizers get located at the interphase, reducing the size of the dispersed phase, improving interfacial adhesion between blend phases and the physical properties of the blends. This method has been implemented in a number of commercial products and appears to be the method of choice for compatibilization.

According to Utracki all commercial blends made from highly immiscible polymers are compatabilized reactively. A block or graft copolymer is formed by coupling of reactive groups on each of the immiscible polymers [45].

Ghijsels and Raadsen comment that there are several problems in compatibilizing multiphase structures with block copolymer in the melt. The viscosity of the block copolymers is high and thus may be difficult to disperse. Moreover these copolymers are very expensive and we have to minimize their concentration [46]. Hobbs *et al.* suggest that the block copolymer added to compatibilize the blend should prefer to lie at the interface rather than form micelles or a separate phase [47].

4. Addition of Low Molecular Weight Coupling Agents

Addition of low molecular weight coupling agents may serve the purpose of compatibilization of polymer blends through copolymer formation. A large number of reagents like bis (2-oxazolines), Peroxides and co-agents, multifunctional epoxy monomers, organo silanes, Aluminium Chloride, bismaleimide, methylene diphenylene di isocyanate etc. have been employed for this purpose.

Compatibilization of a polymer blend can be achieved by the use of low molecular weight reagents or a mixture of low molecular weight co-agents to obtain interfacial reaction between polymer components. During the process some type of graft or block copolymer is formed which plays the role of compatibilizer. When we consider a blend of two polyolefins, we have to add two different functionalized copolymers which may not produce required results. In such cases the ability of a reagent to compatibilise the polymer blend in a single reactive step would be an advantage. A free radical initiator like peroxide can promote reactions on a polyolefin chain leading to compatibilization.

1.5 COMPATIBILIZATION OF POLYOLEFIN BLENDS BY PEROXIDES

Peroxides used in a process of *in-situ* compatibilization of polyolefin blends triggers polymer modifications due to high sensitivity (reactivity) of polyolefins to free radicals. Consider a blend of polyethylene and polypropylene – two common commodity plastics. These two polymers are immiscible due to difference in their molecular structure. When such a blend is treated with peroxide, free radicals produced react in different ways with the two components. Both components form macromolecular free radicals when a molecule of hydrogen is abstracted from them. The macro radicals of polyethylene tend to combine with each other forming larger molecules. This leads to cross linking in polyethylene and the molecular weight increases. But macro radicals of polypropylene undergo reformation of molecular structure leading to β chain scission. This leads to degradation of polypropylene and molecular weight decreases [48].

When a mixture of polyethylene and polypropylene is treated with peroxides, reciprocal grafting reaction between the macromolecules is theoretically possible as below.

$$\mathrm{PE} + \mathrm{R}^* \longrightarrow \mathrm{RH} + \mathrm{PE}^*$$

$$\mathrm{PE}^* + \mathrm{PE}^* \longrightarrow \mathrm{PE}-\mathrm{PE} \quad \text{(Cross linking)}$$

$$\mathrm{PP} + \mathrm{R}^* \longrightarrow \mathrm{PP}^* + \mathrm{RH}$$

$$2\mathrm{PP}^* \longrightarrow \mathrm{PP}= + \mathrm{PP}^* \quad (\beta - \text{scission})$$

$$\mathrm{PE}^* + \mathrm{PP}^* \longrightarrow \mathrm{PE}-\mathrm{g}-\mathrm{PP} \quad \text{(Reciprocal grafting)}$$

Braun *et al.* confirmed that in a solvent containing polyethylene, polypropylene and peroxide, the free radical reaction produced a PE – g – PP copolymer and that polyethylene cross linking and polypropylene degradation were limited. But in a process of melt blending of polyethylene and polypropylene, the free radical reaction produced cross linked polyethylene and degraded polypropylene, and there was no evidence of PE – g – PP copolymer formation [49].

1.6 PREPARATION OF REACTIVE POLYMERS

A reactive group can be incorporated into a polymer chain by –

a. Incorporation into the backbone, side chain and at chain ends as a natural result of polymerization.

b. Co polymerization of monomers containing the desired reactive groups.

c. Chemical modification of pre-formed polymer through a variety of chemical reactions.

Polymerization and co polymerization offer an unlimited number of different products by variations in the architecture of the polymer and in the nature and relative amounts of co monomer units in co polymerization, they require new processes of polymerization which are less favourable industrially. Chemical modification of pre-formed polymers especially in the melt is an attractive technique which has been used extensively in technological applications.

Chemical modification of pre-formed polymers can be conducted in solution or in melt or even in solid state. The modification of polymers during melt processing has a number of advantages – it reduces the cost of solvent removal, recovery and losses and also reduces contamination of the final product. The use of an extruder as continuous reactor / processor offers additional advantages including temperature control and pumping efficiency over a wide viscosity range and also integrates several operations into a single processing device [50 – 52].

Condensation polymers have reactive groups inherent in the backbone and at chain ends like polyamides having carboxylic acid group and / or amine end groups and amide groups in the backbone, polyesters having carboxylic acid group and / or hydroxyl end groups and ester groups in the backbone. Some addition polymers contain potentially reactive groups in their side chains like carboxylic acid group in poly (acrylic acid), ester group in polyacrylates, double bonds in PB and EPDM. In many other cases the polymers need to be functionalized with suitable reactive groups. Various chemical reactions involved are –

1. Free radical catalyzed grafting of malefic anhydride, AA, GMA etc onto a variety of polymers.
2. Substitution reactions such as sulphonation and halogenation.
3. Terminal modification on both addition and condensation polymers.

Reactive polymers undergo chemical reactions seen in normal low molecular weight compounds. In polymer chemistry it is assumed that the reactivity of a functional group does not depend on the size of the molecule to which it is attached. But steric hinderance to the reaction site by the polymer backbone reduces the rate of the reaction [53]. During melt blending rate can also be reduced by the restricted diffusional mobility of the functional groups. The concentration of reactive groups used in reactive compatibilization is normally low and reaction time is short, reducing the possibility of reactive groups encountering each other in the melt for the reaction to take place. Hence to achieve successful compatibilization of polymer blends, the polymers should have sufficiently reactive functional groups; the reaction should be fast, selective and preferably irreversible; and mixing conditions should be such as to minimize mass transfer limitations to reaction. Reactions such as amidation, imidation, esterification, aminolysis, ester – ester interchange, ring opening and ionic bonding can occur at high temperatures are used in reactive compatibilization. Isocyanate and carbodiimide groups are also highly reactive during reactive compatibilization.

Maleic anhydride MAn has been used in polymer industry to promote adhesion and dyeability. It is also used extensively in reactive compatibilization of polymer blends. MAn grafted PP, PE, EPR, EPDM, SEBS etc. have been used to compatibilise a number of blends. When used for polymer blends containing polyamides, improvement in impact strength, tensile strength, permeability, heat resistance etc. are observed. The wide use of MAn functionalized polymers is that MAn can be grafted onto many polymers at normal melt processing temperatures without homo polymerization. We can also use styrene maleic anhydride SMA or MAn copolymers with SAN, ethylene and AC as compatibilizer. MAn functionalized polymers have become highly important in plastic recycling [54].

1.7 REACTIVE EXTRUSION

Today's society and polymer industry demands new properties, lower prices and reuse of polymers. Polymers or plastics are used almost by everybody at home as well as at work. The polymers commonly used are Polyethylene (PE), Polypropylene (PP), and Polystyrene (PS) which ranges to about 25% of the polymer market. These polymers can be extruded without excessive degradation when they contain little impurities. Other commonly used plastics like Polyacetals (POM) and Polyamides (PA 6, PA 66, PA 46, PA 12 and PA 11) have more problems with degradation. Usually the mechanical properties of polymer blends are poor. However research has shown that these properties can be brought back to their original level by adding an additional phase known as compatibilizer.

Polymers are either amorphous or semi-crystalline. A semi-crystalline polymer has an amorphous part and a crystalline part. The crystalline part has a more or less ordered structure where the chains of the polymer are often folded in a non-random fashion. The mechanical properties of semi-crystalline polymers are strongly determined by the crystallites which usually enhance their stiffness (for example PP). Amorphous polymers are either very brittle (PS) or very tough (PC). It is quite difficult to predict the mechanical properties of semi-crystalline polymers since they depend on many parameters such as % of crystallites.

The demands of many applications need a set of properties that no single polymer can fulfill. Rather than synthesizing new specialized polymer systems, we try to meet the demands by mixing two or more polymers. Mixing two or more polymers to get blends or alloys is a well established method to achieve certain physical properties. Well known examples of commercial blends are High Impact Polystyrene (HIPS) and Acrylonitrile – Butadiene – Styrene (ABS). These are tough and have good processability. However when polymers are mixed the blend is often brittle.

Mechanical properties of polymer blends are very important in many applications. Significant for these properties is compatibility between different polymers which is very often defined as miscibility of components on a molecular scale. A large number of miscible polymer pairs are known but only a few have been commercialized such as Polyphenyl ether/Polystyrene (PPE/PS), Polycarbonate/Polyethylene terephthalate (PC/PET), Polycarbonate/Polybutylene terephthalate (PC/PBT). Other type of blend consists of incompatible polymers for which various morphologies can be realized via processing, for instance droplets or fibers in a matrix and stratified or co-continuous structures. These are usually unstable.

Melt mixing of two polymers results in blends which are normally weak and brittle. The incorporation of a dispersed phase into a matrix mostly leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. Improvement of mechanical properties of the blend is usually done by compatibilization which means modification of normally not miscible blends to improve miscibility. The end-use performance has been improved many fold by compatibilization.

Several methods are known to improve the properties of polymers. Many polymer additives are needed to improve the properties like processability and life time (lubricants or stabilizers), modulus and strength (mineral fillers such as chalk, clay, glass beads, mica or glass fiber reinforcement), appearance and colour (pigments), conductivity (conducting fillers like aluminium flakes or carbon) or flammability (flame retardants).

A large part of studies on blending of polymers deals with attempts to obtain a combination of properties of different polymers. But the mechanical properties of blends are usually worse instead of better for many combinations of polymers. The conventional methods for the improvement of these properties are often expensive and do not always meet the required demands. In principle compatibilization is influenced by molecular weight distribution and concentration of the compatibilizer in the dispersed phase in complex ways to influence final blend properties. The best known effect of compatibilization is the reduction in interfacial tension in the melt. It causes an emulsifying effect which leads to an extremely fine dispersion of one phase in the other. A second effect is the increase in adhesion at phase boundaries giving improved stress transfer. A third effect is the inhibition of coalescence of the dispersed phase by modifying the phase boundary interface. These and other effects such as modification of rheology may occur simultaneously which complicates the ongoing of the whole process.

The complexity of interaction of the compatibilizer with the morphology of the blend was studied by Lester and Hope. They mixed HDPE with Nylon 6, Nylon 66, Nylon 6-3T and Polyethylene terephthalate PET with and without low levels of various proprietary compatibilizing agents. The study by SEM as well as tensile testing showed that finest dispersion of blend did not show highest values of ultimate elongation [55].

Barendsen *et al.* studied the compatibilization of PE/PS blend by adding (PS-g-LPDE) graft copolymer of LPDE with PS to the blends of LPDE and PS. They found that adding of 7.5% by weight copolymer caused a substantial reduction in the size of the dispersed phase [56].

It was opined by Herkens *et al.* that difference in the detailed fine structure of copolymers gave rise to large effects on the impact strength, and on the magnitude of the tensile modulus of the blends [57].

Nolley *et al.* used copolymers of propylene and ethylene (EP) displaying residual crystallinity due to long ethylene sequence as compatibilizer for polypropylene / low density polyethylene (PP/LPDE) blends. They found that the amorphous copolymer was less effective as compatibilizing agent [58]. According to Ho and Salovey (1973), a 5% addition of ethylene-propylene rubbers (EPR) to a blend of HDPE/PP was necessary to obtain a linear relation between tensile strength and composition [59].

It must also be noted that there are many examples in the literature where blends prepared from the same types of polymer behave differently. This is due to the high sensitivity of mechanical properties to variation of temperature, composition, morphology of the blend etc.

Utracki *et al.* studied the influence of addition of hydrogenated poly (styrene-b-isoprene) di-block copolymer (SEB) to a blend. [60]. Paul and Barlow independently reviewed the use of block copolymers for the compatibilization of immiscible polymer blends. Addition to PET/HDPE blends variously affected the different physical properties, modulus and yield strength. Addition of block copolymers of the same chemical nature as the two homopolymers of a blend in an obvious choice which when optimized will lead to enhancement of properties [61, 62].

Shilov *et al.* analysed the composition of an immiscible polymer blend as a function of linear dimensions. Between a domain of polymer A and a domain of polymer B exists as interfacial layer, in some cases having a thickness up to 4nm. This interfacial region can be considered as a third phase which has been stabilized in many commercial polymer alloys through selective cross linking, resulting in reproducibility of performance, processability and recyclability. The thickness of this layer depends on thermodynamic interaction, macro molecular segment size, concentration and phase conditions. The interfacial tension and the domain adhesion characterize the interface. The interfacial tension in the integral of the Helmholtz free energy change across the interface which gradually changes over the interfacial area from phase A to B, due to a changing composition of the third phase between both phases [63].

Mixing of two or more polymers to produce blends or alloys in a well known method for achieving a specific combination of physical properties. Mixing means break up of droplets of one polymer to obtain a dispersed phase with a very small size another polymer. This type of mixing is called blending and if the mixture formed has improved mechanical properties, it is called compounding [64].

Blending of polymers became increasingly important after Taylor studied break-up phenomena in liquids [65]. Normally, blending is used to combine the properties of two or more polymers and is performed in extruders. But the material properties are not as good as expected due to poor interfacial adhesion between the minor and major components. Hence we have to look for ways for improving the mechanical properties of such blends.

Polymers are often referred to as compatible if the mechanical properties of blends made by mixing them will have a certain set of required values. This could mean that the blend in strong enough, tough enough or ductile enough. Compatibility is often referred to as miscibility on a molecular scale. The polymer blend is compatible – if the mixture is stable under the normal conditions for its use and nom de-mixing should occur, the dispersed phase has a strong bonding to the surrounding polymer. Adhesion between both phases in a blend can be achieved by addition of a compatibilizer. The compatibilizer is transported to the interface of the dispersed phase by means of mixing and it decreases the interfacial energy.

The morphology of the blends after blending as a function of material and processing parameters have been studied using scanning electron microscopy [66,67].

In reactive compounding chemical bonds are created across the interface. This is generally done by functionalizing one of the components with reactive groups. The method most commonly used is introduction of carboxylic acids and anhydrides on non reactive polymers by means of radically induced graft reaction. These groups react with existing reactive sites of the other component. As an alternate method, both components can be functionalized with mutually reactive sites [68, 69].

The influence of the addition of the monomer and initiator on the morphology of the blend has been investigated. The order in which the reactive media like monomers and initiators are fed during the reactive compounding in extruders is shown to have very distinct influence on the morphology of the dispersed phase and therefore on the material properties [70].

Blom *et al.* reported that PP & HDPE are incompatible and immiscible and that the latter caused deterioration in the elongation at break and impact strengths [71]. Yu *et al.* showed that in the case of gross viscosity mismatch of polymer blends, peroxides can reduce the viscosity of the PP phase by chain scission and increase the viscosity of HDPE phase by cross linking [72].

Stehling *et al.* as well as Choudhary *et al.* showed that a block copolymer of the two homo polymers in the blend can act as compatibilizer of HDPE / PP blend. They used ethylene propylene rubber as compatibilizer for HDPE / PP blends to success [73, 74].

According to Gupta *et al.* EVA is partially compatible with PP. Fang *et al.* found that EVA is partially compatible with HDPE. Blom *et al.* used EVA & EPDM as compatibilizer for HDPE/PP blend and found that EVA improved the impact properties of the blend while EPDM improved the tensile properties [75 – 77].

According to Blom *et al.* compatibilization of iPP / HDPE blend by EPDM or EVA improved the Charpy impact strength and tensile properties [78].

A significant portion of HDPE in the market finds its way into blow moulding applications like milk jugs, water jugs and detergent bottles. When attempts are made to recycle them, a problem arises due to contamination from PP. The presence of excessive amounts of PP will lead to poor mechanical properties of the recycled HDPE and it makes the manufacture of durable articles difficult [79].

Deanin and Sansone (1978), Lovinger and Williams as well as Bartlett *et al.* (1982) reported that the addition of PP to HDPE resulted in a decrease in impact strength and elongation at break [80 – 82].

The recycling of industrial plastics has been an ongoing practice in many industries. More recently environmental, legislative and consumer pressures have led to an increase in research directed towards the recycling of post consumer plastic waste. Industrial scrap is relatively easy to deal with since contamination is unlikely. This is not true for municipal waste which is a mixture of several polymers which makes processing difficult and limits the number of potential applications.

A number of approaches are currently being investigated for dealing with post consumer resin PCR. A number of countries employ incinerators for the purpose of waste-to-energy recovery. Another solution is pyrolysis. Many manufacturers are introducing plastic waste into hydro crackers which convert the polymers to syncrude or naphtha used as feed stock for other applications including polymerization. Yet another approach is the redn of plastic required in articles like packages by down gauging. Many materials and goods are being reused. Lastly there is the approach of converting municipal wastes into resins which can be used to make new articles. For example, HDPE bottles for milk and water are reground and used to make oil and household chemical containers. Shopping bags are being used to make trash bags and lawn bags to collect waste.

Very often the material that emerges from a recycling facility is a blend of two or more homopolymers. This is due to several factors like not sorting the material being recycled and the fact that most articles are constructed from two or more different homopolymers.

Nearly all polymer pairs are immiscible and incompatible. This results in materials which have poor mech properties and undergo phase separation. Consequently these materials cannot beused alone or unmodified but need to be compatabilized in some way [83].

1.8 EXTRUDER AS REACTOR

Carrying out reactions / processes with polymeric materials whose viscosities are typically in the range of 10 to 10000 Pa's is generally not possible in conventional chemical reactors. Extruders offer some attractive features which can be used to advantage.

1. Ease of melt feed preparation
2. Excellent dispersive and distributive mixing
3. Temperature control
4. Control over residence time distribution
5. Reaction under pressure
6. Continuous processing
7. Staging
8. Unreacted monomer and by-product removal
9. Post reaction modification
10. Viscous melt discharge

But in broader application of extruders for processing we come across the following limitations.

1. Difficulty in handling large heats of reaction.
2. High cost for long reaction time.

For reactive extrusion in a single screw extruder, the basic feed is in the solid form. Reaction is unlikely to occur until the polymer has melted. The initial portions of the extruder would be devoted to solids feed transport and melting. The requirements for this initial section are the same as for conventional compounding. After melting, contact of the polymer melt with the reactants may take place in either completely filled channels or in partially starved ones. After reaction and possibly de-volatilization, the product will likely require a pressure generation step for extrusion.

In all extruders, the melt is dragged along the barrel by the rotation of the screws. The drag mechanism is usually best visualized by unwrapping the screw flight as a continuous straight stationary channel, and sliding the barrel in relative motion diagonally over the top of the channel. As noted the extruder is also used to generate pressure to force the viscous melt through some shaping element, such as a sheet or strand die. The pressure required for extrusion also causes a back flow back down the channel. When operated starved, the flight is filled in proportion to the ratio of the actual net flow to the potential drag flow. The melt is somewhat in the form of a rolling bead. Bubbles may be present even in the absence of de-volatilization as the rolling bead induces both entrapment and rupture. Staging between starved zones can be affected by reducing the channel depth of the screw such that complete filling is assured. [84].

Hu *et al.* performed grafting of PP with GMA and blending with PBT in a one step extrusion. The mechanical properties of resulting blends were superior compared to the uncompatabilized blend [85].

Lovinger and Williams studied the relationship between the morphology and tensile properties of HDPE / PP blends. They found that an increase in the stress at yield and ultimate stress was related to a size reduction of spherulites, an increase in crystallinity and the foaming of permeating network. They also reported that the ultimate elongation of all the HDPE / PP blends was lower than that of neat polymers because of the incompatibility of HDPE and PP. The tensile strength at yield increased gradually with increasing PP content.

Similar blend systems have reported different mechanical behaviour. Linear additive properties of pure PE and PP in the modulus and yield stress were observed in HDPE – PP blends by some authors, while others reported a large positive deviation or negative deviation from linearity. The synergism in the modulus and yield stress has been attributed to a reduction in the average spherulite size of PP and an increase in the overall crystallinity introduced by the addition of PE and an increase in tie molecules or intercrystalline links observed by SEM [86].

Negative deviation can be ascribed to the loss of cohesion of the immiscible inclusions in a matrix. It has also been postulated that a small amount of PE may decrease the PP matrix plasticity, and the PE has a marked reinforcing effect resulting in a delay in neck formation and hence an increase in yield stress. Elongation at break has been found to be markedly decreased for the blends compared with homopolymers. [87].

Gahleitner reported that the melt flow rate was related to the weight average molecular weight M_w and molecular weight distribution (ratio M_w / M_n), which can influence the Charpy impact test. When M_w and M_w / M_n increased, the melt flow rate decreased and Charpy impact strength increased [88].

Fellahi *et al.* could improve the stress at break and the impact strength of mixed plastics simply by processing it in the presence of dialkyl peroxide. These improvements are like due to the formation of copolymers acting as compatibilizer by recombination of macro radicals [89].

The deleterious effect of blending on impact strength can be overcome by the creation of a microcellular structure in HDPE / PP blends. The production of a microcellular structure in the blends strongly depended on the blending conditions and the viscoelastic behaviour of the blends which controlled the cell growth and density reduction. For improved impact strength, the cell morphology had to consist of a well developed, uniform microcellular structure which was achieved by foaming at a relatively higher temperature (175°C) for a longer time (30s) with appropriate blend ratios (50 : 50 and 30 : 70 W/W HDPE/PP). The blend with highest HDPE content (70 : 30 W/W HDPE/PP) had poor morphology as the matrix was too soft, causing cell coalescence [90].

1.9 POLYMER COMPOSITES

This radically new class of materials is characterized by the marriage of quite diverse individual components that work together to produce capabilities that far exceed those of their separate elements. Their unique properties make them the enabling materials for major technological advances.

Typically, advanced materials have been characterized by a lengthy development cycle (20 years) [91]. Today the use of composite materials in structures of all kinds is accelerating rapidly in the aerospace industry where the use of composites has directly enhanced the capability of fuel efficient aircraft in the commercial arena and new generation aircraft in the military sphere. The increasing usage of these materials is spreading worldwide, capitalizing on developments that were the direct result of a large investment in the technology over the last two or more decades.

Composites are the result of embedding high-strength, high-stiffness fibers of one material in a surrounding matrix of another material. The fibers of interest for composites are generally in the form of single fibers about the thickness of human hair or multiple fibers twisted together in the form of a yarn or tow. When properly produced, these fibers- usually of a nonmetallic material can have very high values of strength and stiffness. In addition to continuous fibers, there are also varieties of short fibers, whiskers, platelets and particulates intended for use in discontinuous reinforced composites.

Fiber-reinforced composite materials consist of fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces (boundaries) between them. In this form, both fibers and matrix retain their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents acting alone. The fibers are the principal load carrying members, whereas the surrounding matrix keeps them in the desired location and orientation, acts as a load transfer medium between them and protects them from environmental damaged due to elevated temperature or humidity, for example. Even though the fibers provide reinforcement for the matrix, the latter also serves a number of useful functions in a fiber-reinforcement composite material.

Fibers can be incorporated into a matrix either in continuous lengths or in discontinuous (chopped) lengths. The matrix material may be a polymer, a metal or a ceramic. Various chemical combinations, compositions, and micro structural arrangements are possible in each matrix category.

The most common form in which fiber-reinforced composites are used in structural applications is called a laminate. Laminates are obtained by stacking a number of thin layers of fibers and matrix and consolidating them to the desired thickness. Fiber orientation in each layer, as well as the stacking sequence of various layers can be controlled to generate a wide range of physical and mechanical properties for the composite laminate.

Whereas the high properties of the fibres are in part a result of their being in fiber form, as fibers they are not useful from a practical point of view. The key to taking advantage of their uniquely high properties is to embed them in a surrounding matrix of another material. The matrix acts as a support for the fibers, transports applied loads to the fibers, and is capable of being formed into useful structural shapes. The right kind of matrix can also provide ductility and toughness properties that the much more brittle fibers do not possess. The term advanced composites is used to differentiate those with high performance characteristics, generally strength and stiffness, from the simpler forms like reinforced plastic.

The development of any composite requires balancing many factors, including performance, fabrication speed and total cost. With high performance materials, the desire for improved properties is the dominant requirement. For many applications, however, better performance, although desirable, is not the primary need. In fact materials may already be available with properties that meet or even exceed the performance requirements. Instead the problem is to produce parts at sufficient speeds and low enough costs to obtain them cost-effectively. For lack of a better term, such composites can be called cost-performance materials.

Industry representatives believe that they must harness the chemical and physical changes that occur during fabrication to the extent that is required for the processes to be optimized and controlled. Consequently, processing science and on-line process control are key issues for the future.

1.10 COMPOSITES AND THEIR HISTORY

Modern structural composites are blends of two or more materials, one of which is composed of stiff, long fibers and, for polymeric composites, a resinous binder or matrix that holds the fibers in place. The fiber is strong and stiff relative to the matrix and generally it is orthotropic. For advanced structural composites, the fiber is long, with a length-to-diameter ratio of over 100. The strength and stiffness of the fiber are much greater perhaps multiples of those of the matrix material. When the fiber and the matrix are joined to form a composite, they both retain their individual identities and both influence the composite's final properties directly. The resulting composite consists of layers or laminas of fibers and matrix stacked in such a way as to achieve the desired properties in one or more directions.

Modern composite materials evolved from the simplest mixtures of two or more materials to obtain a property that was not there before. The bible mentions the combining of straw with mud to make bricks.

The increases in consumption of composite materials were primarily due to the need for nonconductive electrical components, noncorroding and non-corrosive storage containers and transfer lines, and sporting goods. The technologies for matrices and for the fabrication of useful structures with stronger fiber reinforcement were commercialized in the two decades after 1970. Along with the new fibers, new matrices were developed, and new commercial fabrication techniques were introduced. These developments were due in part to military aircraft designers who were quick to realize that these materials could increase the speed, maneuverability, or range of an aircraft by lowering the weight of its substructures.

1.11 ADVANTAGES OF COMPOSITES

Designers of structures have been quick to capitalize on the high strength-to-weight or modulus-to-weight ratios of composites. The advantages include

- Weight reduction (high strength or stiffness-to-weight ratio)
- Tailorable properties (strength or stiffness can be tailored to be in the load direction)
- Redundant load paths (fiber to fiber)
- Longer life (no corrosion)
- Lower manufacturing costs because of lower part count

- Inherent damping
- Increased (or decreased) thermal or electric conductivity.

The disadvantages include

- Cost of raw materials and fabrication
- Possible weakness of transverse properties
- Weak matrix and low toughness
- Environmental degradation of matrix
- Difficulty in attaching
- Difficulty with analysis.

Generally the advantages accrue for any fiber composite combination, whereas the disadvantages are more obvious with certain combinations. Proper design and material selection can avoid many of the disadvantages.

1.12 GENERAL CHARACTERISTICS OF COMPOSITES

Many fiber-reinforced composite materials offer a combination of strength and modulus that is either comparable to or better than of many traditional metallic materials. Because of their low specific gravity, the strength/weight ratios and modulus/weight ratios of these composite materials are markedly superior to those of metallic materials. In addition, fatigue strength-to-weight ratios, as well as fatigue damage tolerances, of many composite laminates are excellent.

The properties of a fiber-reinforced composite depend strongly on the direction of measurement. For example, the tensile strength and modulus of a unidirectionally oriented fiber-reinforced laminate are maximum when these properties are measured in the longitudinal direction of the fibers. At any other angle of measurement, these properties are lower. The minimum value is observed at 90^0 to the longitudinal direction. Similar angular dependence is observed for other physical and mechanical properties, such as coefficient of thermal expansion (CTE), thermal conductivity, and impact strength. Bi- or multidirectional reinforcement, either in the planar form or in the laminated construction, yields are more balanced set of properties. Although these properties are lower than the longitudinal properties of a unidirectional composite, they will represent a considerable advantage over common structural materials on a unit weight basis.

The anisotropic nature of a fiber-reinforced composite material creates a unique property for tailoring its properties according to the design requirements. This design flexibility can be utilized to selectively reinforce a structure in the directions of major stresses, increase its stiffness in a preferred direction, fabricate curved panels without any secondary forming operation, or produce structures with zero CTEs.

Most fiber-reinforced composites are elastic in their tensile stress-strain characteristics. However the heterogeneous nature of these materials provides mechanisms for high energy absorption on a microscopic scale comparable to the yielding process. Depending on the type and severity of the external loads, a composite laminate may exhibit gradual deterioration in properties but usually does not fail in a catastrophic manner.

Another unique characteristic of many fiber-reinforced composites is their high internal damping. This leads to better vibrational energy absorption within the material and results in reduced transmission of noise and vibrations to neighboring structures. The high damping capacity of composite materials can be beneficial in many automotive applications in which noise, vibration and harshness are critical issues for passenger comfort. CTEs for many fiber reinforced composites are much lower than those of metals. As a result, composite structures may exhibit a better dimensional stability over a wide temperature range. However the differences in thermal expansion between metals and composite materials may create undue thermal stresses when the materials are used in conjunction, for example near an attachment.

Many polymeric matrix composites are capable of absorbing moisture from the surrounding environment, which creates dimensional changes as well as adverse internal stresses within the material. If such behaviour is undesirable in an application, the composite surface must be protected from moisture diffusion by appropriate paints or coatings. Environmental factors that may cause degradation in the mechanical properties of some polymer matrix composites are elevated temperature, elevated fluids, ultra-violet rays. Oxidation of the matrix as well as adverse chemical reactions between the fibers and matrix are of great concern at high-temperature applications [92].

Most materials used in structural applications are polymers, metals, or ceramics, and in many present applications these materials perform satisfactorily in their unmodified or unreinforced form. In many applications where performance is the controlling factor, advanced structural materials are needed that are stronger, stiffer, lighter in weight and more resistant to hostile environments. Unreinforced, the polymer, metal and ceramic materials available today cannot meet many of these requirements. This is especially true if the structural component must be exposed to extremely high temperatures for extended periods of time.

Natural fibers such as cotton and wool are some of the oldest materials used by early humans when strength and light weight were critical. With the development of analytical techniques such as x-ray diffraction, the reasons for the unusual properties of materials in fiber form have been understood. The molecules within fibers tend to align along the fiber axis. This preferred alignment makes the strength and modulus (stiffness) of both natural fibers and synthetic fibers superior to those of the same material in a randomly oriented bulk form. When both natural and synthetic polymers are extruded and/or drawn into fiber form, the processes of extrusion and extension orient the structure along the fiber axis. This results in high strength and increased stiffness for much the same reason that an oriented mass of strings (a rope) is stronger and stiffer than the same mass of strings with no orientation.

Unfortunately, the increased tensile strength of fibers does not come without a penalty. Fibers like rope, display this increased strength only when the load is applied parallel to the fiber axis. Even though the tensile strength parallel to the fiber axis increases as the orientation and structure become more perfect in the fiber direction, this same increase causes a decrease in strength perpendicular to the fiber axis. Also as the orientation of a fiber increases, it often becomes brittle, making it more susceptible to damage by abrasion. Thus, to take advantage of the high strength of fibrous materials in a structure the fibers must be oriented in the direction of the applied load and separated to prevent damage by abrasion.

Mechanical reinforcement of matrices can also be accomplished by using short, randomly oriented fibers, crystal whiskers or particulates. These types of reinforcement offer directionally independent (isotropic) reinforcement, but the degree of reinforcement is not as great as that obtainable from longer continuous-filament fibers.

The major classes of structural composites that exist today can be categorized as polymer matrix composites (PMCs), metal matrix composites (MMC), ceramic matrix composites (CMC), carbon-carbon composites (CCC), inter metallic composites and hybrid composites [93, 94].

Polymer matrix composites are the most developed class of composite materials. They have found widespread applications as they can be fabricated into large complex shapes and have been accepted in a variety of aerospace and commercial applications. They are constructed of components such as carbon or boron fibres bound together by an organic polymer matrix. These reinforced plastics are a synergistic combination of high-performance fibres and matrices. The fibre provides the high strength and modulus while the matrix spread the load as well as offering resistance to weathering and corrosion [95].

Long fibre thermoplastic composites can be divided into three categories. The first is a family of long-and-short fibre materials suitable for injection moulding. Typically, the reinforcement is longer than 6.3 mm but less than 25.4 mm long in the compounded pellets. This result in injection moulded parts with fibre length distributions in the range 2 – 10 times greater than those obtained with the conventional short fibre process. The second category is a class of materials with discontinuous fibres in which the reinforcement length is at least 12.7 mm in the final moulded part. Such composites are based on chopped fibres, chopped strand mat and non-woven fibres. The third class is based on continuous fibre reinforcements, including continuous fibre non-woven as well as woven materials, preimpregnated tapes and preimpregnated or in situ impregnated continuous fibres suitable for filament winding or pultrusion processes [96].

1.13 SCOPE AND OBJECTIVES OF THE PRESENT WORK

The total consumption of plastic like polyethylenes and polypropylene has increased many fold due to their versatile nature during the last decade. A great amount of plastic waste is generated which causes environmental pollution. Due to the immiscible nature of the materials, the blend obtained by recycling the plastic waste has inferior properties – lower tensile properties and impact performance. The literature survey projects the fact that their performance can be improved by the addition of block and graft copolymers, utilization of non-bonding type of interactions, reactive compatibilization and addition of low molecular weight coupling agents. But these methods require large amounts of such reagents to be added.

The blends of commodity plastics are modified in order to upgrade their performance to the grade of engineering plastics in order to develop economically attractive replacements for engineering plastics for the use

In specific applications. In this work we propose to modify blends of HDPE & PP by adding dicumyl peroxide in order to use the blends as matrix for composite preparation. The unmodified and modified blends are proposed to be processed by reactive extrusion as well as injection moulding at two different temperatures to study the effect of the modifier, processing route and processing temperature on the blends prepared. The mechanical, flexural, impact, rheologicacal and thermal properties of the blends are proposed to be studied in order to characterize them and the fracture surfaces are proposed to be investigated by using scanning electron microscope. The literature survey indicates that a variety of short fibre and long fibre composites have been prepared based on HDPE and PP. while the short fibre composites do not show much improvement in properties, the long fibre composites are plagued by the problem of waviness. Hence we propose to use woven nylon mats as reinforcement for developing composites based on unmodified and modified HDPE/PP blends. The mechanical, flexural, impact and thermal properties of the composites are proposed to be studied in order to characterize them. The composites prepared are proposed to be recycled and the mechanical properties of the recycled material are also proposed to be studied.

The specific objectives of this study are

1. To prepare blends of HDPE and PP and to determine their mechanical, thermal and rheological properties.
2. To upgrade the performance of such blends by modification with dicumyl peroxide and to study the mechanical, thermal and rheological properties of the modified blends
3. To investigate the effect of different processing routes on unmodified and modified HDPE/PP blends.

4. To generate recyclable composites based on unmodified and modified HDPE/PP blends and to investigate their mechanical and thermal properties.
5. To investigate the recyclability of such composites.

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CHAPTER 2

MATERIALS AND METHODS

2.1 POLYMERS

Polypropylene homopolymer (PP) (REPOL H 200 MA) with a melt flow index of 20g/10min was supplied by Reliance Industries Ltd. High Density Polyethylene (HDPE) (HD 50 MA 180) with a melt flow index of 18g/10min was supplied by Indian Petrochemicals Ltd. Nylon mesh of different fiber diameter were procured from the open market.

2.2 CHEMICALS

Dicumyl peroxide (DCP – 97% active) used as low molecular weight reagent for blend compatibilization was supplied by M/s FLUKA LABS, Germany. Maleic Anhydride used for grafting was supplied by LOBA CHEMICALS, Bombay.

2.3 BLEND PREPARATION

HDPE and PP granules were placed in an air oven set at 100°C for 4 hours to remove any moisture present and allowed to cool to room temperature in a desicator. Four blend compositions were selected namely 80% HDPE/20% PP; 60% HDPE/40% PP; 40% HDPE/60% PP and 20% HDPE/80% PP and the granules were weighed out. Each mixture was melt blended either with or without the DCP. DCP was added at different amounts to give 0.1, 0.2, 0.3, 0.4 and 0.5phr respectively. The granules were fed into the mixing chamber of a Thermo Haake Rheomix 600P blender set at 180°C. The blender is fitted with Roller Rotor blades counter rotating at 3:2 speed ratio made to rotate at 30 rpm. When the granules melted, the torque reading became steady and DCP was added. A mixing time of 5 minutes was allowed to complete the reaction. During this time the torque would become steady. The hot polymer blend taken out from the mixing chamber was passed through a laboratory size two roll mill. The sheet form so obtained was cut to small pieces and subjected to extrusion in a Thermo Haake Rheomex 252P extruder or subjected to injection moulding in a semiautomatic plunger type injection moulding machine.

Thermo Haake has a mother unit Thermo Haake Rheocord 300P. It is fitted with a motor of 4kW capacity and can work at a speed up to 250rpm. The blending can be done up to a torque of 300Nm. The blender has a mixing chamber of capacity 120cm^3 without the rotors and 69cm^3 with the rotors. The rotors are Roller Rotor type and work counter rotating. The mixing chamber is provided with three separate heaters and can be heated to a temperature of 450°C and the rotors can handle a torque of 160Nm. The best mixing efficiency is obtained when the mixing chamber is about 70% filled. If the melt density of the test substance is known we can determine the sample weight as follows

$$\text{Sample weight} = \text{melt density} \times \text{chamber volume} \times 0.7$$

$$= \text{melt density} \times 69 \times 0.7$$

A sample weight of 40g was chosen for each mixing.

The cut samples from the blender are fed into a Thermo Haake Rheomex 252P extruder connected to Thermo Haake Rheocord. The extruder has a cylinder of diameter 19.05mm with an effective cylinder length 25 x D. The cylinder has 3 heating zones and can be heated up to 450°C. The cylinder can withstand a pressure of up to 700 bars. In our experiment the barrel temperature is set as 160°C – 170°C – 180°C and the temperature at the die head was 180°C. The die used is ribbon type with a width of 50mm and opening of 0.5mm. The extrudate is led away on a conveyer belt and tensile samples were cut out as per ASTM norms.

2.4 MECHANICAL PROPERTIES

2.4.1 Tensile Properties

The tensile properties were determined as per ASTM D 638. The dumb bell shaped samples were tested on a Shimadzu AG 1 Universal Testing Machine with a load cell of capacity 50kN. The jaws of the UTM were placed 40mm apart for all measurements and moved at a cross head speed of 50mm/min. At least six samples were used for each data point. The observations were made to compare tensile strength, elongation at break and tensile modulus.

2.4.2 Flexural Properties

The flexural properties of the injection moulded samples were measured on a Shimadzu AG 1 Universal Testing Machine with a load cell of capacity 50kN as per ASTM D 790. The cross head speed was 5mm/min. Specimen of 1/8" x 1/2" x 5" is placed on two supports and a load is applied at the center. The load at yield is the sample material's flexural strength. The observations were made to compare flexural strength, flexural strain and flexural modulus.

The sample to be tested was placed on a Shimadzu Autograph AG I Universal Testing Machine fitted with a 50 kg load cell and the load allowed to move at a speed of 5mm / min. the flexural stress – strain response of the sample was observed and the flexural stress, flexural strain and flexural modulus determined.

2.4.3 Impact Strength

The Izod impact strength of the injection moulded samples was measured using CEAST RESIL Impactor. The hammer of energy 4J traverses at a speed of 3.46 m/s and hits the sample. The energy required to break the sample is noted and impact strength calculated.

2.5 THERMAL BEHAVIOUR

2.5.1 Thermogravimetric Analysis (TGA)

The thermal stability of the blends was investigated using TGA and derivative thermo gravimetry (DTA). The instrument TGA Q 50 of TA Instruments was used for the study. The material was heated from room temperature to 800°C. The heating rate was 20°C/min. The temperature at which the decomposition rate is maximum, the highest rate of decomposition, time for 50% decomposition of sample and the amount of residue were noted. The test was conducted using samples weighing 10 – 12mg, nitrogen gas was used to purge the heating chamber.

2.5.2 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analyzer Q800 of TA Instruments was used for the study. Rectangular samples of specification 50mm length, 12mm breadth and 3mm thickness were used for the analysis. The analysis was made in dual cantilever mode with a constant frequency of 1 Hz. The temperature ramp was run from 30°C - 140°C at a rate of 3°C/min. The Loss Modulus, Storage Modulus and the mechanical damping (tan δ) were measured fixed dynamic analysis technique.

2.5.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry DSC Q 100 (TA Instruments) was employed to study the crystallization characteristics of the polymer blends. Indium was used for temperature calibration (T_m = 156.6°C and $\Delta H_m = 28.4\ Jg^{-1}$). All samples were dried prior to the measurements. The analysis were done in an atmosphere of nitrogen in aluminium pans. Samples were exposed to temperature scans at a rate of 20°C per minute to 200°C and then cooling to 50°C at the same rate.

2.6 MELT RHEOLOGY

2.6.1 Melt Flow Measurements

The melt flow measurements were carried out on a capillary rheometer connected to a Shimadzu AG 1 Universal Testing Machine with a load cell of capacity 50kN. The plunger was set to move at six set speeds ranging from 1 – 500mm/min. A capillary made of tungsten carbide with a capillary of length 40mm and diameter 1mm (L/D ratio = 40) was placed inside the barrel at an angle of entry 90°. The material was loaded in the barrel of the rheometer and allowed to melt. The melt was then forced through the capillary by the moving plunger. The initial position of the plunger was kept constant during all measurements. The shear viscosities at six different shear rates were obtained from a single charge of the material. The measurements were carried out at three different temperatures 170°C, 180°C and 190°C.

Shear stress is calculated using the relation,

$$\tau_w = P\ R / 2\ l$$

where τ_w is shear stress, P is the pressure drop at the wall, R is the radius of the capillary and l is the length of the capillary.

Shear rate at the wall was calculated using the equation,

$$\gamma_w = 32\ Q / \pi\ d^3$$

where γ_w is the shear rate, Q is the volumetric flow rate ($mm^3\ s^{-1}$) and d is the diameter of the capillary used.

Viscosity of the melt is calculated using the relation

$$\eta = \tau_w / \gamma_w.$$

2.6.2 Die Swell Studies

The extrudate from the capillary rheometer were carefully collected taking care that no deformation of extrudate took place. This was done at all six shear rates in each case. The samples were allowed to cool and the diameter of the extrudate was measured after 24 hours using a traveling microscope. The die swell ratio was determined according to the ratio,

Die swell ratio = Diameter of the extrudate/Diameter of the capillary

$$= (d_e)/(d_c)$$

2.7 COMPOSITE PREPARATION

80% HDPE/20% PP as well as 20% HDPE/ 80% PP blends were prepared using Thermo Haake Rheomix blender. The hot molten blend from the blender was pressed between metal plates in a hydraulic press to make them into sheets. The blends were modified with dicumyl peroxide (0.3 phr) as well as with maleic anhydride (5 phr) in presence of dicumyl peroxide (0.3 phr) and converted to sheets. The sheets were cut to 100 mm x 100 mm size and nylon fibre in mesh form of different fibre size [Mat A = 0.2 mm; Mat B = 0.4 mm and Mat C = 0.6 mm diameter] were placed between two such sheets. The material was placed in a previously heated mould and placed into a hydraulic press heated to 180°C. Pressure was applied to remove excess polymer and then the mould was allowed to cool. The composite sheets were taken out and cut as per specification for further studies.

2.8 MORPHOLOGICAL STUDIES

The morphology of the tensile fracture surface of the blends as well as composites was studied with the help of JEOL JSM 840A Scanning Electron Microscope. The specimens were mounted on a metallic stub with the help of a conducting carbon tape and placed in a JEOL – 1100E ion sputtering device and gold sputtered for 6 minutes at an ion current of 10 mA. The samples were placed inside the scanning microscope and an electron beam was made to fall on the fractured surface. A secondary electron detector was used which operated at 20 kV. The imaging was done at 1000x magnification for blends and 750x magnification for the composites.

CHAPTER 3

MECHANICAL PROPERTIES OF UNMODIFIED AND MODIFIED HDPE/PP BLENDS

3.1 INTRODUCTION

During the first half of the 20th century, one of the most interesting developments was the discovery of synthetic polymers. This was based on the new understanding of polymer synthesis and the commercialization of economic manufacturing methods making use of a wide range of monomers. The polymers commonly used now were developed in early 1950's and by 1970 most of the known monomers were exploited for polymer synthesis.

Polymers are classified on the basis of their application as commodity plastics [PP, PE's, PS and PVC], technical plastics [PC, PBT, PET, PA, ASA, SAN, PMMA, PUR etc] and high-performance plastics [LCP, PEEK, PEI, PPS, PAR, PES etc]. A study conducted by the plastic industry in 1975 showed that by the year 1995, high-performance plastics will occupy about 50% of market share of polymer industry and commodity plastics and technical plastics will account for 10% and 40% respectively. But the true picture of 1995 was entirely different. Commodity plastics were worth 81% of the polymer market while high-performance plastics accounted only for 0.25%. This was due to the fact that the commodity plastics were modified to meet the high-performance needs expected from technical and speciality plastics. This shows the growing importance of commodity plastics in the years to come.

During the same period polymer blending industry flourished. It was gradually accepted that new monomers were less likely and scientists began to think about combining the existing polymers. This was due to the fact that most of the monomers could not be co-polymerized to get a product of intermediate property, but their polymers could be melt mixed to a polymer blend of intermediate property. The composition of the blend could be varied so as to obtain a blend of desired properties.

But most of the polymer pairs are immiscible and incompatible which results in poor mechanical properties. The properties of the polymer blends can be improved by adding several classes of modifiers. Dicumyl peroxide [DCP] is a widely used modifier in HDPE and PP for optimization of mechanical, thermal and rheological properties of these polymers. Use of DCP as a modifier to optimize the mechanical properties of HDPE/PP blends is proposed to be investigated in this chapter.

3A.TENSILE STRENGTH OF EXTRUDED AND INJECTION MOULDED SAMPLES

3A.1 EXPERIMENTAL

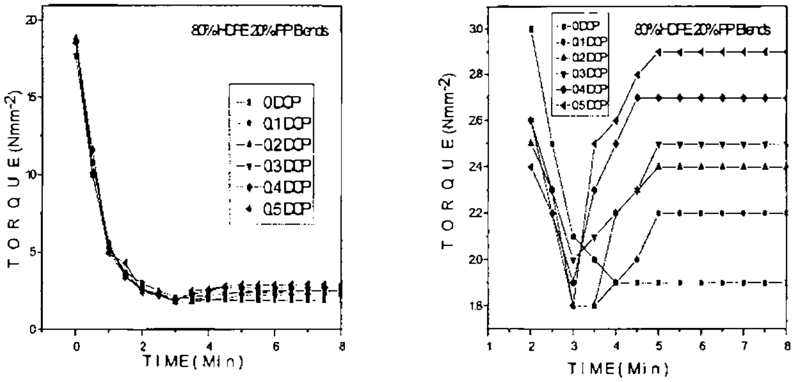
Blends of HDPE and PP were prepared in the composition of 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP. The blends were prepared by melt mixing the two polymers in the above composition using a Rheomix 600P attached to Thermo Haake Rheocord 300 set at a chamber temperature of.180°C. The rotor speed was set at 30rpm. Each mixture was treated with the modifier at different concentration levels. The modifier concentrations used were 0.1, 0.2, 0.3, 0.4 and 0.5phr. The torque-time curves for melt mixing of different polymer mixtures with different DCP concentration were taken and plotted. A mixing time of 8minutes was fixed since the torque became steady within that time interval. The experiment was repeated at 170°C.

The blends so obtained were subjected to extrusion in a Rheomex 252P extruder connected to Thermo Haake Rheocord 300 at 170°C and 180°C. The extrudate was cut when hot to obtain dumb bell specimens which were cooled and used to study the mechanical properties. The blends were also injection moulded at 170°C and 180°C using a semi automatic injection moulding machine to obtain dumb bell specimens which were used to study the tensile properties.

3A.2 RESULTS AND DISCUSSION

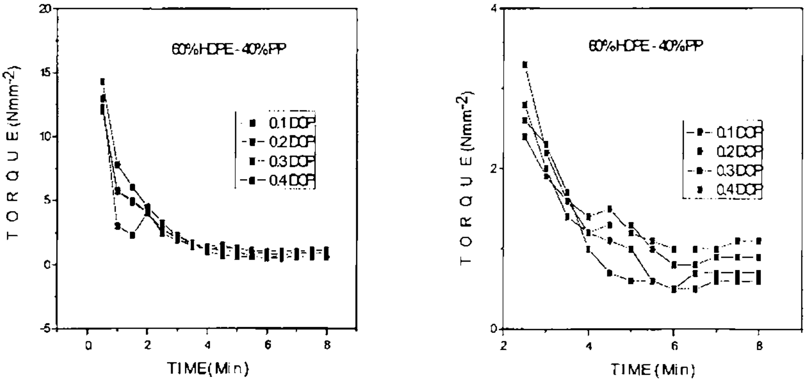
3A.2.1. Torque studies

Fig 3.1 [A] shows the Torque-Time mixing curves of unmodified and modified 80% HDPE/20% PP blends at various modifier concentrations. The initial torque for the mixture is found to be high which decreases and become steady within 3 minutes when the modifier is added. The initial high value of the torque is due to the solid nature of the polymers which becomes soft on heating. In the case of HDPE rich blends a slight increase in torque is observed on the addition of modifier and the value becomes steady at a higher value than that of the blend alone [Fig..3.1& 3.2 A & B]. This indicates that the modifier induces cross-linking in the blend. In the case of PP rich blends the reverse trend is observed which shows that the modifier induces chain scission in such blends [Fig.3.3 & 3.4 A & B].



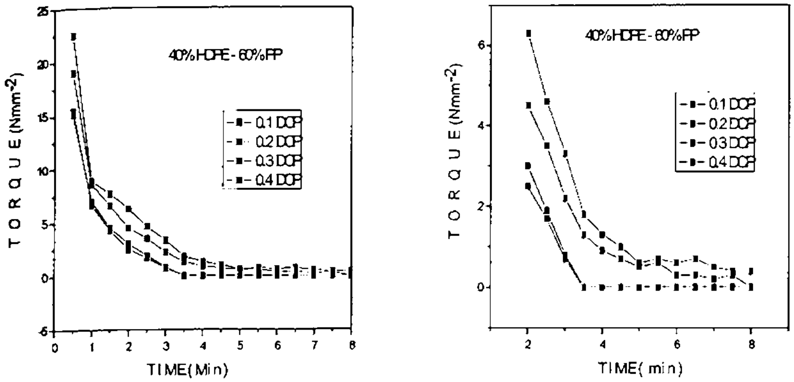
[A] [B]

Figure 3.1: [A] Torque – Time graph for 80% HDPE/20% PP Blends, [B] Torque – Time graph after addition of modifier.



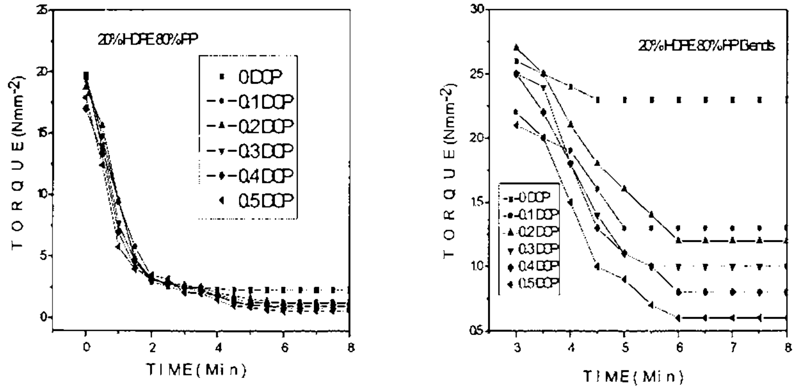
[A] [B]

Figure 3.2: [A]. Torque – Time graph for 60% HDPE/40% PP Blends [B]. Torque – Time graph after addition of modifier.



[A] [B]

Figure 3.3: *[A] Torque – Time graph for 40% HDPE/60% PP Blends [B] Torque – Time graph after addition of modifier.*



[A] [B]

Figure 3.4: *[A] Torque – Time graph for 20% HDPE/80% PP Blends [B] Torque – Time graph after addition of modifier.*

The stabilization of torque towards the end of mixing indicates that there is no degradation taking place during melt mixing.

3A.2.2 Tensile properties of samples extruded at 180°C

The tensile strength of high density polyethylene [HDPE] samples prepared by extrusion at 180°C is found to be 26.31 N/mm^2. Addition of polypropylene [PP] to HDPE is found to increase the tensile strength of the blend as expected since PP has a higher strength [Fig. 3.5].

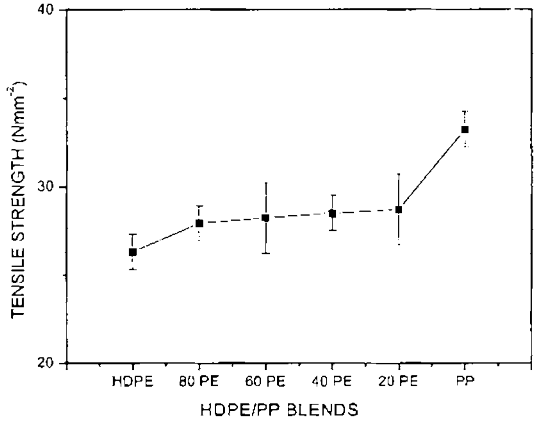
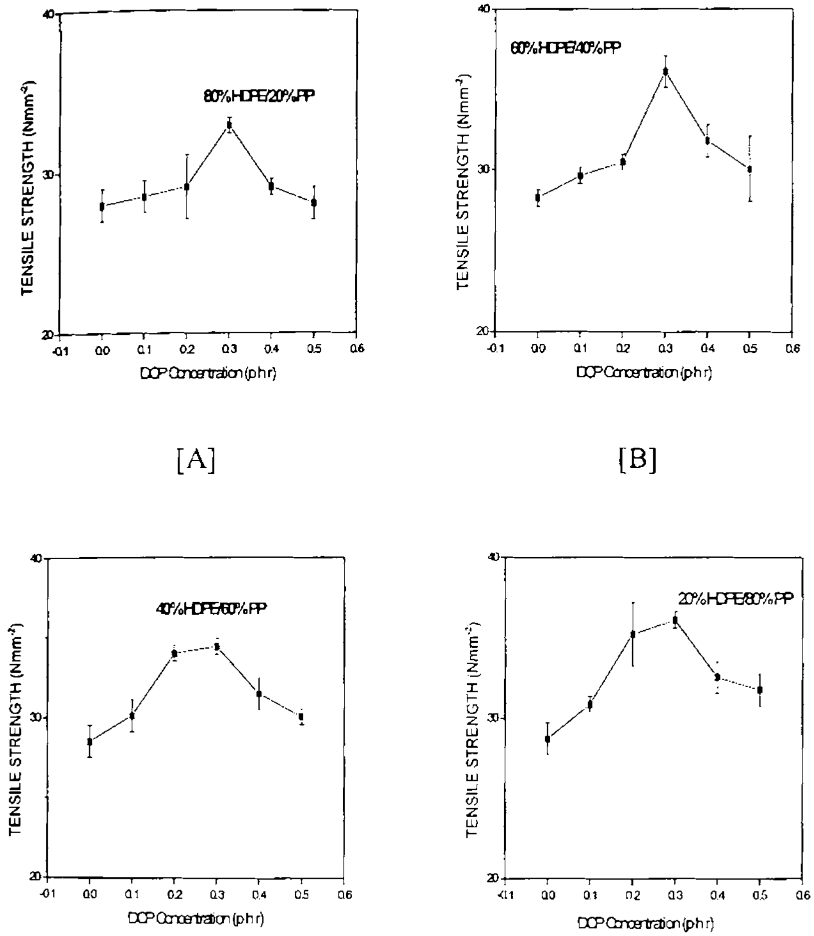


Figure 3.5: Variation in tensile strength of HDPE/PP blends with blend composition.

It has been observed that the addition of modifier improves the tensile strength of HDPE/PP blends and the maximum improvement is at a concentration of 0.3 phr of the modifier. The highest improvement is observed in the case of 20% HDPE/80% PP blend [Fig. 3.6A]. The tensile strength improves with increase in modifier concentration, reaches a maximum at 0.3phr and then decreases. This behaviour is observed in the case of all the blends [Fig. 3.6 B, C, & D].



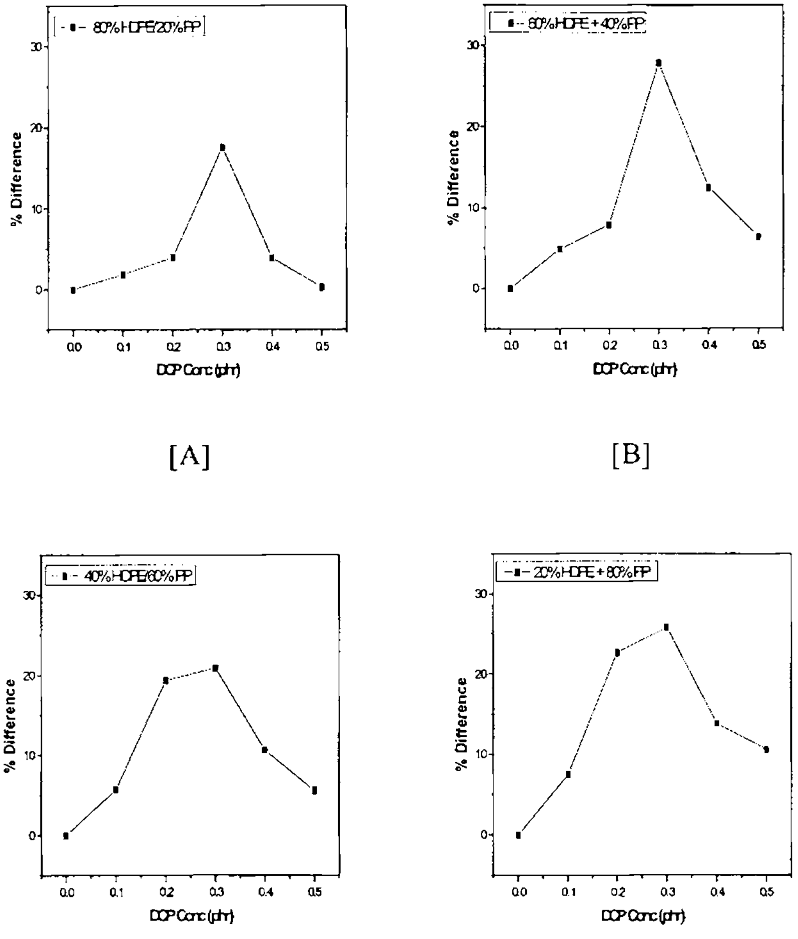
[A] [B]

[C] [D]

Figure 3.6: [A – D] Variation in tensile strength of HDPE/PP blends with DCP concentration.

It is observed that addition of 20% PP to HDPE [80% HDPE/20% PP blend] improves the tensile strength of HDPE by 6.2% and further addition of PP to the extent of 40% improves the tensile strength by

7.34%. The 20% HDPE/80% PP blends show the maximum tensile strength and at this combination the tensile strength of HDPE is improved by 14.2%.



[A] [B]

[C] [D]

Figure 3.7: [A – D]. % Variation in Tensile Strength of blends with DCP concentration

The highest increase in tensile strength is found in the case of 80% HDPE/20% PP blend. The addition of 0.3phr DCP to the blend improves the tensile strength of the blends to such an extent that it becomes nearly equal to or greater tensile strength of pure PP [Fig. 3.7 A].

The unmodified blend 80% HDPE/20% PP has tensile strength improved by 6.2% than pure HDPE but is weaker by 16% than pure PP. But addition of DCP to the blend is found to enhance the tensile strength and 0.3phr DCP improves the tensile strength by 17.6% than that of the unmodified blend. This value is found to be 1% below the tensile strength of pure PP.

The blend 60% HDPE/40% PP has its tensile strength improved by 8% than pure HDPE. This blend has its tensile strength lower than pure PP. But addition of DCP improves the tensile strength of the blend and 0.3phr DCP improves the tensile strength by 8.5% than pure PP [Fig. 3.7 B]. In the case of 40% HDPE/60% PP blend the tensile strength of the unmodified blend is 14% lower than that of pure PP. Addition of DCP is found to enhance the tensile strength of the blend–in fact 0.2phr and 0.3phr DCP in the blend improves the tensile strength to be greater than pure PP by 5.4% and 6.9% respectively [Fig. 3.7 C].

The blend 20% HDPE/80% PP shows best results in terms of tensile strength. The unmodified blend has a tensile strength lower by 13% than pure PP but addition of 0.3phr DCP enhances the tensile strength to be 13% greater than that of pure PP [Fig. 3.7 D].

3A.2.3 Elongation at break

The elongation at break of HDPE is found to be 11.91% and that of PP is found to be 7.79. It is also found that the addition of PP to HDPE lowers the elongation at break of the blends. Addition of 20% PP to HDPE reduces the elongation at break by 6% while addition of 80% PP to HDPE lowers the value by 15% [Fig. 3.8].

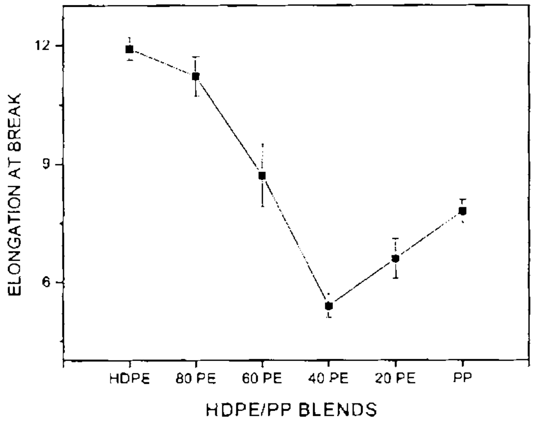
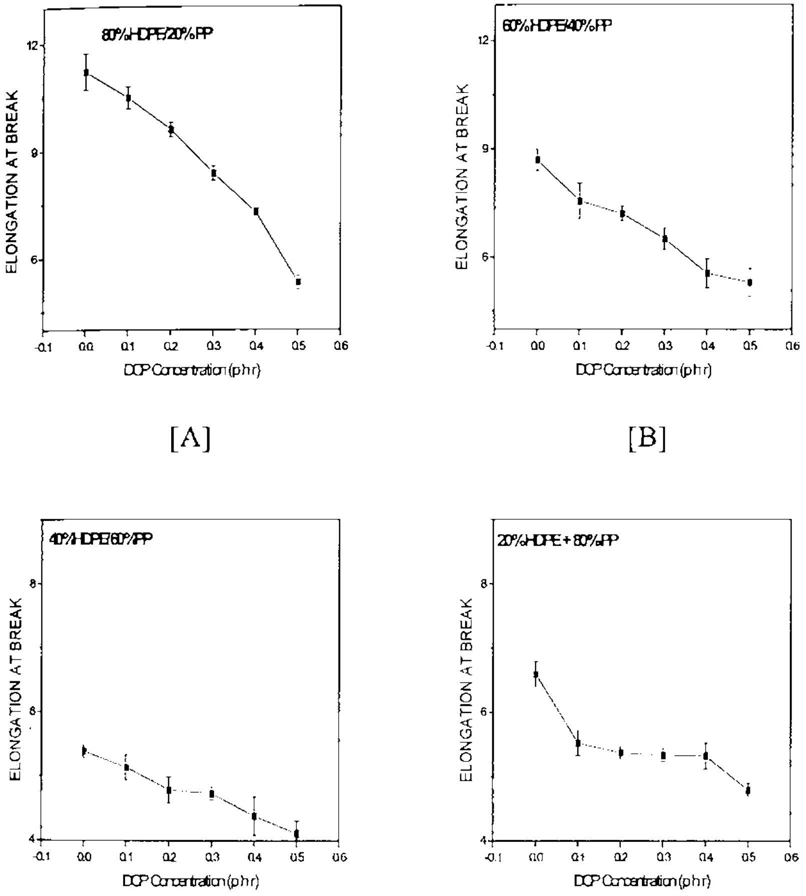


Figure 3.8: Elongation at Break of HDPE, PP and their blends with blend composition.

The addition of DCP to the blends further reduces the elongation at break of all the four blends studied. The deterioration produced in HDPE rich blends is much higher than in PP rich blends. Addition of 0.5phr DCP to 80% HDPE/20% PP blend leads to a lowering in elongation at break by 52.5% while in the case of 20% HDPE/80% PP blend, it is only 27%. The blend 60% HDPE/40% PP shows a decline of

39% while 40% HDPE/60% PP blend shows a decline of 23.74% [Fig. 3.9 A – D].



[A] [B]

[C] [D]

Figure 3.9: *[A-D] Variation in elongation at break of blends with DCP concentration.*

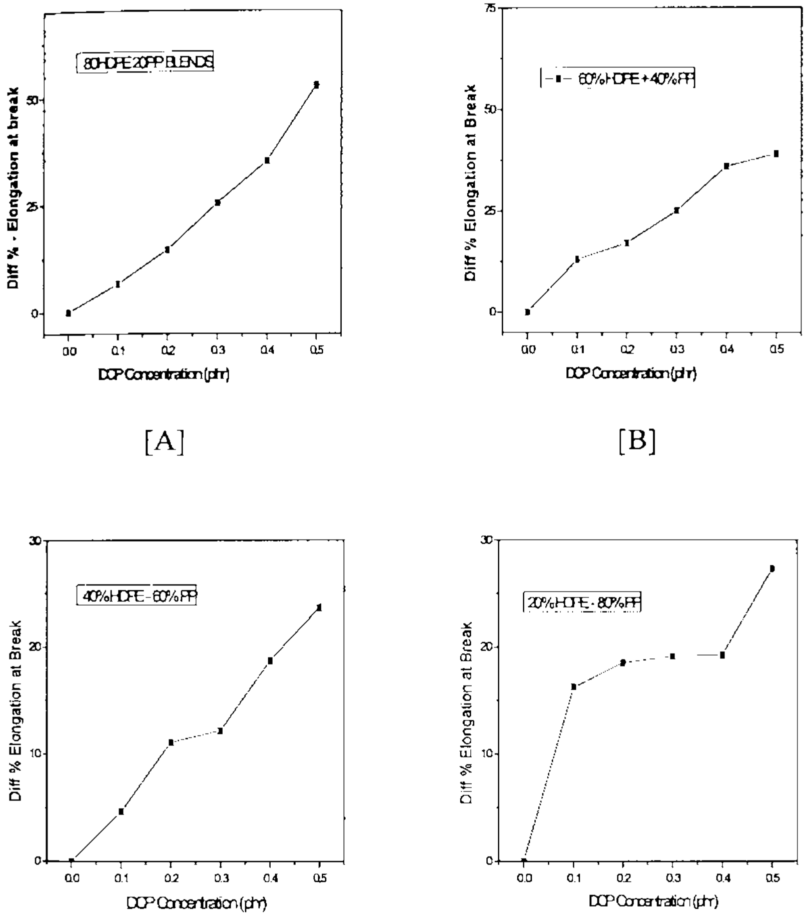
Comparison of elongation at break of HDPE, PP and their blends – 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP – on extrusion at 180°C show that addition of PP to

HDPE bring out a decline in elongation at break. Melt mixing produces incompatible blends with poor adhesion between domains of pure components or lower dispersion of one polymer in the other.

It is observed that addition of DCP to all these blends produce a declining trend for elongation at break. In the case of 80% HDPE/20% PP blend, addition of each 0.1phr DCP causes a decrement of about 7 – 10% in the value of elongation at break. Addition of 0.5phr DCP to this blend has brought out a large decrement in the value of elongation at break. The difference between the values for 0.4 and 0.5phr DCP is about 17%. This large difference is not shown by the other blends studied [Fig. 3. 10 A].

Even though addition of 0.1phr DCP to 60% HDPE/40% PP blend produces 13.1% decline in elongation at break, further addition of DCP in 0.1phr increments do not cause large deviations [Fig. 3. 10 B]. For 40% HDPE/60% PP blend, the largest deviation for elongation at break values are shown by addition of 0.1 and 0.2phr DCP – 6.5% – while the difference between the values of 0.2 and 0.3phr DCP modified blends is only 1% [Fig. 3. 10 C].

20% HDPE/80% PP blend modified by 0.1phr DCP shows a decline of 16.24% in elongation at break. Further increments of DCP show only slight variations – blends modified by 0.2, 0.3 and 0.4phr DCP has nearly equal elongation at break values. The next increment of DCP ie. 0.5phr DCP shows about 8% decline in elongation at break values. PP rich blends shows much lower decline in elongation at break on addition of DCP when compared to HDPE rich blends [Fig. 3. 10 D]. The addition of DCP to HDPE/PP blends cause cross linking in HDPE and chain scission in PP. The cross linking in HDPE lower the elongation at break of HDPE rich blends.



[A] [B]

[C] [D]

Figure 3.10: [A-D]. Percentage Variation in Elongation at break of blends with DCP concentration.

3A.2.4 Modulus of blends

Modulus of PP used is found to decrease on addition of HDPE while that of HDPE increases on addition of PP. All blends studied have modulus in between that of the pure components [Fig. 3.11].

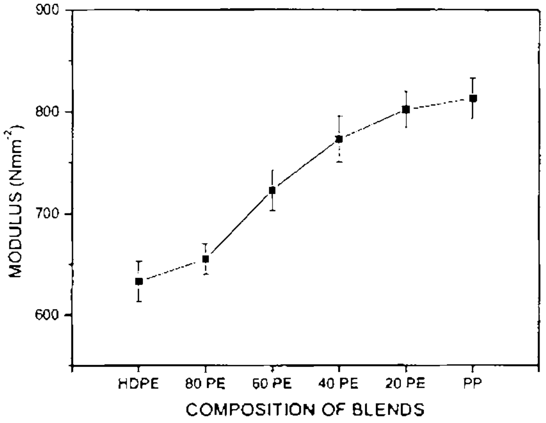
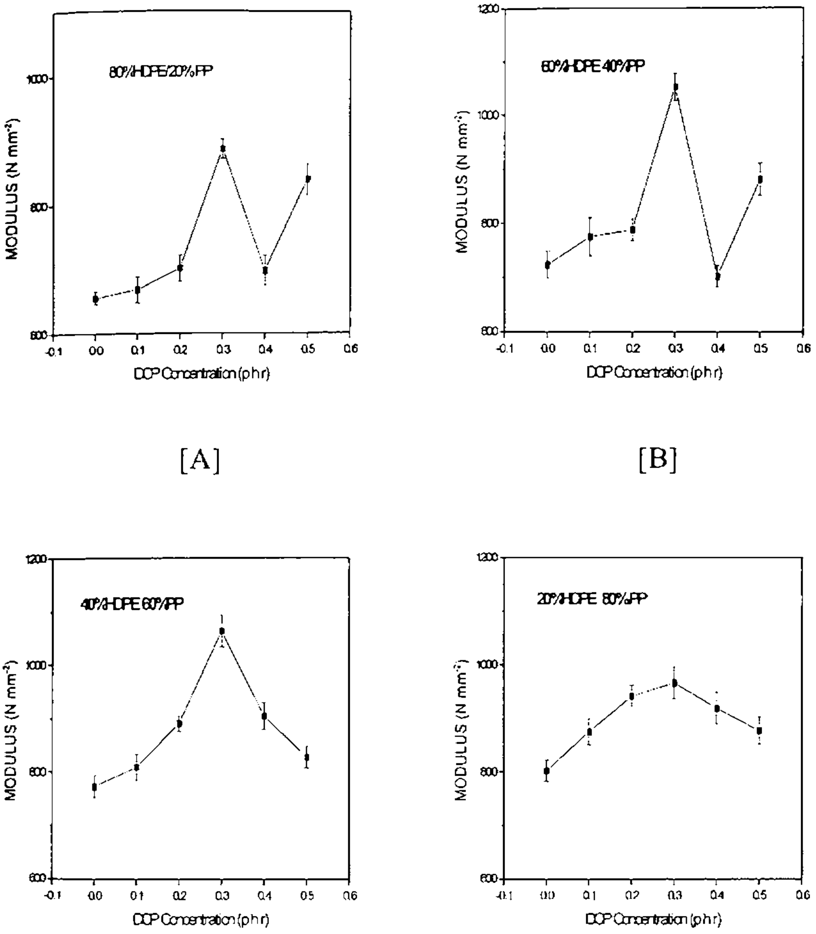


Figure 3.11; *Modulus of HDPE, PP and their blends.*

Studies on the modulus of all four blends show similar trends. Addition of DCP brought out improvement in modulus up to 0.3phr DCP and further addition showed a decline in modulus. The HDPE rich blends show improvement in modulus when 0.4 and 0.5phr DCP modifications are compared. The 0.4phr DCP modified 60% HDPE/40% PP blend has its modulus reduced by 3% than the unmodified blend.



[A] [B]

[C] [D]

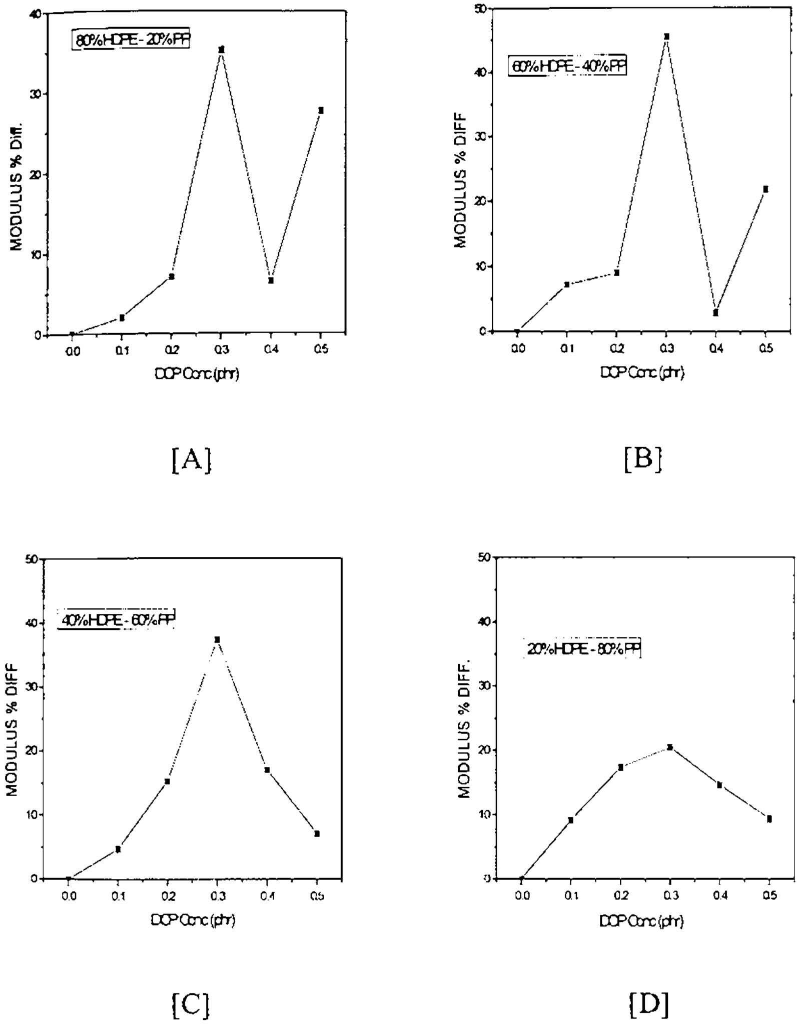
Figure 3.12: [A – D]. Variation in Modulus of HDPE/PP blends with DCP concentration.

The modulus of HDPE is found to increase on addition of PP. The presence of 20% PP in the blend improves the modulus by 3.5% while 40% PP can produce an increase of 14.2%. For PP, the addition of HDPE produces a decline in modulus. Addition of 20% HDPE to PP has brought out a decline of 1.4% while 40% HDPE produces 4.9% decline. The improvement in strength of HDPE on addition of PP may be due to stronger PP in the blend.

The addition of DCP to 80% HDPE/20% PP blend shows modulus to improve up to 35% for 0.3phr DCP and then decrease. Addition of lower amounts of DCP can bring out only slight improvement in modulus. Addition of DCP to 60% HDPE/40% PP blends bring out larger improvement in modulus. 0.3phr DCP modified blend is found to have its modulus enhanced by 46% and this combination had the best value among all blends studies.

Larger variations in modulus are observed in the case of PP rich blends. Addition of 0.1phr DCP to 40% HDPE/60% PP blend improves the modulus by 4.7% while for 20% HDPE/80% PP blends, it is 9%. The addition of 0.2phr DCP improves the modulus by 15.3 and 17.3% respectively. 0.3phr DCP in 40% HDPE/60% PP blend can bring out an improvement of 37.6% while in 20% HDPE/80% PP blend it has only 20.4% improvement. In fact the least improvement in modulus is observed in 20% HDPE/80% PP blend.

The improvement in modulus of blends on addition of DCP can be attributed to morphology changes taking place. DCP can modify the blends to an extent of 0.3phr addition. Further addition of DCP causes damage to the phase morphology and hence the decrease in modulus.



[A] [B]

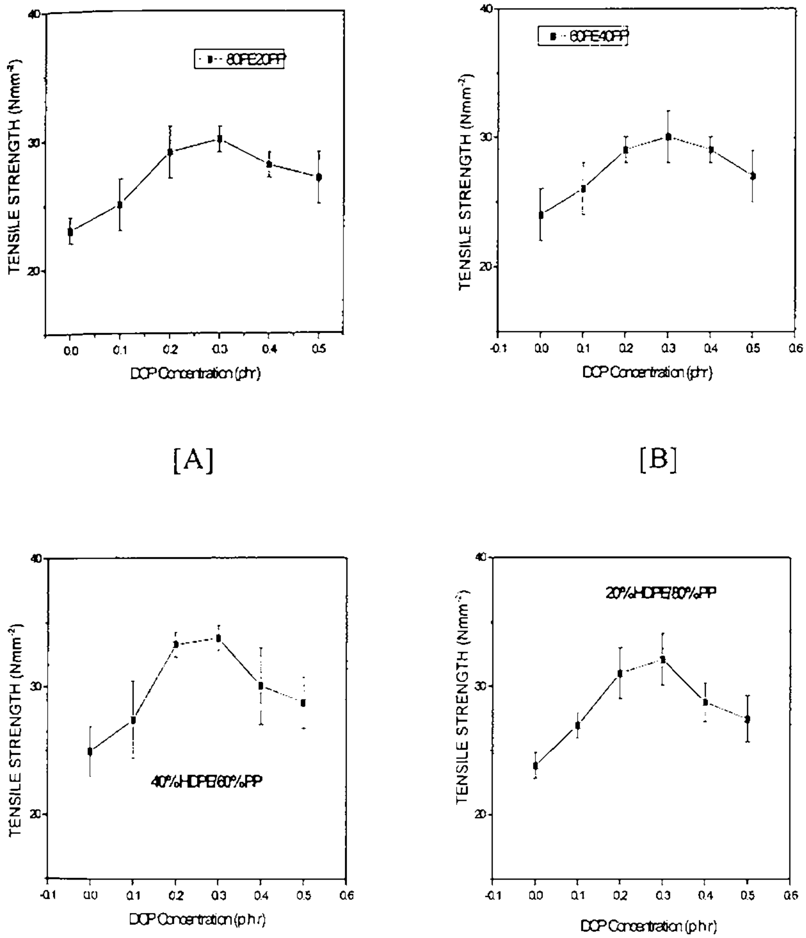
[C] [D]

Figure 3.13: *[A – D]. Percentage variation in Modulus of HDPE/PP blends with DCP concentration.*

3A.2.5 Tensile properties of samples extruded at 170°C

The unmodified 80% HDPE/20% PP blend exhibits a tensile strength of 23.01 N/mm^2 which is 17.6% lower than the tensile strength at 180°C. The addition of DCP enhances the tensile strength but in all cases the tensile strength values are lower for extrusion at 170°C. This is true for other three blends also and the trends are as in the case of blends at 180^{0}C *ie.* the presence of 0.3phr DCP produces the best effect on tensile strength. The tensile strength of each blend enhances with each increment of DCP, reaches a maximum at 0.3phr DCP and then further addition of DCP causes a decline in the value of tensile strength. The same pattern is shown by all the blends (Fig. 3.14 [A – D]).

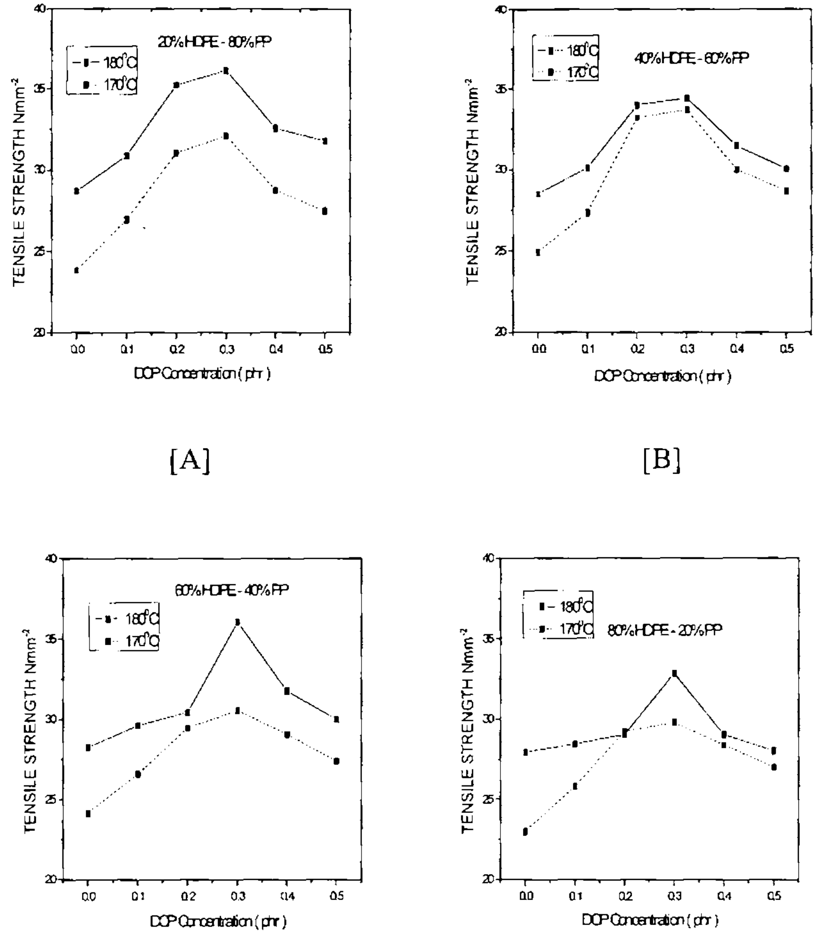
Comparison of tensile strength values of the four blends studied i.e. 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP shows that the tensile strengths of samples obtained by extrusion at 180°C are higher than the values at 170°C. The difference in tensile strength values of each blend extruded at two different temperatures - 180°C and 170°C – are summarized as follows (Fig. 3.15 [A – D]).



[A] [B]

[C] [D]

Figure 3.14: [A – D]. Variation in Tensile Strength of HDPE/PP blends with DCP concentration at 170°C.



[A] [B]

[C] [D]

Figure 3.15: [A – D]. Comparison of tensile strength of HDPE/PP blends on extrusion at two different temperatures.

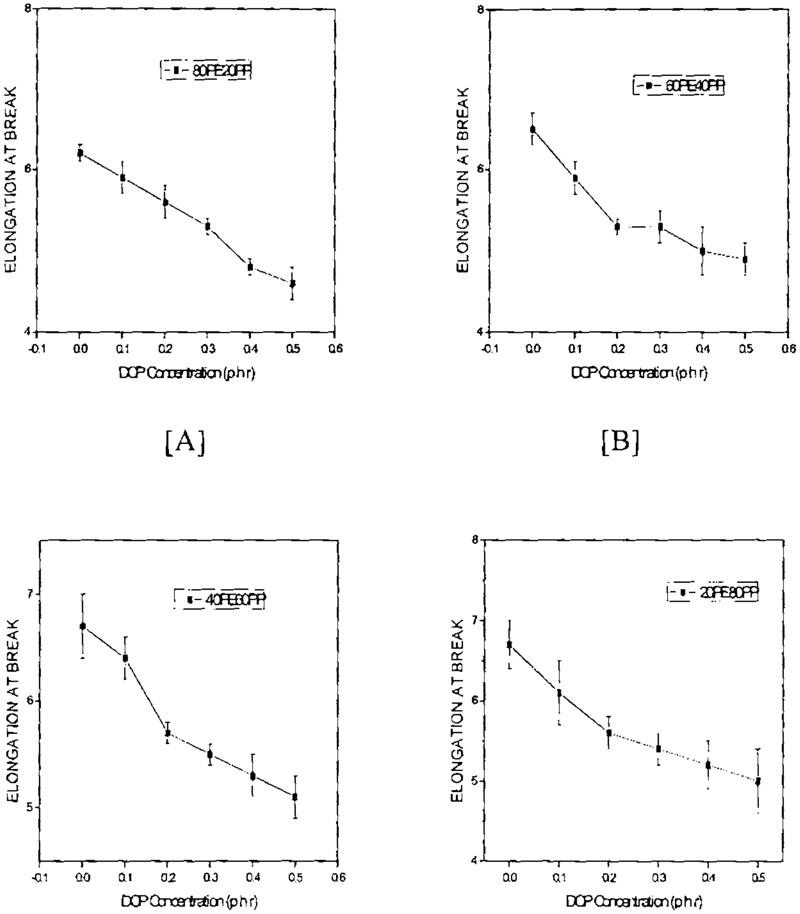
In the case of HDPE rich blends, the blends containing 0.3phr DCP shows the largest difference in tensile strengths at the two temperatures while in the case of PP rich blends, the blends containing

0.3phr DCP shows the lowest difference. In the case of HDPE rich blends, combinations with 0.1, 0.2, 0.4 and 0.5phr DCP show only slight difference in tensile strengths where as in the case of PP rich blends, the difference is larger. In all cases the values of tensile strength of samples extruded at 180°C are higher than those for samples extruded at 170°C (Fig. 3.15 [A – D]).

3A.2.6 Elongation at Break

The elongation at break values for all the blends are curtailed by addition of DCP and the values decline with increase in concentration of DCP. These observations show similar trends as in the case of extrusion at 180°C.

The elongation at break values in the case of HDPE rich blends - 80% HDPE/20% PP and 60% HDPE/40% PP – are lower than the values obtained in the case of samples prepared by extrusion at 180°C. The elongation at break value in the case of PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – are higher than the values obtained in the case of samples prepared by extrusion at 180°C (Fig. 3.16 [A – D]).



[A] [B]

[C] [D]

Figure 3.16: *[A – D] Variation in Elongation at Break with DCP concentration for blends extruded at 170°C.*

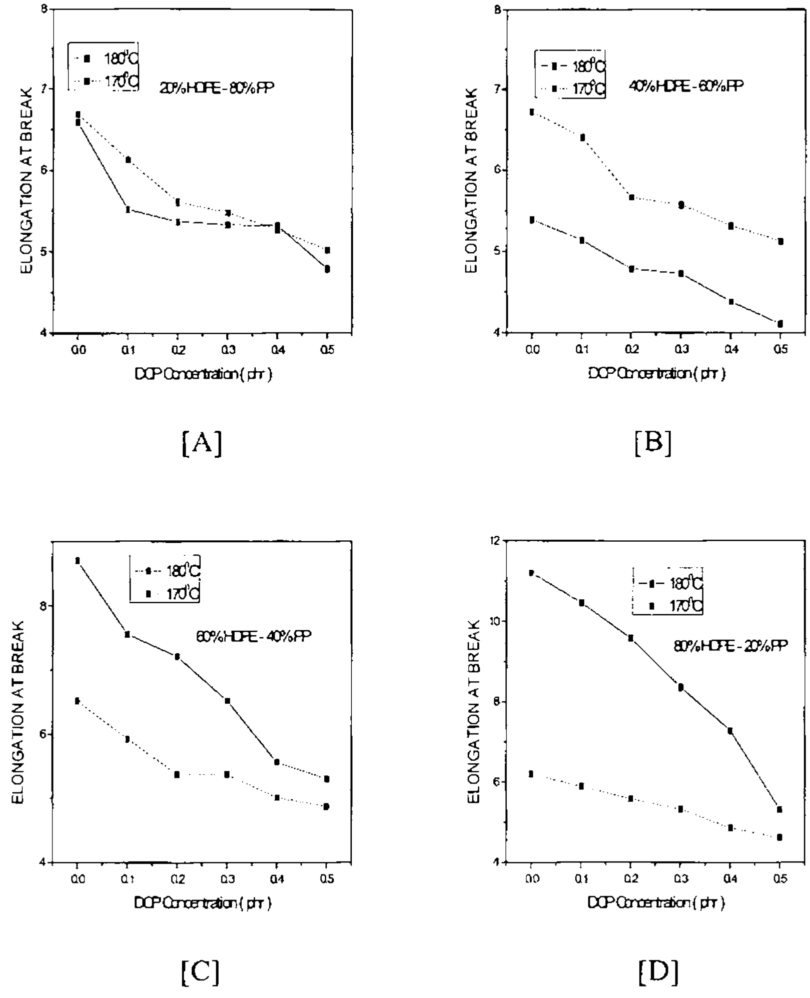
Comparison of elongation at break values of the four blends studied – 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP – shows that the elongation at break values of

HDPE rich blends are higher at 180°C while for PP rich blends, the values are higher for extrusion at 170°C.

The largest lowering of elongation at break value is observed in the case of unmodified 80% HDPE/20% PP blend, where the value is nearly half for the sample extruded at 170°C. The introduction of DCP to the mixture reduces the difference in elongation at break values and this reduction increases with increase in concentration of DCP. The presence of 0.5phr DCP in the blends shows the smallest difference in elongation at break values.

In the case of 60% HDPE/40% PP blend, the utmost depreciation in elongation at break values are shown by the unmodified blend as well as the blend containing 0.2phr DCP. In all other cases the depreciation in the elongation at break values for extrusion at lower temperature is much lower and the least depreciation is observed when 0.5phr was added.

For 40% HDPE/60% PP blend, the increment in elongation at break values for lower temperature extrusion (170°C) decreases with increase in concentration of DCP. The lowest increment is for the presence of 0.3phr DCP (18%) while the highest increment is for the unmodified blend (24.7%).



[A] [B]

[C] [D]

Figure 3.17: *[A – D] Comparison of elongation at break of HDPE/PP blends on extrusion at two different temperatures.*

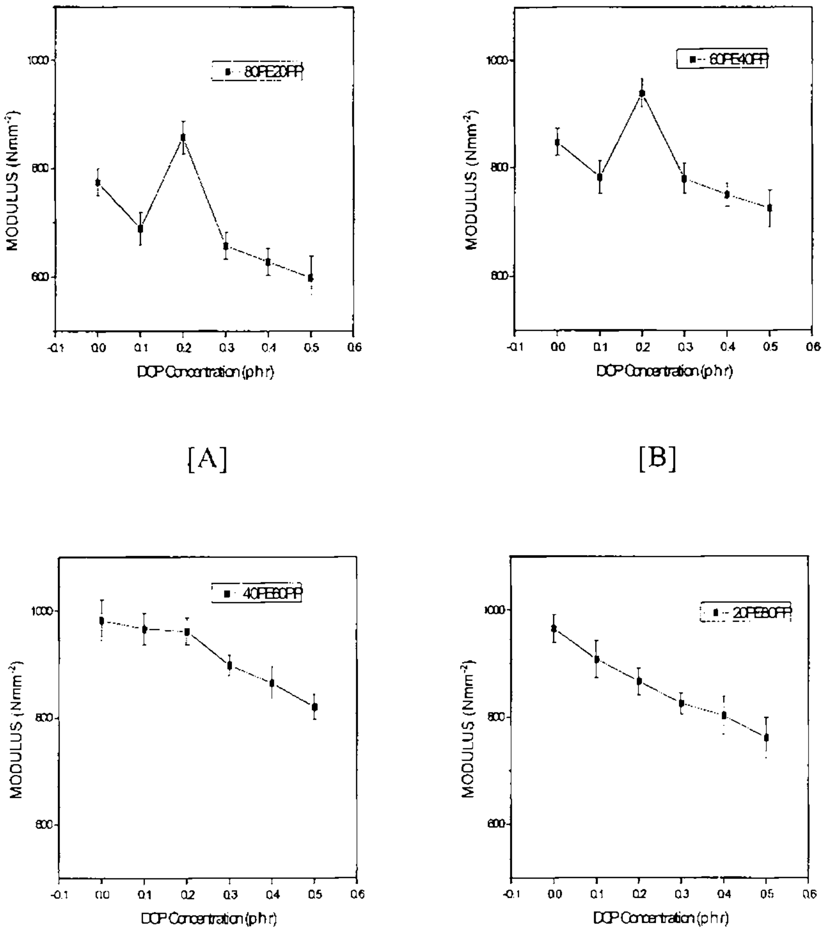
For 20% HDPE/80% PP blends, the blend with 0.4phr DCP extruded at 170°C has a slightly lower value of elongation at break than for extrusion at 180°C, where as in all other cases the extrusion at 170°C has higher values. But the increment observes in the case of this blend is much lower than in the case of 40% HDPE + 60% PP blend (Fig. 3.17 [A – D]).

3A.2.7 Modulus of Blends

The modulus of 80% HDPE/20% PP blend with varying composition of DCP is found to increase to a maximum at 0.2phr and then decreases. The highest value is 10.5% greater than the unmodified blend. Further addition of DCP is found to be lower the modulus of the blend.

For 60% HDPE/40% PP blend, increment in concentration of DCP is found to augment the modulus of the blend which happens up to addition of 0.2phr DCP. The maximum value is 20% greater than that of the unmodified blend. Further addition of DCP curtails the modulus of the blend.

But in the case of PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – the modulus decreases with increase in the concentration of DCP. The lowest value is obtained in the case of addition of 0.5phr DCP for both the blends (Fig. 3.18 [A – D]).



[A] [B]

[C] [D]

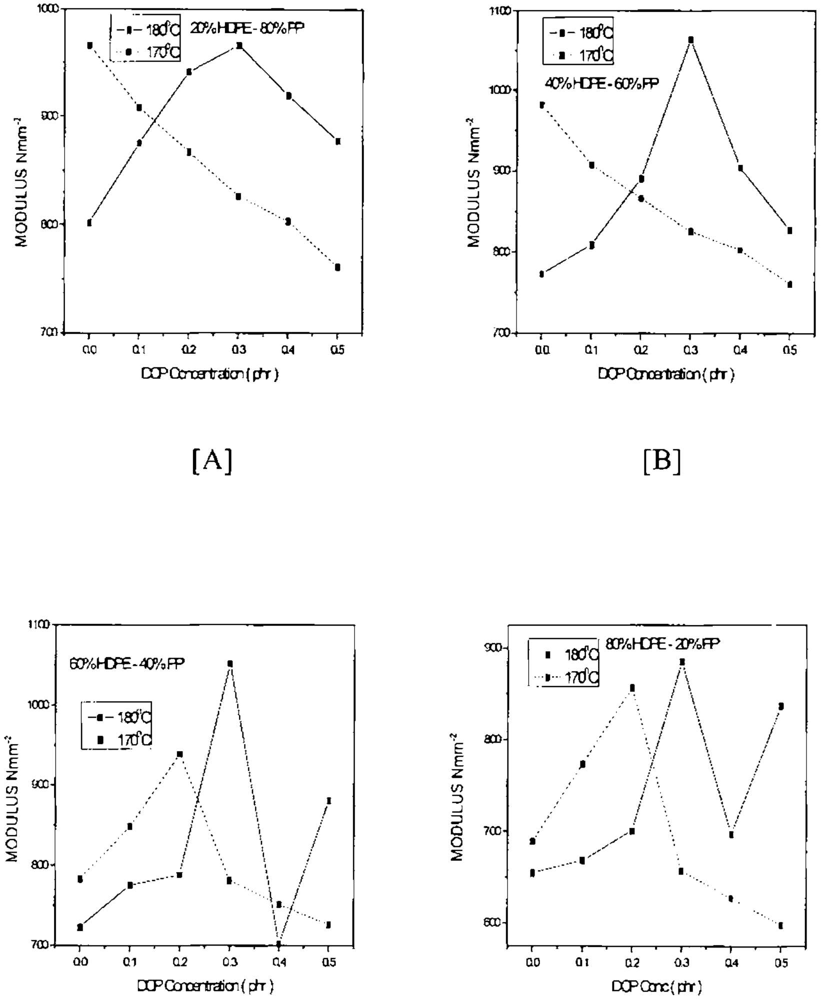
***Figure 3.18:** [A – D] Variation in Modulus with concentration of DCP for blends extruded at 170°C.*

The modulus of the four blends studied – 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP prepared at two different temperatures 180°C and 170°C are compared and the following observations are made.

For 80% HDPE/20% PP blends the modulus for blending at 170°C are greater than for blending at 180°C up to addition of 0.2phr DCP. Further addition of DCP shows that the values for blending at 180°C are higher. The largest difference in values was found at 0.3phr DCP content.

Similar trend is shown by 60% HDPE/40% PP blend. Up to 0.2phr DCP, the modulus of blends prepared at 170°C are higher than that of blends prepared at 180°C and further addition of DCP shows the reverse trend. Like 80% HDPE/20% PP blend, the largest difference in values is observed for addition of 0.3phr DCP.

For PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – modulus for blending at 170°C is higher than for blending at 180°C for unmodified blend and blend containing 0.1phr DCP. In all other cases the value is higher for blends prepared at 180°C. Once again blends containing 0.3phr DCP shows large difference in values – lower by 22% for 40% HDPE/60% PP blend and 15% for 20% HDPE/80% PP blend.



[A] [B]

[C] [D]

Figure 3.19: [A – D] - Comparison of modulus of HDPE/PP blends on extrusion at two different temperatures.

3A.2.8 Injection moulding at 180°C

(a) Tensile strength:-

The tensile strength values of all blends processed by injection moulding are found to be lower than those for blends processed by extrusion. The tensile strength of PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – are found to be in between the tensile strength of pure HDPE and pure PP where as the tensile strength of HDPE rich blends – 80% HDPE/20% PP and 60% HDPE/40% PP – has lower values than pure HDPE [Fig. 3.20]. As in the case of extrusion the tensile strength of all four blends increases with each increment of DCP, is found to reach the maximum at 0.3phr DCP and further increments of DCP lowers the tensile strength of the blend (Fig. 3.21 [A – D]).

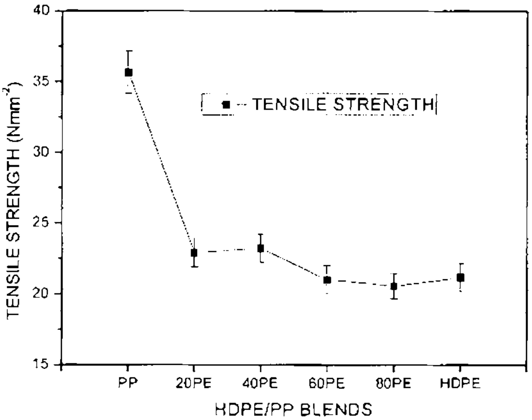
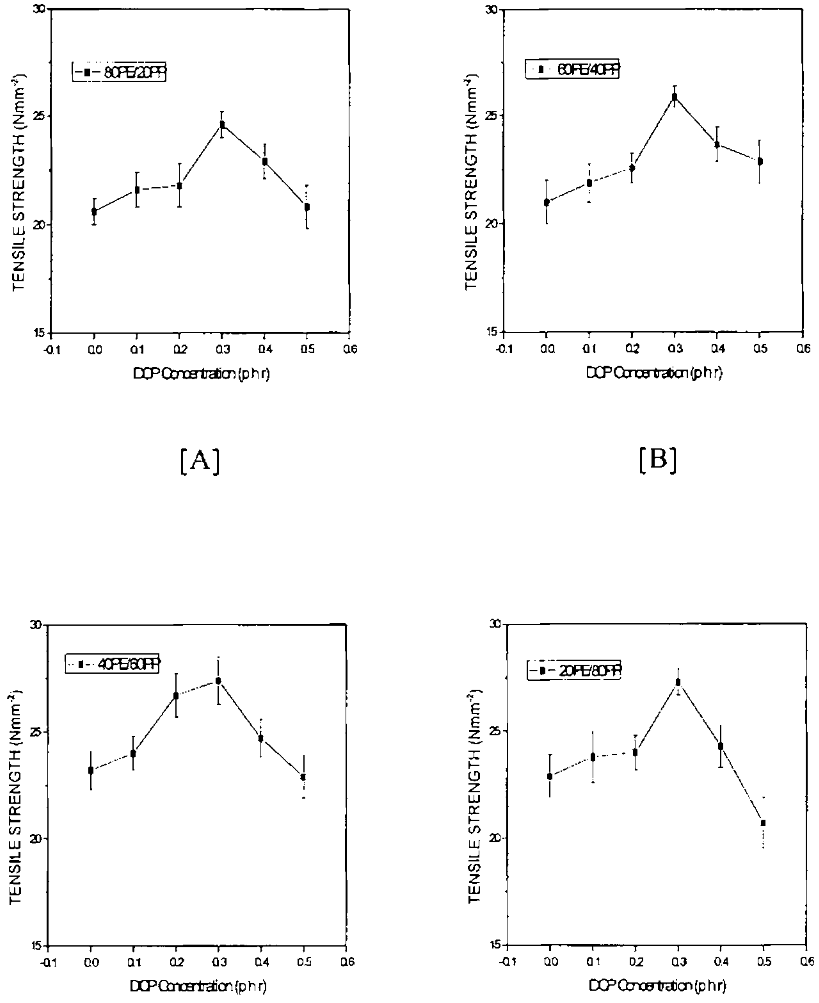


Figure 3.20: Tensile strength of HDPE/PP blends with blend composition.



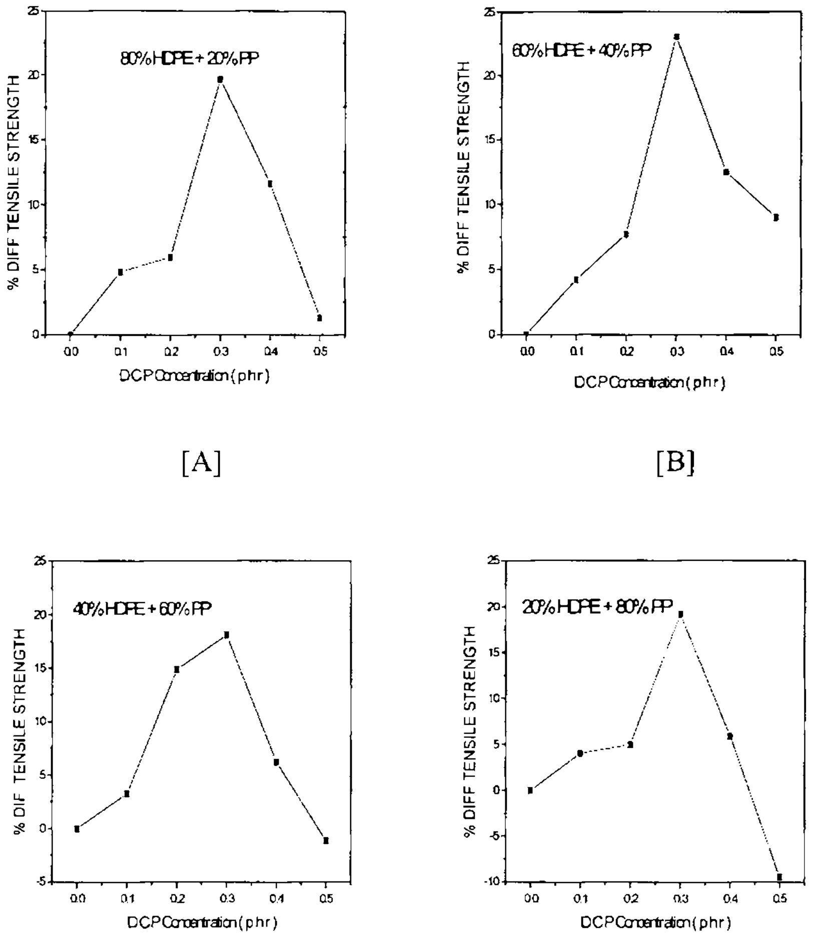
[A] [B]

[C] [D]

Figure 3.21: *[A – D] Variation in Tensile Strength with concentration of DCP for HDPE/PP blends injection moulded at 180°C.*

The tensile strength values of all four blends processed by injection moulding are compared and are found that the tensile strength in the case of extrusion is higher than in injection moulding. This can be attributed as due to better polymer chain orientation in the case of extrusion. The tensile strength of the blend increases with increase in concentration of DCP to a maximum and then decrease. The largest increment in tensile strength is for the addition of 0.3phr DCP and the largest enhancement of 23% is observed in the case of 60% HDPE/40% PP blend followed by 19.6% for 80% HDPE/20% PP blend and by 19.1% for 20% HDPE/80% PP blend. Addition of 0.5phr DCP to PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – lowers the tensile strength by 9.4 and 1.16% respectively than the unmodified blend. In all other cases the tensile strength of blends are increased than for unmodified blends.

The lowering of tensile strength in the case of PP rich blends may be attributed to chain scission of PP by DCP. The lower the molecular weight due to scission, the lower is the strength of the material. The enhancement of tensile strength in the case of HDPE rich blends can be attributed to cross-linking in HDPE caused by addition of DCP.



[A] [B]

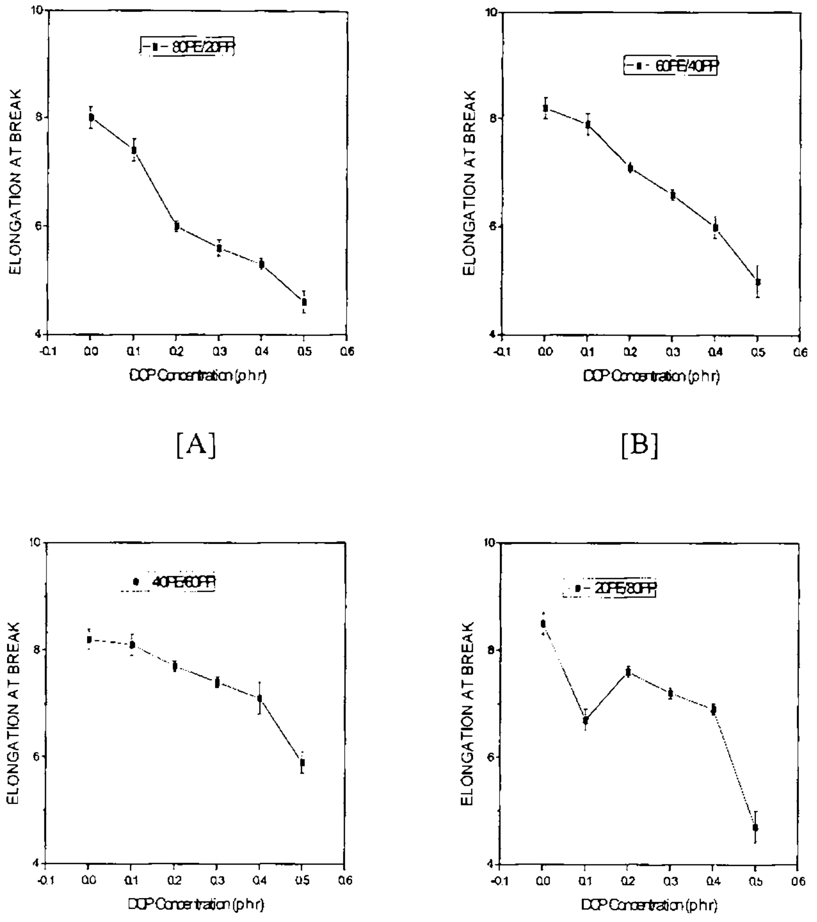
[C] [D]

Figure 3.22: [A – D] % Variation in Tensile Strength of HDPE/PP blends with concentration of DCP for blends injection moulded at 180°C.

(b) Elongation at break

The elongation at break of all four blends studied – 80% HDPE/ 20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP – show a regular depreciation on enhancement of concentration of DCP. The largest depreciation of 44% is observed in the case of 80% HDPE/20% PP blend followed by 43% in the case of 20% HDPE/80% PP blend both when 0.5phr DCP is added to the blend. The elongation at break of both extruded and injection moulded samples show similar trend. The depreciation in the elongation at break shown by PP rich blends – 40% HDPE/60% PP and 20% HDPE/80% PP – are much lower than those for HDPE rich blends (Fig. 3.23 [A – D]).

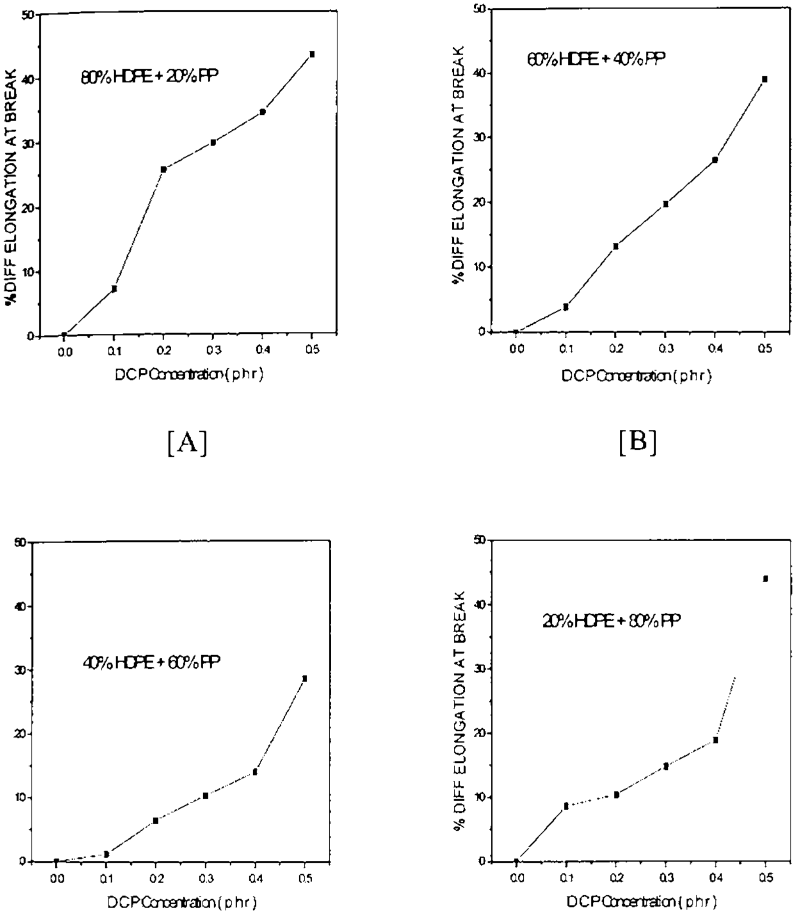
Comparing the values of elongation at break of blends on injection moulding at 180°C, it is observed that of all the four blends, the unmodified blend has the highest elongation at break. The elongation at break of HDPE is lowered by addition of PP as well as the addition of HDPE to PP. In all cases the values are in between those for pure HDPE and pure PP.



[A] [B]

[C] [D]

Figure 3.23: *[A – D] Variation in Elongation at break of HDPE/PP blends with DCP concentration for blends injection moulded at 180°C.*



[A] [B]

[C] [D]

Figure 3.24: *[A – D] % Variation in Elongation at Break of HDPE/PP blends with concentration of DCP for blends injection moulded at 180°C.*

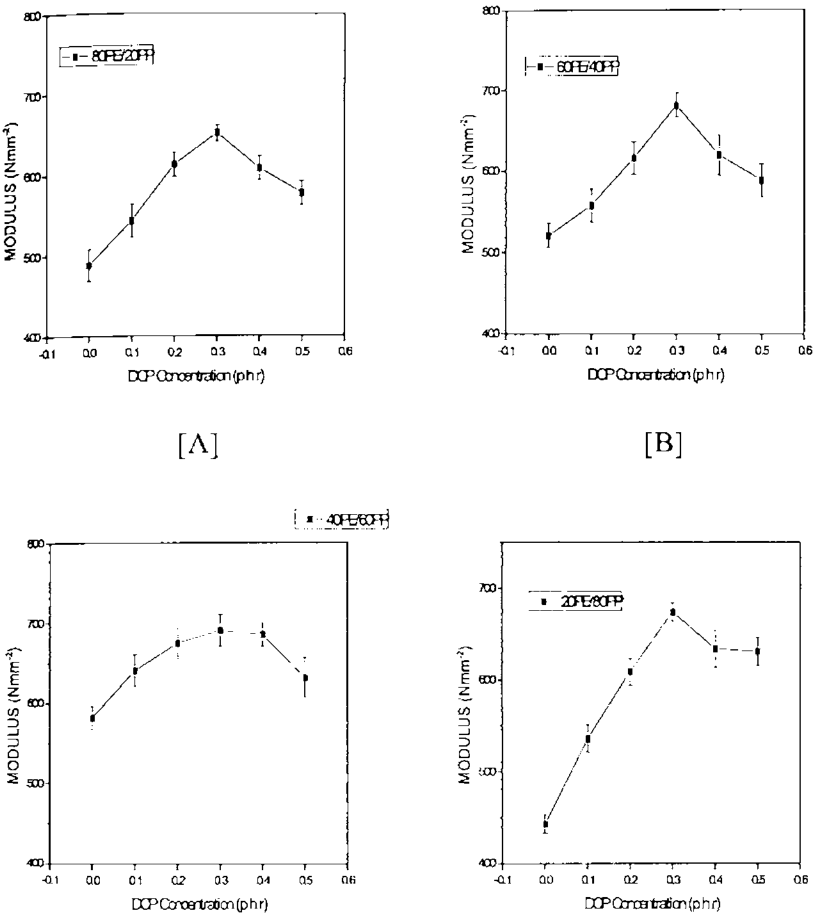
It is observed that the addition of PP to HDPE causes an enhancement of elongation at break and the value increases with increase in PP content. The elongation at break values kept decreasing on the enhancement of concentration of DCP. The depreciation in elongation at break for addition of 0.1phr DCP is high in the case of 80% HDPE/20% PP and 20% HDPE/80% PP blends – 7.12% and 8.64% respectively while 60% HDPE/40% PP and 40% HDPE/60% PP blends shows only narrow increase – 3.8% and 1.22% respectively (Fig. 3.24 [A – D]).

(c) Modulus of blends

The modulus of all four blends increase with increase in concentration of DCP, reach a maximum value at 0.3phr DCP and then decrease. The largest enhancement of 52.1% is observed in the case of 20% HDPE/80% PP blend for the addition of 0.3phr DCP. In the case of 80% HDPE/20% PP blend, the largest enhancement is by 33.4%, for 60% HDPE/40% PP it is 30.7% and for 40% HDPE/60% PP it is only 18.7% which is much lower that for other blends (Fig. 3.25 [A – D]).

On comparing the values of modulus of blends on injection moulding at 180°C, it is observed that of all the four blends have enhanced modulus on addition of DCP, reach a peak value at 0.3phr DCP and then decrease.

In the case of 80% HDPE/20% PP, 60% HDPE/40% PP and 20% HDPE/80% PP blends, each increment in the amount of DCP brought about considerable change in values but for 40% HDPE/60% PP blend, the change is much low even though the trend is kept up.

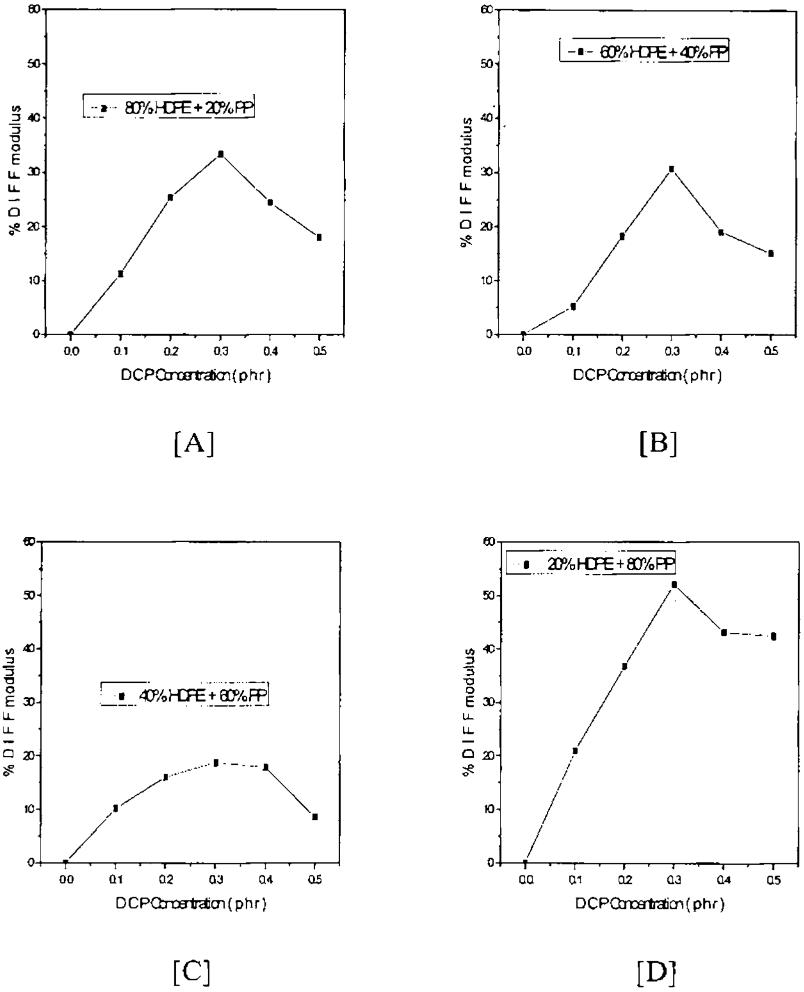


[A] [B]

[C] [D]

***Figure 3.25:** [A – D] Variation in Modulus of HDPE/PP blends with DCP concentration for blends injection moulded at 180°C.*

The maximum enhancement in the case of 40% HDPE/60% PP blend is only 18.7% compared to 30.7, 33.4 and 52% enhancement in the case of 60% HDPE/40% PP, 80% HDPE/20% PP and 20% HDPE/80% PP blends respectively (Fig. 3.26 [A – D]).



[A] [B]

[C] [D]

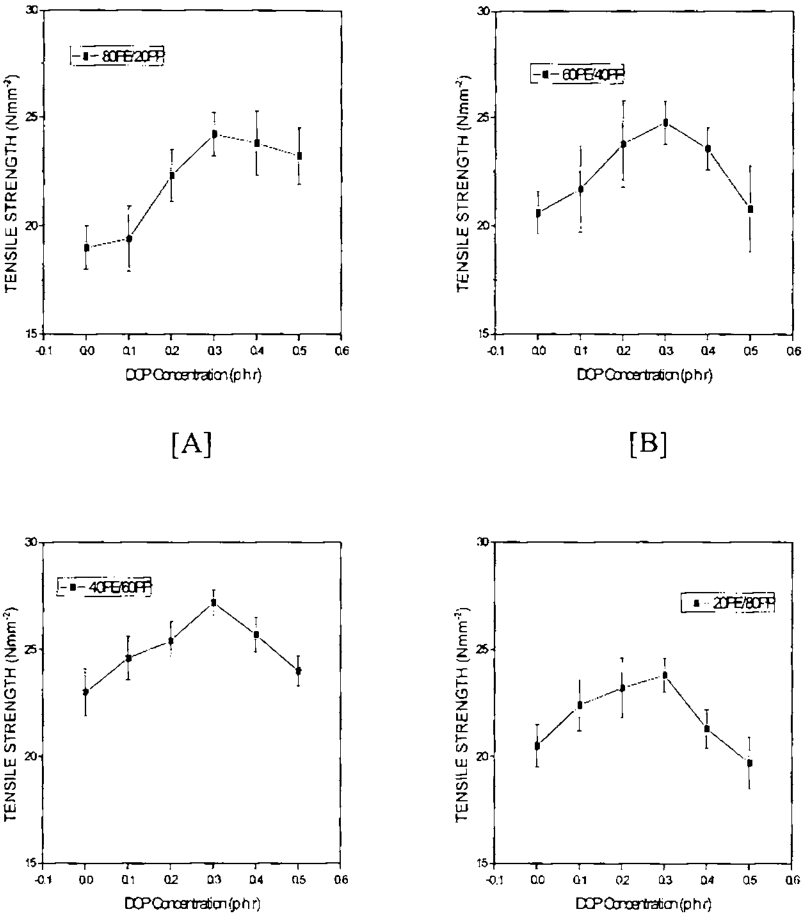
Figure 3.26: *[A – D] % Variation in Modulus of HDPE/PP blends with DCP concentration for blends injection moulded at 180°C.*

3A.2.9 Injection moulding at 170°C

(a) Tensile strength

The tensile strength values of all blends processed by injection moulding are found to be lower than those for blends processed by extrusion. The tensile strength values of all unmodified blends are found to be in between the tensile strengths of the pure components. The tensile strength of HDPE rich blends are higher than pure HDPE while that of PP rich blends are lower than that of pure PP. The tensile strength of HDPE increases with increase in PP content. It is also observed that 40% HDPE/60% PP blend has the highest tensile strength and shows highest values even on DCP modification (Fig. 3.27 [A – D]).

The tensile strength values of all blends processed by injection moulding are found to be lower than those for blends processed by extrusion. The tensile strength of all four blends increases with increase in concentration of DCP, reaches a peak value and then decreases. This observation is true even in the case of injection moulding at 180°C as well as for extrusion.



[A] [B]

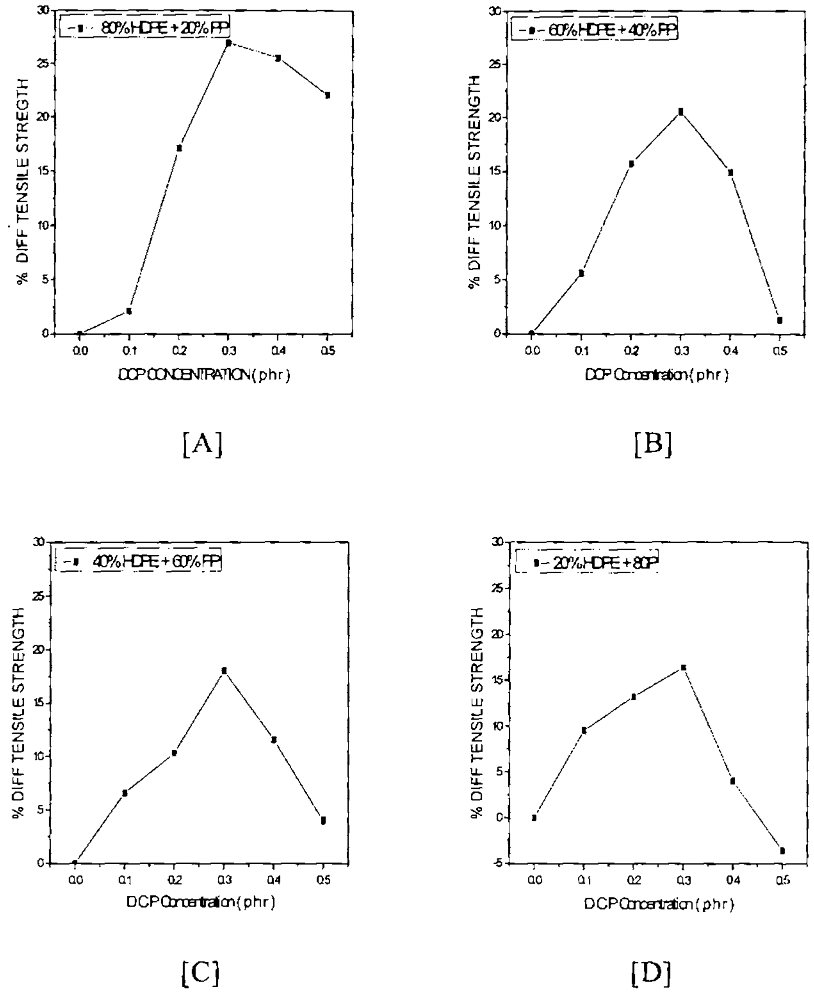
[C] [D]

Figure 3.27: *[A – D] Variation in Tensile Strength of HDPE/PP blend with DCP concentration.*

Addition of 0.1phr DCP to 80% HDPE/20% PP blend is found to bring out only a small increase of 2.16% in tensile strength, whereas for other blends considerable change is observed. Further addition of DCP is found to produce greater variation in tensile strength in the case of 80% HDPE/20% PP blend. Least variation in tensile strength is observed in the case of 20% HDPE/80% PP blend. It is also observed that addition of 0.5phr DCP to 20% HDPE/80% PP blend lowers the tensile strength than the unmodified blend. Addition of 0.5phr DCP causes only slight variation in tensile strength for 60% HDPE/40% PP and 40% HDPE/60% PP blends (Fig. 3.28 [A – D]).

Comparison of tensile strengths of blends processed by injection moulding at 180°C and 170°C show the following variations. In all cases the tensile strength of the blends increases with increase in concentration of DCP to a maximum at 0.3phr level and then decreases. The tensile strength of 20% HDPE/80% PP blend processed at 170°C has lower values than the blend processed at 180C for all DCP combinations. This may be attributed to better alignment of polymer chains at higher temperatures (Fig. 3.29 [A – D]).

For 80% HDPE/20% PP blend, higher DCP concentrations – 0.4 and 0.5phr – at 170°C are found to produce better results than for processing at 180°C. It is observed that blend with 0.5phr DCP processed at 170°C has 11.4% greater tensile strength than the blend processed at 180°C.

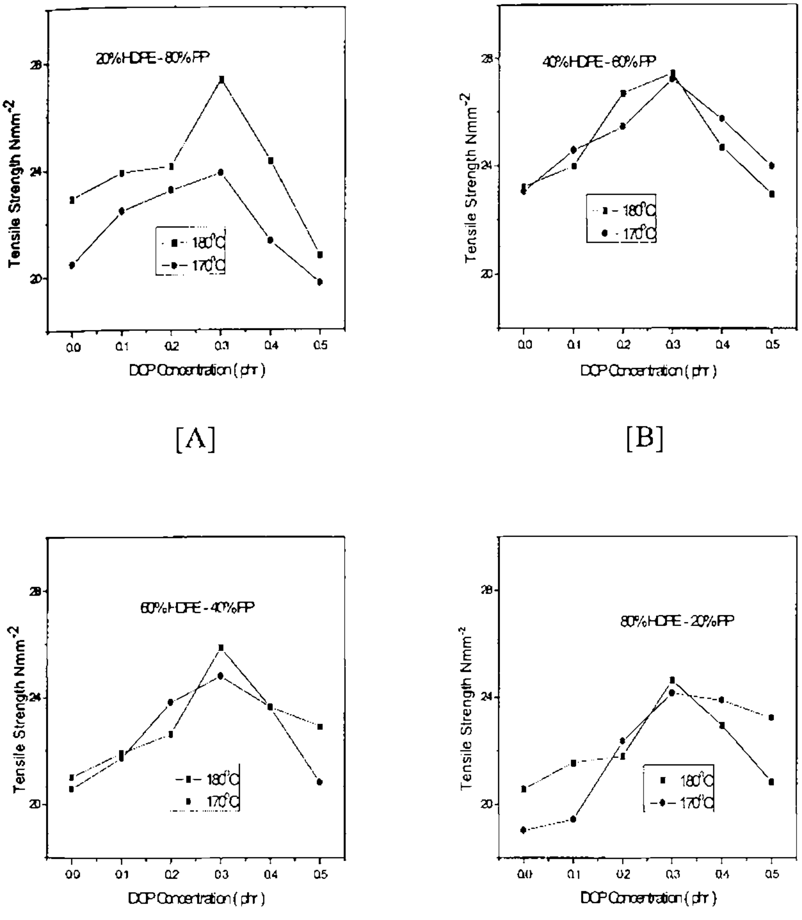


[A] [B]

[C] [D]

Figure 3.28: *[A – D]. % Variation in Tensile Strength of HDPE/PP blends with DCP concentration for blends injection moulded at 170°C.*

For 60% HDPE/40% PP blend, the presence of 0.2phr DCP improves the tensile strength for moulding at 170°C by 5.2%. In the case of 40% HDPE/60% PP blend, the results are similar to 80% HDPE/20% PP blend, the increase is only 4.4%.



[A] [B]

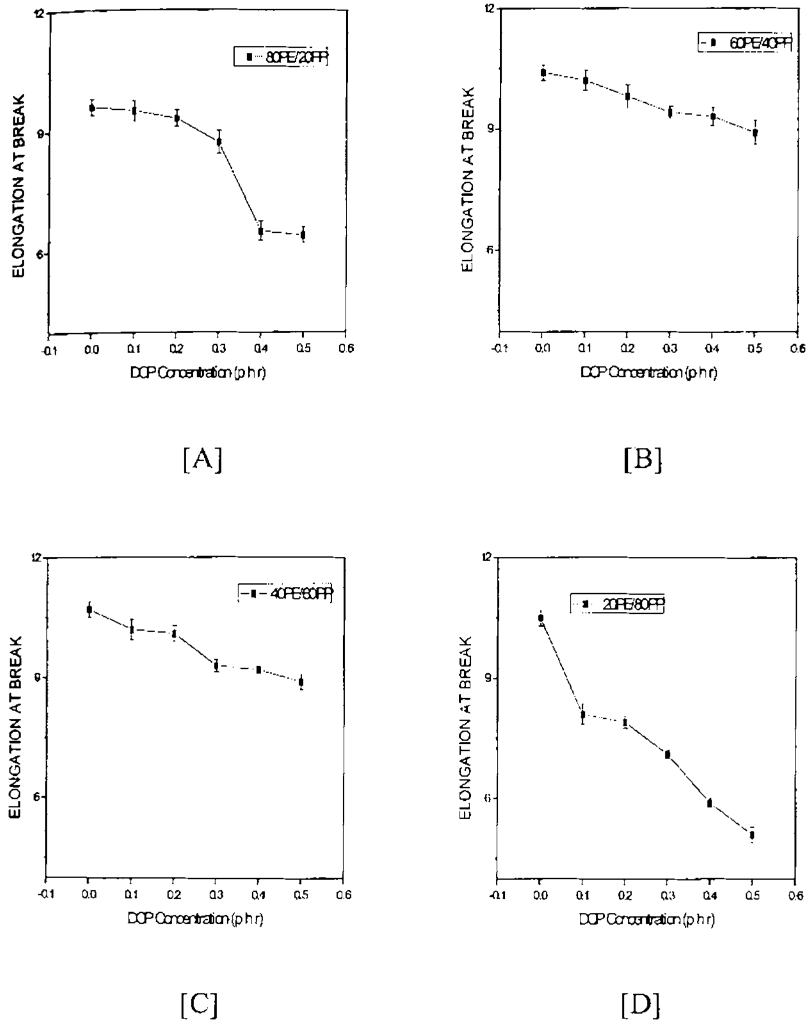
[C] [D]

Figure 3.29: *[A – D]. Comparison of tensile strength of HDPE/PP blends on injection moulding at two different temperatures.*

The increase in tensile strength of these blends on addition of DCP can be due to better dispersion of one polymer in the matrix of the other. In fact peroxides bring out chain scission in PP and cross linking in HDPE which brings about a matching of viscosities which leads to better dispersion of the two polymers. At higher DCP concentrations the curtailment of tensile strength can be due to higher degree of degradation of the components.

(b) Elongation at break

Measurement of elongation at break of samples prepared by injection moulding at 170°C show that the values obtained are lower than that for pure components. The values also show a decreasing trend on addition of DCP. The HDPE and PP rich blends – 80% HDPE/20% PP and 20% HDPE/80% PP – show larger deviations while the other two blends shows only lower deviations. The 60% HDPE/40% PP and 40% HDPE/60% PP blends show a gradual decrease in elongation at break but for 80% HDPE/20% PP and 20% HDPE/80% PP blends, each increment in DCP bring out large variations (Fig. 3.30 [A – D]).



[A] [B]

[C] [D]

Figure 3.30: [A – D] Variation in Elongation at break of HDPE/ PP blend with DCP concentration.

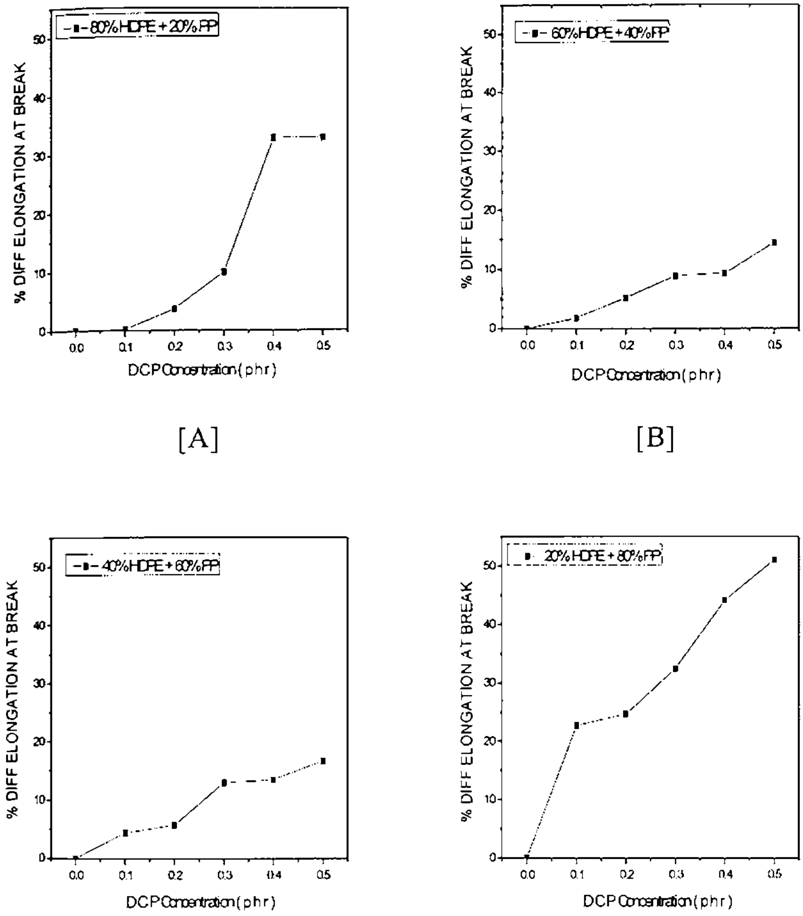
Addition of DCP is found to curtail the elongation at break for all blends studied. In the case of 20% HDPE/80% PP blend, addition of 0.5phr DCP lowers the elongation at break by 50% and for 80%

HDPE/20% PP blend, the lowering is 33%. The other two blends show much lower curtailment of elongation at break.

In the case of 60% HDPE/40% PP blend, addition of 0.1phr DCP decreases the elongation at break by 1.8% and for 40% HDPE/60% PP blend it is 4.4%. A much lower deviation of 0.2% is observed for 80% HDPE/20% PP blend but later the decrement is similar to 20% HDPE/80% PP blend. The effect of 0.4 and 0.5phr DCP are similar (Fig. 3. 31 [A – D]).

Comparison of injection moulded samples prepared at two different temperatures, 180°C and 170°C shows the following variations. The elongation at break of all blends at both temperatures decrease with increase in DCP content. In most cases samples prepared by injection moulding at lower temperature give higher elongation at break.

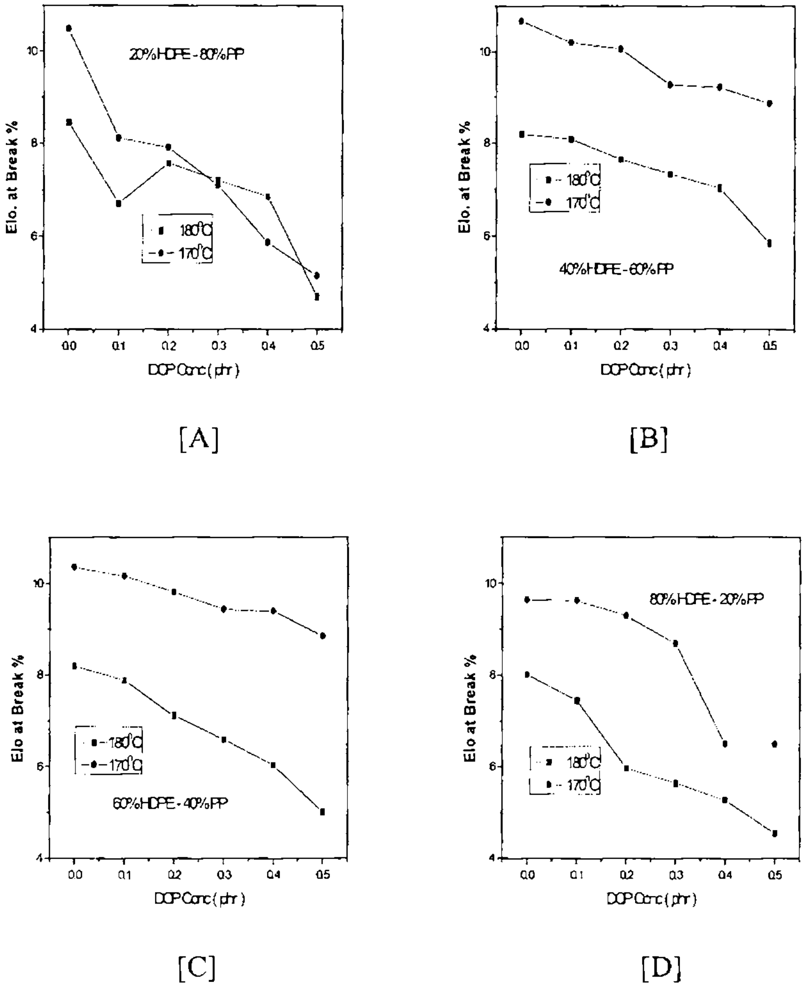
Comparing the elongation at break of 80% HDPE/20% PP blend, it is observed that the presence of 0.2 and 0.3phr DCP in the blend bring out a large increment in value of elongation at break when moulded at 170°C. For 60% HDPE/40% PP blend the increase is observed for each addition of DCP in the case of moulding at 170°C. As the concentration of DCP increases, the increase is found to become larger. In the case of 40% HDPE/60% PP blend, the increase in elongation at break for moulding at 170°C is about 25 – 30% than for moulding at 180°C. The presence of 0.5phr DCP bring out about 50% increase for moulding at 170°C (Fig. 3. 32 [A – D]).



[A] [B]

[C] [D]

Figure 3.31: *[A – D]. % Variation in Elongation at break with DCP concentration for blends injection moulded at 170°C.*



[A] [B]

[C] [D]

Figure 3.32: [A – D]. Comparison of Elongation at break of HDPE - PP blends at 170° and 180°C.

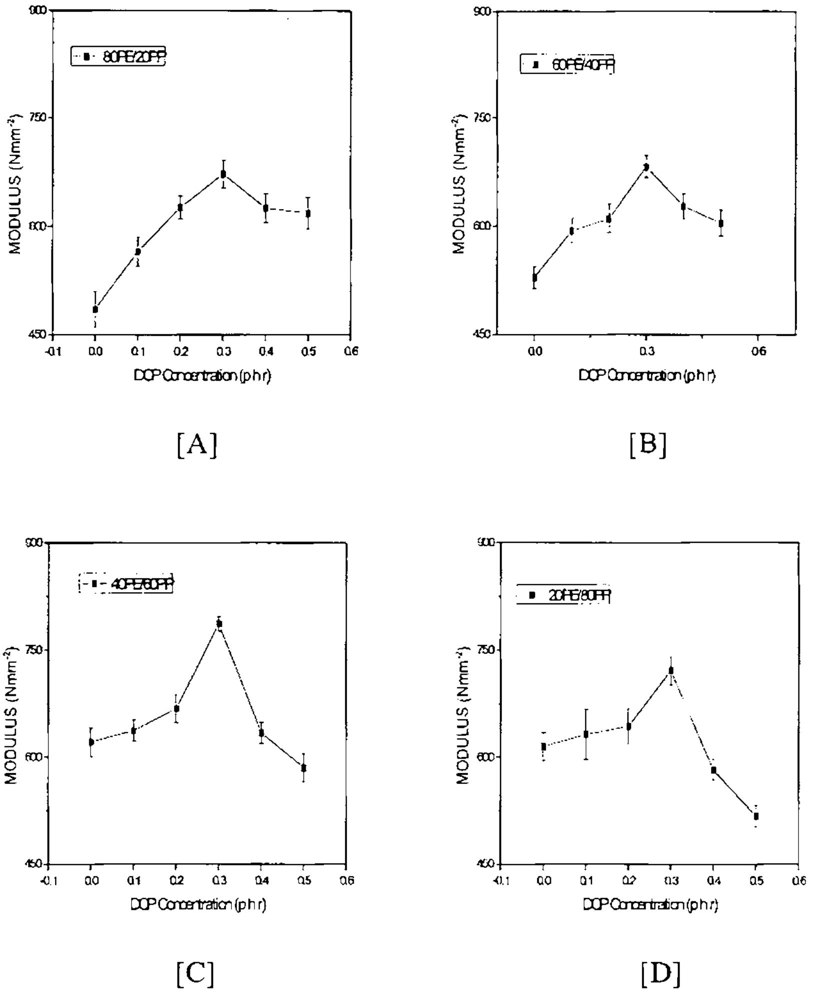
In the case of PP rich blends – 20% HDPE/80% PP – it is observed that the elongation at break for blends containing 0.2 and 0.3phr DCP are lower for moulding at 170°C.

(c) Modulus

The modulus of all four blends studied show an increasing trend on addition of DCP, reach a peak value and then decrease. The maximum increment is observed in the case of addition of 0.3phr DCP and is shown by 80% HDPE/20% PP blend. The modulus values in the case of HDPE rich blends are found to be higher than unmodified blend for all DCP combinations while for PP rich blends, higher DCP combinations – 0.4 and 0.5phr – show lower value than the unmodified blend (Fig. 3. 33 [A – D]).

The modulus of all four blends studied at 170°C show an increasing trend on addition of DCP, reach a peak value and then decrease. In the case of HDPE rich blends, each addition of DCP produces considerable change in modulus values. Addition of 0.3phr DCP to the blends bring out an increase of 38.6% in 80% HDPE/20% PP blend, 29.1% in 60% HDPE/40% PP blend and 26.7% in 40% HDPE/60% PP blend. But in the case of 20% HDPE/80% PP blend, the increase is only 17.2%.

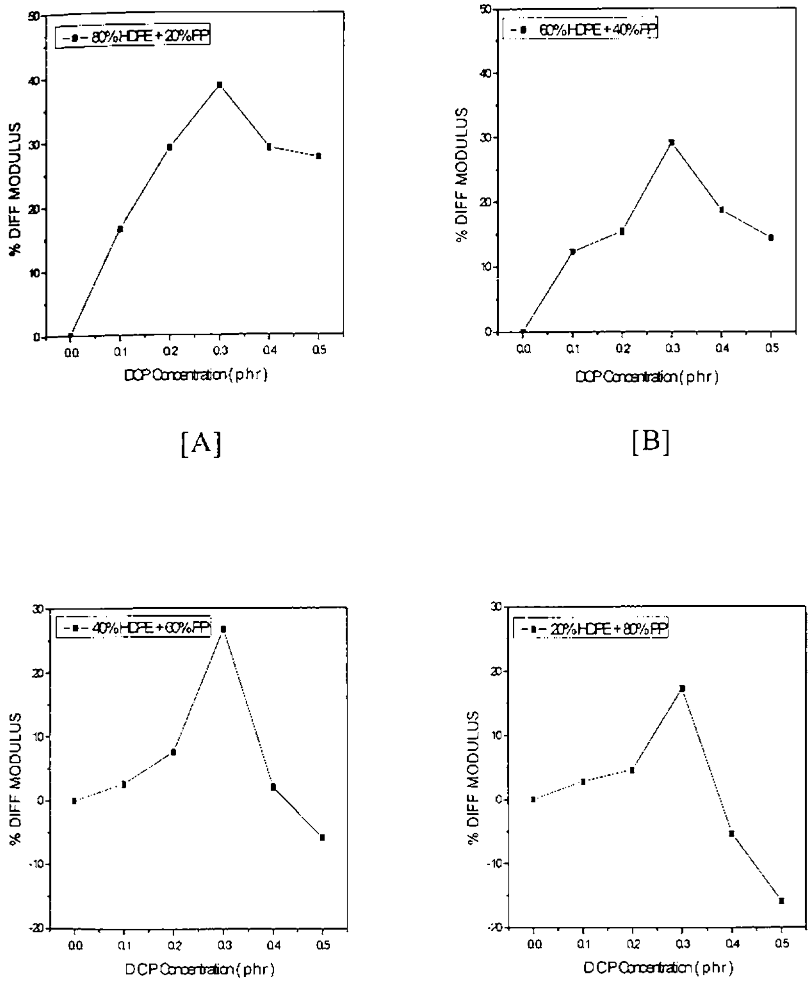
The modulus of all DCP combinations are higher than that of unmodified blend in the case of HDPE rich blends while for PP rich blends high DCP combinations shows the blend to deteriorate in terms of modulus. Addition of 0.5phr DCP to 40% HDPE/60% PP blend curtails modulus by 6% than the unmodified blend. In the case of 20% HDPE/80% PP blend, 0.4phr DCP produce 5.4% and 0.5phr DCP produce 16% curtailment in modulus than the unmodified blend (Fig. 3. 34 [A – D]).



[A] [B]

[C] [D]

Figure 3.33: *[A – D]. Variation in Modulus of HDPE/PP blend with DCP concentration injection moulded at 170°C.*



[A] [B]

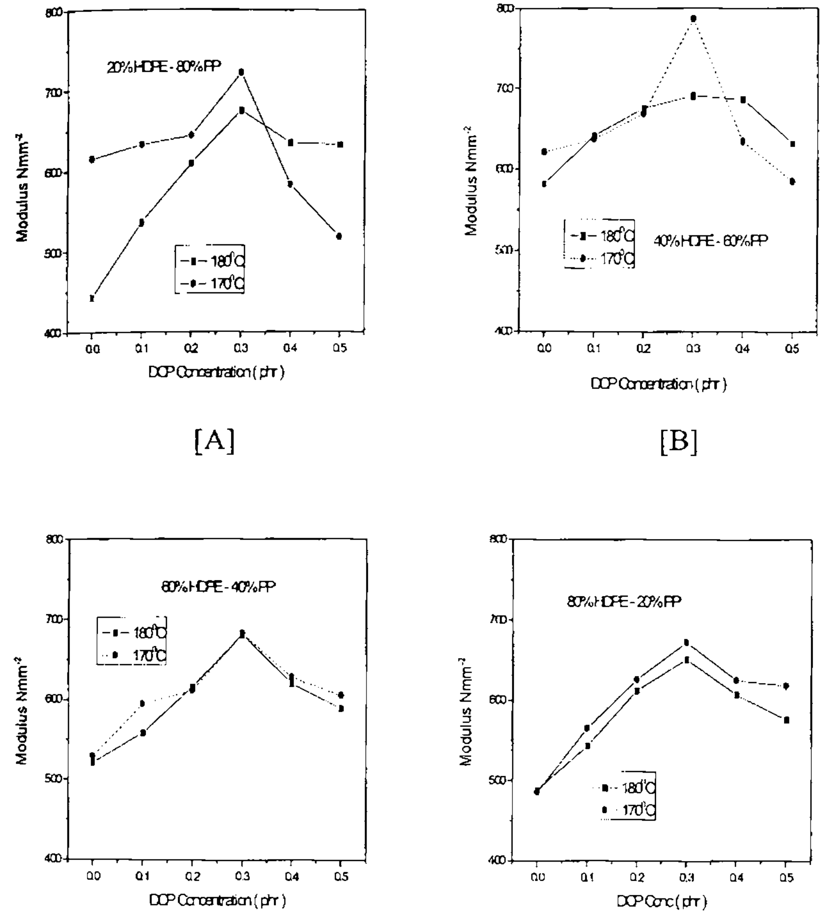
[C] [D]

Figure 3.34: *[A – D]. % Variation in Modulus with concentration of DCP for blends injection moulded at 170°C.*

Comparison of modulus of injection moulded samples prepared at two different temperatures – 180°C and 170°C – show the following observations. At both temperatures, modulus first increases with increase in concentration of DCP and then decreases. The highest value is observed when 0.3phr DCP is added.

Unmodified 80% HDPE/20% PP blend moulded at both temperatures show the same values but when modified with DCP, modulus at 170°C is slightly higher than at 180°C and the increase is 5%. In the case of 60% HDPE/40% PP blend, it is observed that only the composition containing 0.1phr DCP shows some enhancement in modulus when moulded at lower temperature. The composition containing 0.2phr DCP shows decrease in modulus by less than 1% when moulded at lower temperature and in all other cases a slight enhancement is observed.

For 40% HDPE/60% PP blend, low phr DCP combinations shows around 1% decrease in modulus while higher DCP combinations showed around 7.5% decrease. The unmodified blend and blend containing 0.3phr DCP shows enhancement when moulded at 170°C. The 20% HDPE/80% PP blend shows that at low DCP content there is considerable enhancement when moulded at lower temperature while for high DCP content, there is a considerable decrease in modulus when moulded at lower temperature. In fact the unmodified blend shows the highest deviation of 38% increase for moulding at lower temperature (Fig. 3. 35 [A – D]).



[A] [B]

[C] [D]

***Figure 3.35:** [A – D]. Comparison of modulus of HDPE/PP blends on injection moulding at two different temperatures*

3B. FLEXURAL TESTING OF HDPE/PP BLENDS

3B.1 EXPERIMENTAL

The blends of 80% HDPE/20% PP as well as 20% HDPE/80% PP as well as their DCP modifications were subjected to injection moulding in a semi automatic injection moulding machine. The bars so prepared are loaded on a Shimadzu AG II Universal Testing Machine and subjected to three point bending test.

3B.2 RESULTS AND DISCUSSION

3B.2.1 Flexural Strength

Rectangular specimens prepared from 80% HDPE/20% PP as well as 20% HDPE/80% PP blends by injection moulding are subjected to a 3-point bending test on a Shimadzu Autograph AG II Universal Testing Machine and the results are compared. The flexural strength of HDPE as well as PP is curtailed on addition of the other. The flexural strength of 80% HDPE/20% PP shows improvement on addition of DCP. The best result is observed in the case of 0.3phr DCP modification. There after the value shows a slight decline (Fig.3. 36).

The blend 20% HDPE/80% PP on DCP modification shows an improving trend in flexural strength. The flexural strength of 0.3phr DCP modification is nearly equal to that of pure PP and further addition of DCP is found to improve the value. The PP rich blend shows the trend similar to pure PP (Fig.3. 37).

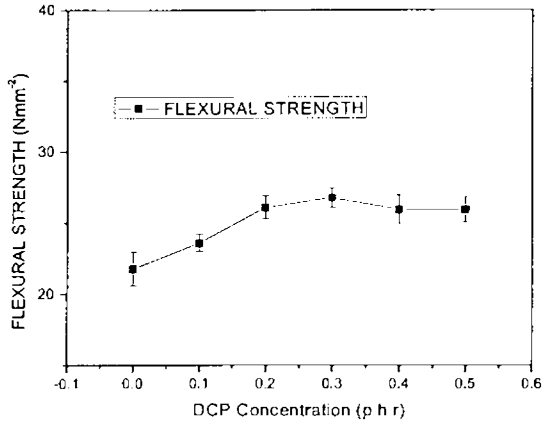


Figure 3.36: Variation in flexural strength of 80% HDPE/20% PP blend with DCP concentration.

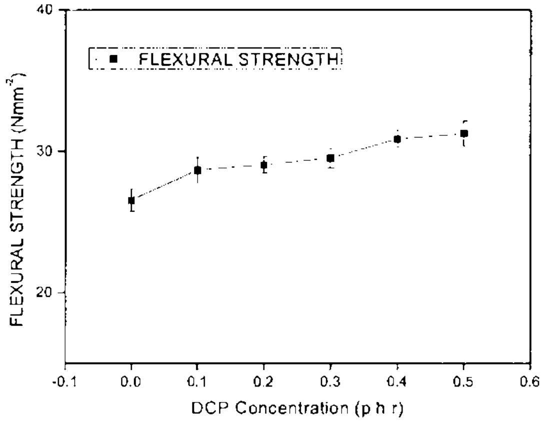
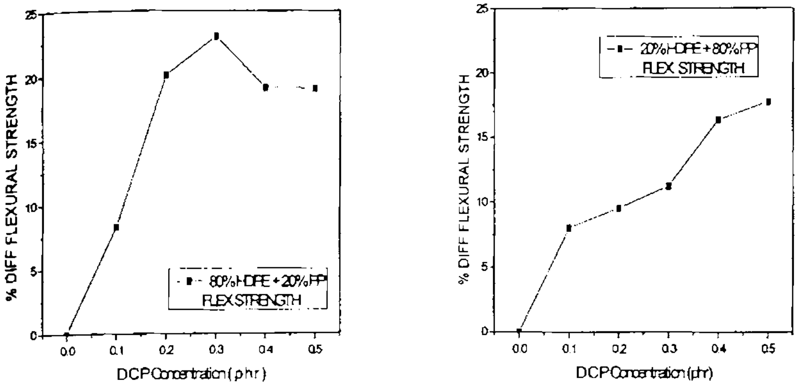


Figure 3.37: Variation in flexural strength of 20% HDPE/80% PP blend with concentration.

The flexural strength of 80% HDPE/20% PP blend is lower than the flexural strength of both pure components. Addition of DCP to the blend is found to enhance the flexural strength, but the values are still lower than that of pure components. Addition of 0.1phr DCP enhances the flexural strength of the blend by 8% and 0.2phr by 20%. The largest improvement of 23% is in the case of the blend containing 0.3phr DCP. Further addition of DCP is found to curtail the flexural strength (Fig.3. 38 [A]).

HDPE and PP form incompatible blends which is the reason for the lowering of flexural strength of the blend. The compatibilizing agent DCP can improve the flexural strength to an extent which is about 7% lower than pure HDPE.

The flexural strength of 20% HDPE/80% PP blend is also lower than that of pure components but DCP is able to modify the blend to such an extent that the flexural strength is higher than that of pure components. It is found that blends containing 0.3, 0.4 and 0.5phr DCP has better values than the pure components. This can be attributed to better compatibilization in the case of this blend in terms of flexural strength (Fig.3. 38 [B]).



[A] [B]

Figure 3.38: *[A] %Variation in flexural strengths of 80% HDPE/20% PP & [B] 20% HDPE/80% PP blends with DCP concentration.*

3B.2.2 Flexural Strain

Pure HDPE and pure PP show a flexural strain of 8.05 and 7.35% respectively. The flexural strain of HDPE is enhanced by the addition of PP while that of PP is curtailed by addition of HDPE. Both blends show similar trends. The flexural strain increase with increase in concentration of DCP, reach a peak value for 0.3phr DCP and then decline. The variation shown by 80% HDPE/20% PP blend (Fig. 3. 39) was much higher than the variation shown by 20% HDPE/80% PP blend (Fig. 3. 40). 80% HDPE/20% PP blend shows a maximum increment of 46.5% over unmodified blend when 0.3phr DCP is added.

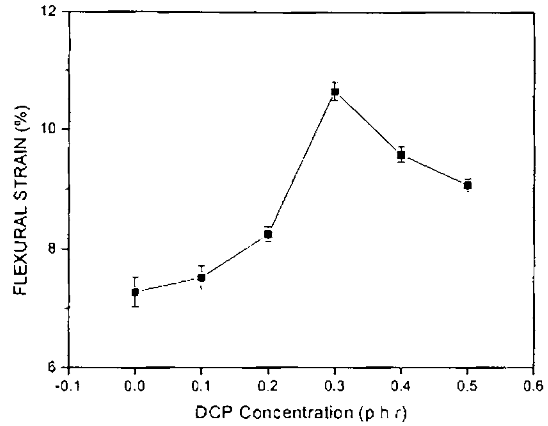


Figure 3.39: Variation in flexural strain of 80% HDPE/20% PP blend with DCP concentration.

The addition of 0.3phr DCP to 20% HDPE/80% PP blend can produce only 17.5% increase.

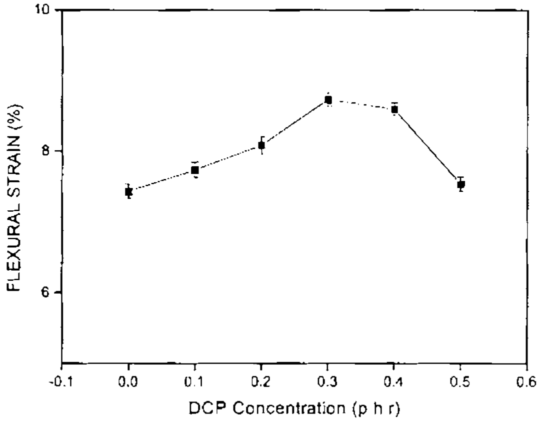
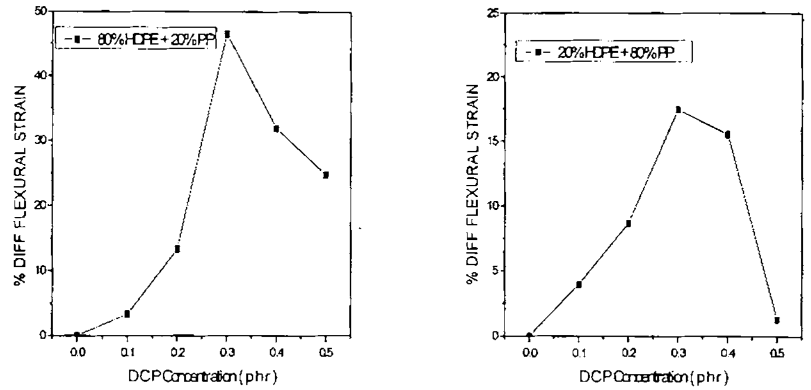


Figure 3.40: Variation in flexural strain of 20% HDPE/80% PP blend with DCP concentration.

The flexural strain of 80% HDPE/20% PP blend is lower than that of pure PP as well as HDPE while for 20% HDPE/80% PP blend the value is in between that of PP and HDPE. The addition of DCP increases the flexural strain for both blends.

Addition of 0.1phr DCP to 80% HDPE/20% PP blend enhances the flexural strain by 3.3% and 0.2phr DCP by 13.3%. The addition of 0.3phr DCP is found to increase the flexural strain by 46.5%. This large increase can be attributed to better phase morphology in the case of blend containing 0.3phr DCP. The flexural strain of blend modified by 0.2, 0.3, 0.4 and 0.5phr DCP are higher than pure HDPE (Fig. 3. 41 [A]).

The 20% HDPE/80% PP blend shows relatively lower improvement on DCP modification when compared to 80% HDPE/20% PP blend. The maximum increment of 17.5% is shown by the blend modified with 0.3phr DCP. The modifications with 0.2, 0.3 and 0.4phr DCP show higher values than pure HDPE. The relatively low improvement in flexural strain of this blend can be attributed to the chain scission taking place in PP, the major component of the blend. This is also supported by the fact that the flexural strain of pure PP decreases with increase in concentration of DCP (Fig. 3. 41 [B]).



[A] [B]

Figure 3.41: *%Variation in flexural strain of [A] 80% HDPE/20% PP and [B] 20% HDPE/80% PP blends with DCP concentration.*

3B.2.3 Flexural Modulus

The flexural modulus is found to be below the value of pure components in the case of both blends. The incorporation of DCP into the blend improves the flexural modulus, the values are still below than that of the pure components. The value is increased with the increase in concentration of DCP, reaches a peak at 0.3phr DCP and then declines (Fig. 3.42). The PP rich blend show larger improvement than HDPE rich blend. The flexural modulus of 20% HDPE/80% PP blend containing 0.3phr DCP is only 2.8% below than that of PP (Fig. 3. 43).

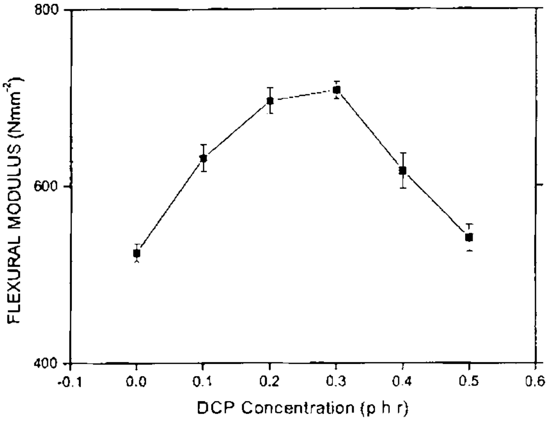


Figure 3.42: Variation in flexural modulus of 80% HDPE/20% PP blend with DCP concentration

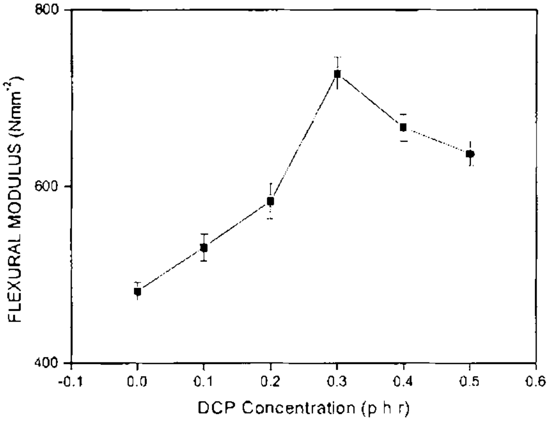
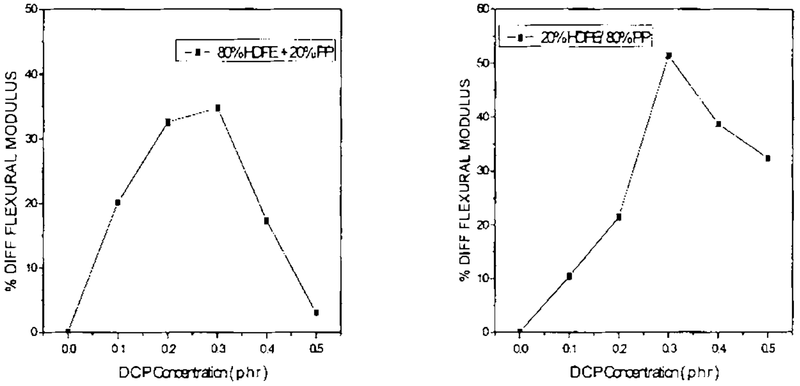


Figure 3.43: Variation in flexural modulus of 20% HDPE/80% PP blend with DCP concentration

The flexural modulus of pure HDPE and PP are 749 and 618 N/mm^2 respectively. Their blends 80% HDPE/20% PP and 20% HDPE/ 80% PP have flexural modulus of 525 and 481 N/mm^2 in order.

The addition of DCP to both blends shows an increasing trend up to 0.3phr and then a receding trend. 80% HDPE/20% PP blend shows a peak value which has an increment of 34.8% than the unmodified blend (Fig. 3. 44 [A]). In the case of 20% HDPE/80% PP blend the peak value is 51.4% above than that of unmodified blend. In all cases the values are below than that of unmodified HDPE (Fig. 3. 44 [b]).



[A] [B]

Figure 3.44: %Variation in flexural modulus of [A] 80% HDPE/20% PP and [B] 20% HDPE/80% PP blends with DCP concentration.

Pure HDPE on modification with DCP shows a steady decrease in flexural modulus while pure PP shows an increasing trend. For 80% HDPE/20% PP blend, the increase in flexural modulus can be attributed to better phase morphology of the blend due to compatibilization by DCP. The larger variation in the case of 20% HDPE/80% PP blend may be attributed to two factors –

1. Compatibilization of the blend by DCP.
2. Increasing trend in flexural modulus of PP on adding DCP.

3C. IMPACT STRENGTH OF HDPE/PP BLENDS

3C.1 EXPERIMENTAL

The blends of 80% HDPE/20% PP as well as 20% HDPE/80% PP as well as their DCP modifications were subjected to injection moulding in a semi automatic injection moulding machine. The bars so prepared were loaded on a RESIL Impact Testing Machine and impact strength measured.

3C.2 RESULTS AND DISCUSSION

The impact strength of polymer blends are studied with the aid of injection moulded specimens. The studies are conducted on 80% HDPE/20% PP and 20% HDPE/80% PP blends. The testing is done using a RESIL Junior Impact Tester. Both blends are modified adding 0.1, 0.2, 0.3, 0.4 and 0.5 phr dicumyl peroxide and impact strength measured (Fig. 3. 45).

It is observed that the impact strength of the HDPE rich blend increases with increase in concentration of DCP, reaches a maximum at 0.3phr and then decreases. In the case of PP rich blend, each increment of DCP shows deterioration in impact strength (Fig. 3. 46).

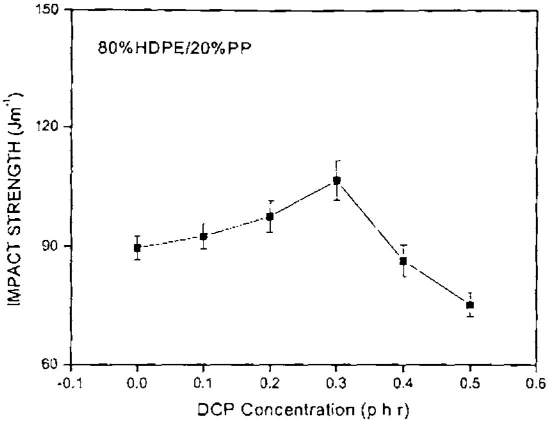


Figure 3.45: *Variation in impact strength of 80% HDPE/20% PP blends with DCP concentration.*

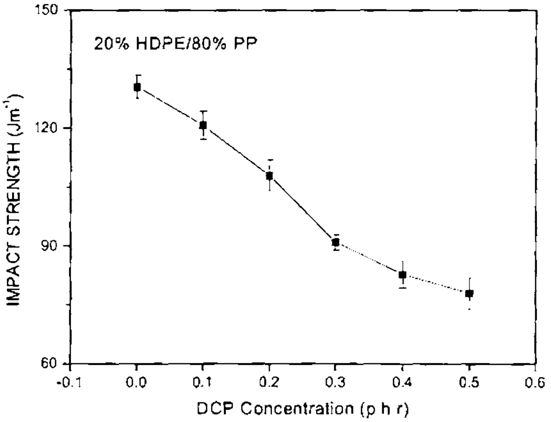


Figure 3.46: *Variation in impact strength of 20% HDPE/80% PP blends with DCP concentration.*

Impact strength of unmodified 80% HDPE/20% PP blend is measured to be 89.5 J/m. Addition of 0.1 phr DCP to the blend shows the impact strength to increase by 3.2% while for 0.2 phr DCP, the increment is 8.8%. A maximum enhancement of 19% is observed for 0.3 phr DCP. Further addition of DCP decreases the impact strength values. The impact strength of the sample modified by 0.4 phr DCP is 3.6% lower than the unmodified blend while for 0.5 phr DCP modification; the value is 15% less (Fig. 3. 47).

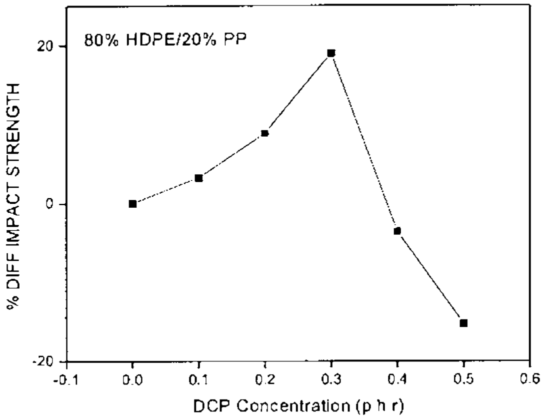


Figure 3.47: % Variation in impact strength of 80% HDPE/20% PP blend with DCP concentration.

Impact strength of 20% HDPE/80% PP blend shows deterioration for DCP modification, the strength decreases with increase in concentration of the modifier. Addition of 0.1 phr DCP loweres the impact strength by 7.5% while for 0.2 phr, the decrease is 17.3% and for 0.3 phr DCP, the value is 30% for 0.4phr, while for 0.5 phr, the value is 40% lowered (Fig. 3. 48).

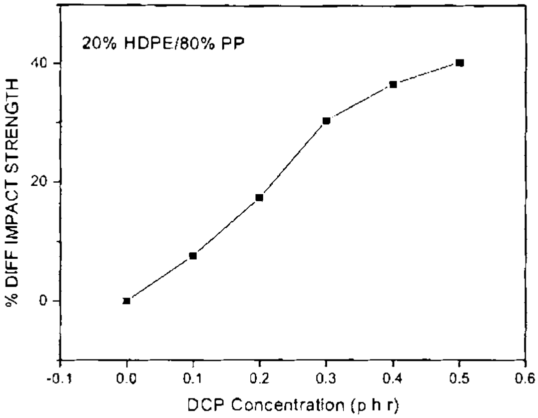


Figure 3.48: *Variation in impact strength of 20% HDPE/80% PP blend with DCP concentration.*

It has been reported that the addition of PP to different PE's improve the Young's modulus and yield stress of the blend [1]. Comparison of tensile strength as a function of melt temperature as well as composition of HDPE/PP blends shows that making blends is a good way to achieve high performance materials with high stiffness and high toughness as well [2]. They shows that the composition as well as melt temperature greatly affects the tensile strength of blends.

It has been reported by Blom *et.al.* that additions of up to 5.5% EPDM to PP resultes in slight increase in impact strength values while the flexural modulus remains nearly the same [3]. The tensile strength of the mixture increases up to 1.1% EPDM concentration and further addition of EPDM shows a decline in property.

The literature survey indicates that addition of EPDM to HDPE/PP blend decreases the flexural modulus. There is no change in the tensile yield strain while yield stress slightly decreases. The impact strength is found to increase with EPDM. The addition of EPDM to about 1% causes increase in ultimate tensile strength, but further addition makes no change. The elongation at break increases with increase in EPDM concentration. The same results are reported by Choudary and others [4].

It has been reported that the addition of 30% PP to HDPE of low melt flow index (HDPE 5) resulted in about 75% increase in flexural modulus and about 70% decrease in impact strength. During addition of PP to HDPE of higher melt flow index (HDPE 65) a slight increase in flexural modulus is observed with increasing PP content. Impact strength reduces drastically. The tensile properties changes with PP concentration [5].

According to Blom *et.al.* flexural modulus of PP is lowered on addition of 7.5% of post consumer resin (PCR), further addition causing no change. Impact strength is increased sharply at this concentration. Further addition of PCR slightly lowers the value which then remains constant. The impact strength of blends is found to be higher than that of i-PP or PCR. This increase is not observed in PP/HDPE blends [6]. It is also observed that EPDM is more effective in improving impact and tensile properties of HDPE / PCR blends but unable to improve them to unmodified HDPE levels [7].

Studies on the properties of 90% HDPE/10% PP blend prepared by extrusion shows that extrusion increases strain at break. Elongation at break as well as impact strength decreases with increase in PP content.

But Young's modulus shows an increasing trend with PP% [8]. These results are consistent with results published by Bartlett *et.al.* [9] and Blom *et.al.* [5].

According to Hettema *et al.*, the addition of peroxide leads to strong deterioration in the mechanical properties. The strain at break and the impact strength shows low values at low concentration of peroxide (0.05phr). A same observation is made by Cheung *et.al.* for the blends of LLDPE and PP. At higher peroxide concentration, cross linking of HDPE phase is predominant showing increase in die-pressure and torque [10].

Studies have shown that for PP – virgin HDPE blend as well as PP – recycled HDPE blend the Young's modulus increases with the HDPE content to a maximum and then decreases due to smaller spherulites. Elongation at break shows no significant changes which reflected incompatibility of the blends. Low impact strength values show poor interfacial adhesion. Studies on blends prepared with 5 to 20% ethylene – propylene copolymer as modifier shows Young's modulus values to decrease on addition of modifier up to 5%, further addition shows the value to be same as for blend without copolymer [11].

A decrease in interfacial thickness leads to a reduction in interfacial tension, due to the action of the block copolymer, its molecular weight and orientation of blocks in the interface [12].

The tensile strength of HDPE/PP blends obtained by oscillating packing injection moulding increases with PP content to 10% and then decreases with further addition of PP. The value is more or less steady after 25% PP. Molecular 'architecture and phase behaviour play an important role in chain orientation; hence, the tensile strength. In the case

PP with a methyl group attached to the carbon – carbon backbone, sser enhancement is seen. When molecular orientation is induced in the mple via oscillating packing injection moulding, the enhancement of nsile strength is achieved [13].

Two major mechanisms prevail in determining the fracture resistance of polymeric materials [14]. One primary contribution comes from the energy required to extend polymer chains, or some subsection thereof to the point of rupture. The deformation and fracture energy can be evaluated by two major experiments – stress-strain and impact resistance. In a stress-strain experiment, the sample is elongated until it breaks. The stress is recorded as a function of elongation. This measurement is relatively slow to the order of a few mm per minute. Impact strength measures the materials resistance to a sharp blow and by definition is a faster experiment. In both experiments, energy is absorbed within the sample by viscoelastic deformation of the polymer chains and finally by the creation of new surface areas [15]. Energy may be absorbed by shear yielding, crazing or cracking.

The crack can grow through the polymer either by breaking the chains or by viscoelastic flow of one chain past the other or by a combination of both these processes. While chain scission is important in the deformation and fracture of many polymers, this micro mechanism normally consumes only a small fraction of the fracture energy but its appearance limits the extent of viscoelastic energy dissipation. Thus for tougher materials, chain scission should be delayed or avoided in favour of molecular relaxations [16].

Investigations on the effect of semi-crystalline PS-b-PB copolymers on the compatibilization of PS/PE blends shows that the impact strength is independent of interfacial strength, but rather controlled by gross phase morphology. The effect of varying the copolymer molecular weight on impact strength of blends containing 5% copolymer were studied and compared the value with that of PS and PS/PE blend. The observed trend was just the reverse of what is expected if the copolymer molecular weight is to determine the impact strength via an increase in interfacial strength. If the molecular weight of the copolymer increased, the phase morphology is found to change from relatively small PS inclusions in PE matrix to large PS inclusions to co-continuous to PS matrix for the blend. As soon as PS forms a continuous phase in the blend, the impact strength of the blend becomes similar to that of pure PS [17].

3D. MORPHOLOGICAL STUDIES

Fig. 3.49 [A & B] show the SEM of unmodified 80% HDPE/20% PP blend and its 0.1phr DCP modified version.

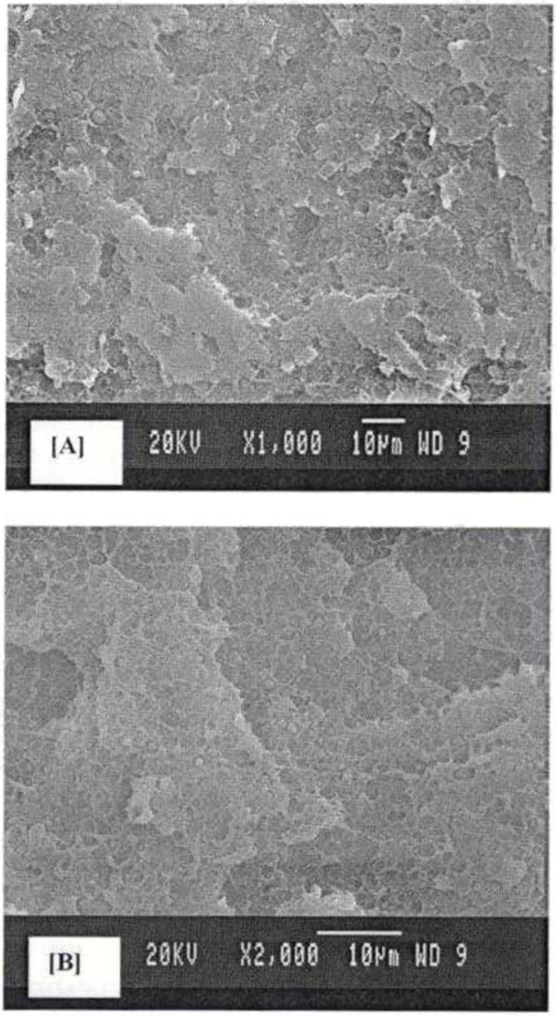


Figure 3.49 *SEM pictures of 80% HDPE 20% PP blend [A] without DCP, [B] with 0.1 phr DCP.*

Introduction of DCP into the blend shows lowering in domain size indicating better dispersion than the unmodified blend – both pictures indicating phase separated morphology.

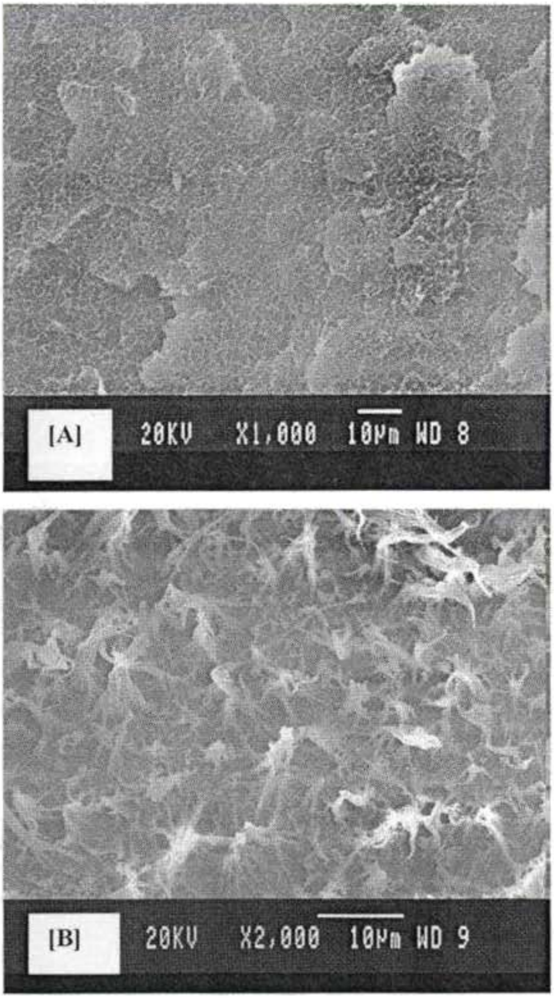


Figure 3.50 *SEM pictures of 80% HDPE 20% PP blend [A] with 0.2 phr DCP, [B] with 0.3 phr DCP.*

Fig. 3.50 [A] shows the 0.2phr DCP modified version of the blend which indicates still smaller domains. Fig. 3.50 [B] shows a regular britlle fracture surface indicating a better phase morphology than the other versions.

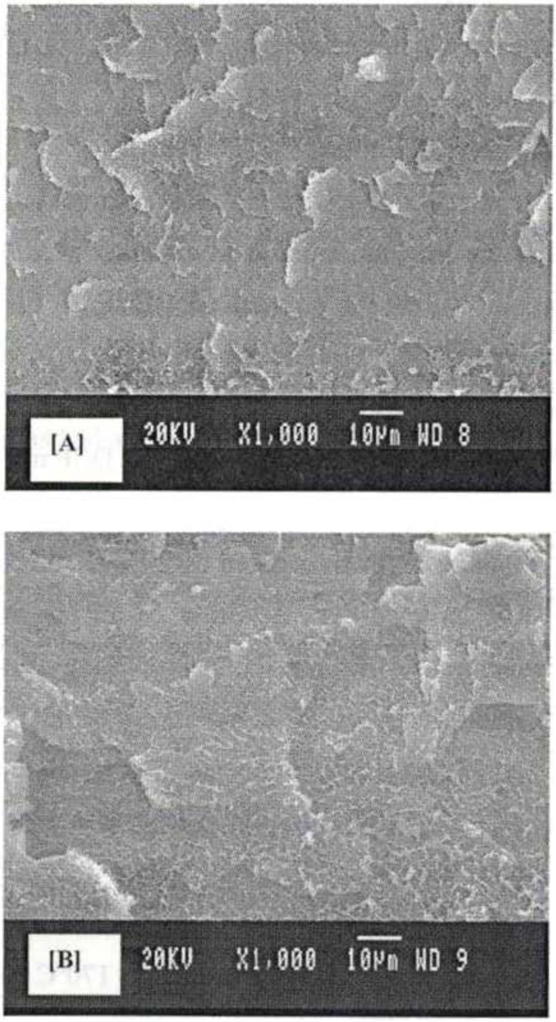


***Figure 3.51** SEM pictures of 80% HDPE 20% PP blend*

·[A] with 0.4 phr DCP, [B] with 0.5 phr DCP.

Fig. 3.51 [A & B] show the 0.4 and 0.5phr DCP modified versions of the blend respectively. These pictures show phase separated morphology.

3.2 CONCLUSIONS

The torque is found to increase for HDPE rich blends and decrease in PP rich blends on addition of DCP.

3.2.1 Extrusion at 180°C

The tensile strength of HDPE is found to increase with incorporation of PP and the maximum value is obtained at 20% HDPE/80% PP combination. The tensile strength of HDPE/PP blends increase with concentration of DCP reaches a peak value at 0.3phr DCP and then decreases. 0.2 and 0.3 phr DCP modifications of 20% HDPE/80% PP as well as 40% HDPE/60% PP and 0.3 phr DCP modifications of 60% HDPE/40% PP shows greater tensile strength than pure PP. The highest tensile strength is recorded by 20% HDPE/80% PP blend with 0.3phr DCP as modifier. Addition of PP to HDPE lowers the elongation at break of the blends. Incorporation of DCP further lowers the elongation at break. The modulous of HDPE increases with increase in PP level in the blend. The modulous of each blend increases with DCP concentration, reaches a maximum value at 0.3phr DCP and then decreases.

3.2.2 Extrusion at 170°C

Tensile strength of the blends extruded at 170°C shows similar trend with extrusion at 180° C .The values were lower at 170°C. Elongation at break shows similar trend, the values lower at 170°C. The modulous of PP rich blend decreases on incorporation of DCP whereas for HDPE rich blends, no regular pattern is obtained.

3.2.3 Injection moulding

Injection moulding at 170° and 180°C show 40% HDPE/60% PP blend to have the highest tensile strength. The modulous showed a trend similar to tensile strength. The values obtained are lower at 170°C.

3.2.4 Flexural strength of blends

The flexural strength, strain and modulous of 80% HDPE/20% PP blend increase with increase in DCP concentration and a peak value is obtained at 0.3 phr DCP level. The flexural strength and strain of 20% HDPE/80% PP blend increases with DCP concentration.The flexural modulous had a peak value at 0.3phr DCP and then decreases.

3.2.5 Impact Strength

The impact strength of 80% HDPE/20% PP blend increases with DCP to a peak value at 0.3phr level and then decreases. The impact strength of 20% HDPE/80% PP blend decreases with increase in DCP concentration

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CHAPTER 4

RHEOLOGICAL AND THERMAL STUDIES OF UNMODIFIED AND MODIFIED HDPE/PP BLENDS

4A. RHEOLOGICAL PROPERTIES

4A.1 INTRODUCTION

Most plastic melts, solutions or dispersions exhibit pseudoplastic flow behaviour. At rest, long chain molecules of a plastic melt, solution or dispersion are engaged into stable association as a consequence of chain entanglement and due to molar cohesion. At low shear rates the stress required to overcome or undo the effect of chain entanglement is relatively high, but proportionaly lower stress is required to allow the melt, solution or dispersion flow at higher strain rate once the molecules are set in motion with respect to each other. The entanglement effect becomes virtually non-existent and almost Newtonian behaviour is shown at higher shear rates depending on the exact nature of fluid materials. If allowed to stand at rest, the fluid material set again and is called thixotropy.

During processing of plastics at different temperatures and different pressures by different approaches and techniques such as extrusion, injection and compression moulding, blow moulding etc, we come across diverse flow behaviour of the material. Each process or technique involves at different stages of operation, a critical and delicate relation between temperature, applied stress and viscosity of the material. Thus a thorough study of rheological characteristics is necessary for the satisfactory operation and control of such processes. The reduction of viscosity with increasing shear rate is taken advantage in many types of equipment without raising the temperature to detrimental levels.

Measurement of rheological properties of fluids takes into account two points –

1. The fluid must be sheared at measurable rates and
2. The stress developed must be known. This can be accomplished using a capillary or extrusion rheometer or rotational rheometer.

Capillary or extrusion rheometers are useful in the studies of melt viscosities of thermoplastics and selected elastomer systems if selection of appropriate range of temperature and shear rates is permissible. A sample in powder, granule or other form is loaded into an extrusion cylinder or chamber and is heated to a specific temperature using thermostatic control. On attainment of temperature equilibrium, the melt is forced by a plunger through a cylinder or a capillary die attached at the bottom. The pressure on the plunger is a measure of shear stress. The plunger is allowed to move at a constant pre-set speed covering the desired range of shear rate. The amount of fluid extruded per unit time is a measure of the rate of shear.

4A.2. EXPERIMENTAL

4A.2.1 Blend preparation

Four blend compositions – 80% HDPE/20% PP; 60% HDPE/40% PP; 40% HDPE/60% PP and 20% HDPE/80% PP – unmodified as well as modified are prepared by melt blending. DCP is added at different amounts to give 0.1, 0.2, 0.3, 0.4 and 0.5phr concentrations respectively and blended in the mixing chamber of a Thermo Haake Rheomix 600P blender set at 180°C to form the modified blends. The hot polymer blend taken out from the mixing chamber is passed through a laboratory size two roll mill. The sheet form so obtained was cut to small pieces and subjected to rheological studies.

4A.2.2 Rheological studies

The melt flow measurements are carried out on a capillary rheometer connected to a Shimadzu AG I Universal Testing Machine with a load cell of capacity 50kN. The plunger is set to move at six set speeds ranging from 1–500mm/min. A capillary made of tungsten carbide with a capillary of length 40mm and diameter 1mm (L/D ratio = 40) is placed inside the barrel at an angle of entry 90°. The shear viscosities at six different shear rates are obtained from a single charge of the material. The measurements are carried out at three different temperatures 170°C, 180°C and 190°C.

4A.2.3 Extrudate swell studies

The extrudate from the capillary rheometer are carefully collected at all six shear rates. The samples are allowed to cool and the diameter of the extrudate is measured after 24 hours using a traveling microscope. The extrudate swell ratio is determined according to the ratio,

Extrudate swell ratio = Diameter of the extrudate / Diameter of the capillary.

4A.3. RESULTS AND DISCUSSION

Melt viscosity data of HDPE/PP blends of four different compositions namely 80% HDPE/20% PP; 60% HDPE/40% PP; 40% HDPE/60% PP and 20% HDPE/80% PP are obtained from the capillary rheometer studies at three different temperatures 170°C, 180°C and 190°C.

4A.3.1 Effect of Shear Stress on Shear Viscosity

It is observed that shear viscosity values decreases with increase in shear stress. This behaviour is exhibited by all four blends as well as their peroxide modifications at the three study temperatures 170°C, 180°C and 190°C.

The shear viscosity of 20% HDPE/80% PP blend at 170°C [Fig 4.1] is 2.9×10^{4} Nmm^{2} at a shear rate of $13.33 s^{-1}$ which decreases to 2.2×10^{5} Nmm^{2} at a shear rate of $6667 s^{-1}$. This decrement is observed for the blend modified with 0.1 and 0.2 phr dicumyl peroxide. But the blend modification with 0.3, 0.4 and 0.5 phr dicumyl peroxide shows only lesser depreciation.

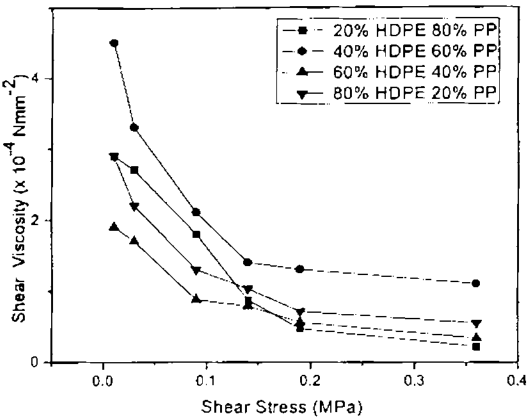


Figure 4.1: *Variation of Shear Viscosity with Shear Stress for the HDPE/PP blends at 170°C.*

The same trend in shear viscosity against shear stress is observed in the case of 40% HDPE/60% PP blend. The shear viscosity of 4.5 x 10^{4} Nmm^{-2} decreases to 1.1 x 10^{4} Nmm^{-2} as the shear rate of 13.33 s^{-1} increases to 6667 s^{-1}. Similar depreciation is observed for all DCP modifications of the blend.

In the case of 60% HDPE/40% PP blend, the shear viscosity varies from 1.9 x 10^{-4} Nmm ^{2} to 3.4 x 10^{-5} Nmm^{-2} for the same change in shear rate while for 80% HDPE/20% PP blend, the decline is from 2.9 x 10^{4} Nmm^{-2} to 5.5 x 10^{-5} Nmm^{-2}.

The same trend is observed for viscosity measurements at 180^{0}C [Fig.4.2]. For 20% HDPE/80% PP blend, the change is from 2.39 x 10^{-4} Nmm ^{2} at a shear rate of 13.33/s to 3.3 x 10^{5} Nmm^{-2} at 6667 s^{-1}. In the case of 40% HDPE/60% PP blend, the fall is from 4.38 x 10^{4} Nmm^{-2} to 7.8 x 10^{-5} Nmm ^{2}, for 60% HDPE/40% PP blend, 1.8 x 10^{4} Nmm ^{2} to 3.5

x 10^{-5} Nmm^{-2} and for 80% HDPE/20% PP blend, the change is from $2.82x10^{-4}$ Nmm^{-2} to 3.2 x 10^{-5} Nmm^{-2}. On moving from a shear rate of 13.33 s^{-1} to 6667 s^{-1}, there is a depreciation of around 600%.

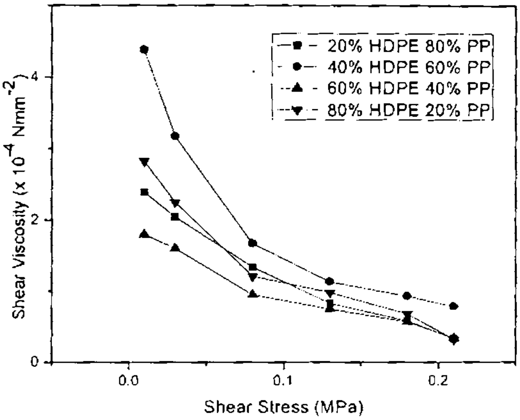


Figure 4.2: Variation of Shear Viscosity against Shear Stress for the HDPE/PP blends at 180°C.

Similar trend is observed when viscosity is measured at 190°C [Fig.4.3]. The reduction in viscosity of 20% HDPE/80% PP blend is from $2.29x10^{-4}$ Nmm^{-2} to 3.9 $x10^{-5}$ Nmm^{-2}, 40% HDPE/60% PP blend shows a reduction from $2.41x10^{-4}$ Nmm^{-2} to $4.5x10^{-5}$ Nmm^{-2}, 60% HDPE/40% PP blend shows a decline from $1.73x10^{-4}$ Nmm^{-2} to 2.5x 10^{-5} Nmm^{-2} while for 80% HDPE/20% PP blend, the value retrenches from $2.51x10^{-4}$ Nmm^{-2} to $3.2x10^{-5}$ Nmm^{-2}.

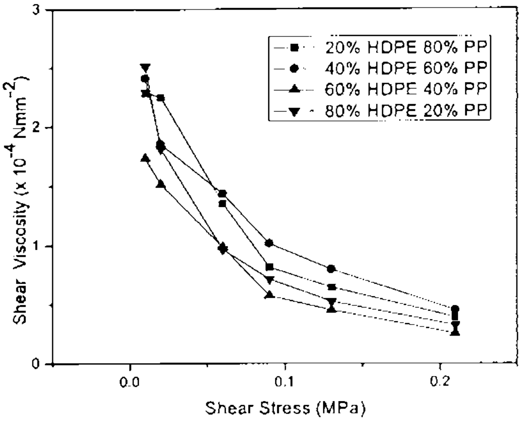


Figure 4.3: *Variation of Shear Viscosity against Shear Stress for the HDPE/PP blends at 190^{0}C.*

4A.3.2 Effect of Temperature on Shear Viscosity

The shear viscosity values of the blends are studied at a shear rate of 1333s^{-1} [Fig.4.4] shows that 40% HDPE/60% PP blend has high viscosity at 170^{0}C, 180^{0}C and 190^{0}C. The value of shear viscosity is 1.4x 10^{-4} Nmm^{-2} at 170^{0}C, 1.13x10 ^{4} Nmm ^{2} at 180^{0}C and 1.01x10 ^{4} Nmm ^{2} at 190^{0}C. The lowest value of shear viscosity is for 60% HDPE/40% PP blend, the values being 7.9x10 ^{5}, 7.5x10^{-5} and 5.7x10^{-5} Nmm^{-2} at 170^{0}C, 180^{0}C and 190^{0}C respectively.

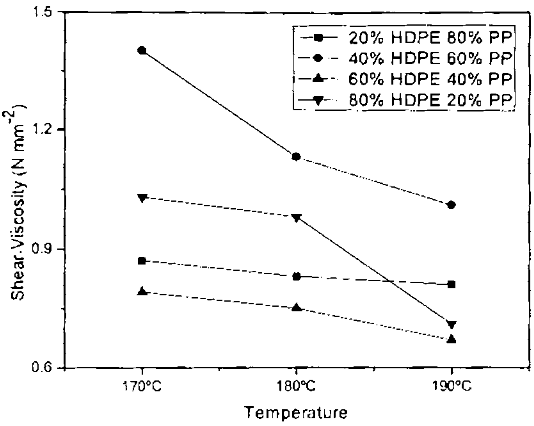


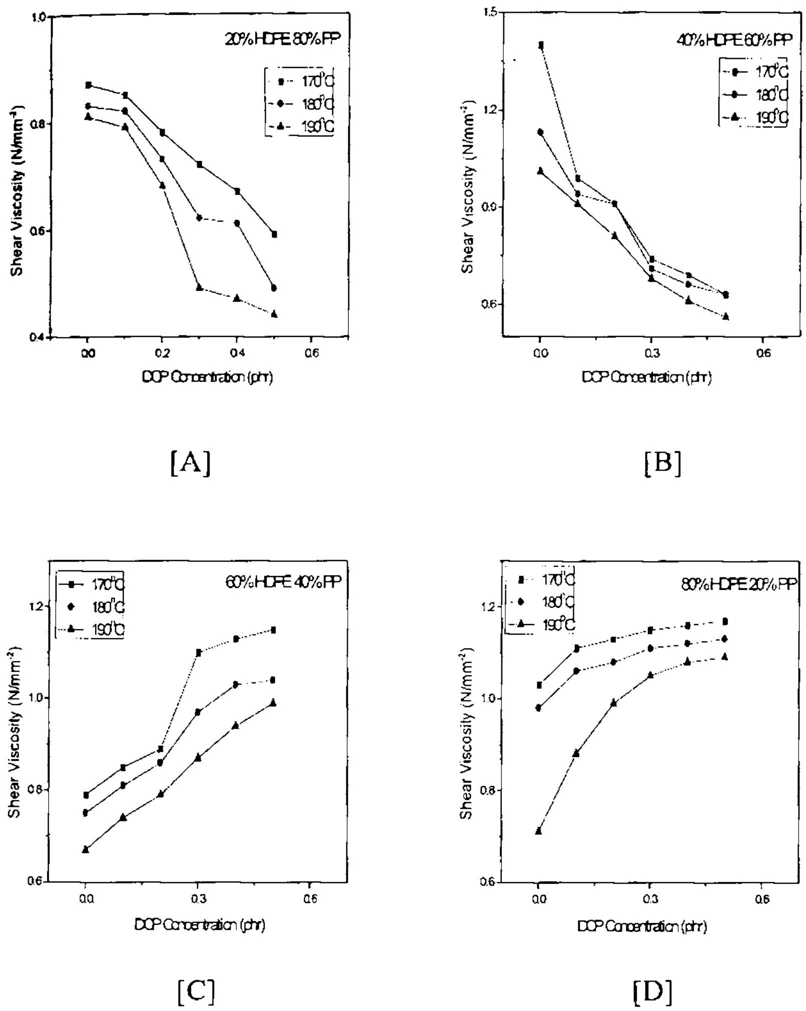
Figure 4.4: Variation of Shear Viscosity with Temperature for HDPE/PP blends.

The shear viscosities for 20% HDPE/80% PP blend are 8.7x10^{-5}, 8.3x10^{-5} and 8.1x10^{-5} Nmm^{-2} at 170^{0}C, 180^{0}C and 190^{0}C whereas for 80% HDPE/20% PP blend, the values are 1.03x10^{-5}, 9.8x10^{-5}, and 7.1x 10 ^{5} Nmm^{-2} at 170^{0}C, 180^{0}C and 190^{0}C respectively.

4A.3.3 Effect of Dicumyl Peroxide Modification on Shear Viscosity

All the four combinations of the blend are modified using DCP at different compositions such as 0.1, 0.2, 0.3, 0.4 and 0.5 phr and viscosity is measured at three different temperatures - 170^{0}C, 180^{0}C and 190^{0}C.

It is observed that in the case of PP rich blends - 20% HDPE/80% PP and 40% HDPE/60% PP blends – shear viscosity shows a fall as the concentration of DCP increases. In the case of 60% HDPE/40% PP blend, the addition of DCP increases the shear viscosity up to a concentration of 0.3 phr and then decreases. But for 80% HDPE/20% PP blend, the shear viscosity values show a steady augmentation on addition of DCP [Fig.4.5 A – D]. The same is observed at all shear rates.

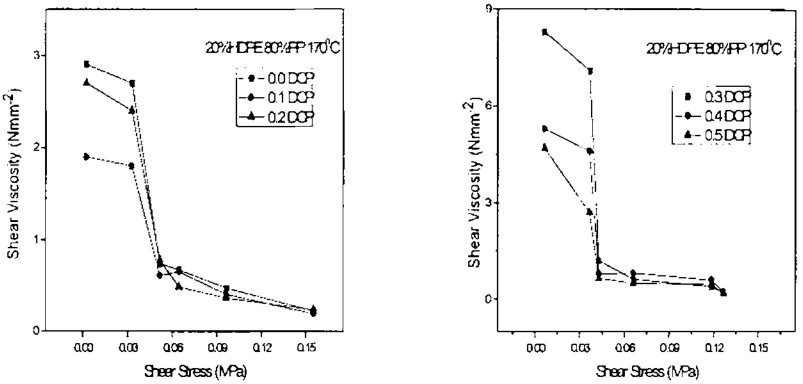


[A] [B]

[C] [D]

Figure 4.5: *[A – D] Variation of Shear Viscosity with DCP concentration for the HDPE/PP blends at a shear rate of 1333s^{-1}.*

When 20% HDPE/80% PP blend is modified using DCP, the shear viscosity of unmodified blend shows a value of 2.9x10^{-4} Nmm^{-2} which decreases to 1.1x10^{-4} Nmm^{-2} at a shear rate of 13.33s^{-1}; 2.7x10^{-4} Nmm^{-2} to 9.1x10^{-5} Nmm^{-2} at 133.33s^{-1}; 1.8x10^{-4} Nmm^{-2} to 6.4x10^{-5} Nmm^{-2} at 666.7s^{-1}; 8.7x10^{-5} Nmm^{-2} to 5.9x10^{-5} Nmm^{-2} at 1333s^{-1}; 4.7x 10^{-5} Nmm^{-2} to 3.8x10^{-5} Nmm^{-2} at 2666s^{-1} and 2.2x10^{-5} Nmm^{-2} to 1.9x 10^{-5} Nmm^{-2} at 6667s^{-1} [Fig 4.6 A & B].

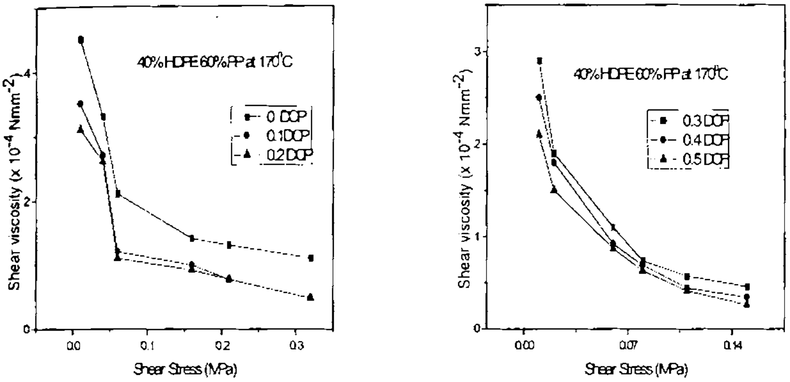


[A] [B]

Figure 4.6: *[A & B] Comparison of Shear viscosity with Shear Stress variation of 20% HDPE/80% PP blend at different concentrations of DCP at 170°C.*

A similar trend in depreciation of shear viscosity is observed in the case of 40% HDPE/60% PP blend. The decrement observed is from 4.5x10^{-4}Nmm^{-2} to 2.1x10^{-4} Nmm^{-2} at a shear rate of 13.33s^{-1} for DCP concentration increasing from 0 to 0.5 phr. Shear viscosity of the blend is lowered from 1.1x10^{-4} Nmm^{-2} to 2.6x10^{-5} Nmm^{-2} at a shear rate of 6667s^{-1} [Fig. 4. 7 A & B].

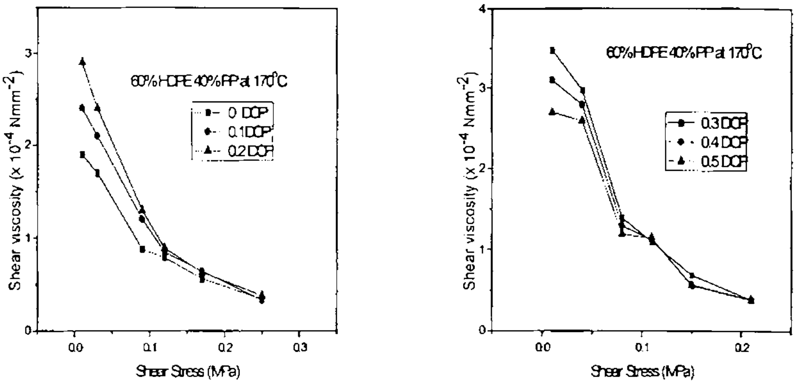
The shear viscosity determination of 60% HDPE/40% PP blend shows a different trend from the previous two blends examined. At low shear rates of 13.33, 133.33 and 666.7s^{-1}, viscosity increases to a maximum at 0.3 phr DCP and then decreases.



[A] [B]

Figure 4.7: [A & B] Comparison of Shear viscosity with Shear Stress variation of 40% HDPE/60% PP blend at different concentrations of DCP at 170°C.

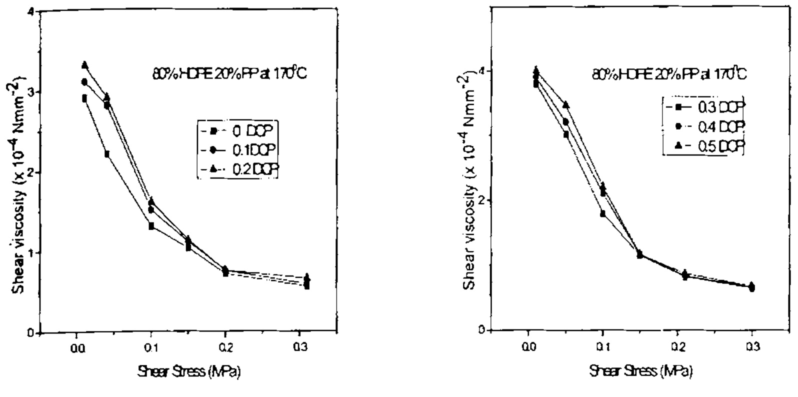
At the lowest shear rate of 13.33s^{-1}, the shear viscosity of unmodified blend measures 1.9 x 10^{-4} Nmm^{-2} which increases to 3.48 x 10^{-4} Nmm^{-2} at 0.3 phr DCP and then decreases to 2.7 x 10^{-4} Nmm^{-2} at 0.5 phr DCP. Similar trend is observed at other shear rates too. At a shear rate of 1333s^{-1}, the shear viscosity shows a steady augmentation at all DCP concentrations. Even at 0.5 phr DCP, the modified blend has shear viscosity greater than for the neat blend [Fig. 4.8 A & B].



[A] [B]

Figure 4.8:[A & B] Comparison of Shear viscosity with Shear Stress variation of 60% HDPE/40% PP blend at different concentrations of DCP at 170°C.

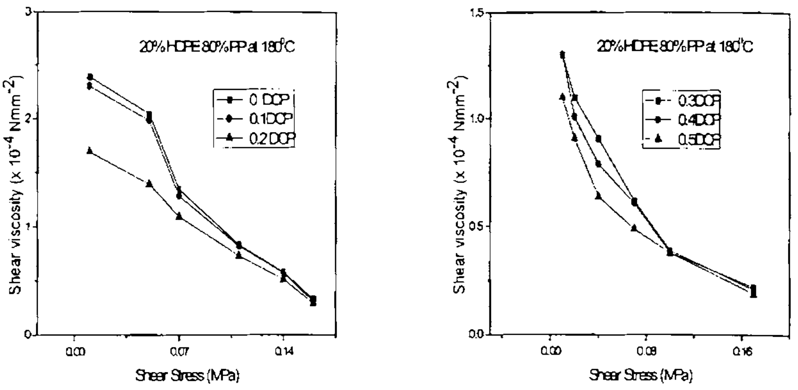
When 80% HDPE/20% PP blend is studied at 170°C, the shear viscosity values enhances with increase in concentration of DCP. The enhancement are 2.9 x 10^{-4} Nmm^{-2} to 4.0 x 10^{-4} Nmm^{-2} at 13.33s^{-1}, 2.2 x 10^{-4} Nmm^{-2} to 3.46 x 10^{-4} Nmm^{-2} at 133.3s^{-1}, 1.3 x 10^{-4} Nmm^{-2} to 2.2 x 10^{-4} Nmm^{-2} at 666.7s^{-1}, 1.03 x 10^{-4} Nmm^{-2} to 1.17 x 10^{-4} Nmm^{-2} at 1333s^{-1}, 7.1 x 10^{-5} Nmm^{-2} to 8.7 x 10^{-5} Nmm^{-2} at 2666s^{-1} and 5.5 x 10^{-5} Nmm^{-2} to 6.8 x 10^{-5} Nmm^{-2} at 6667 s^{-1} [Fig. 4.9 A & B].



[A] [B]

Figure 4.9:[A & B] Comparison of Shear viscosity with Shear Stress variation of 80% HDPE/20% PP blend at different concentrations of DCP at 170°C.

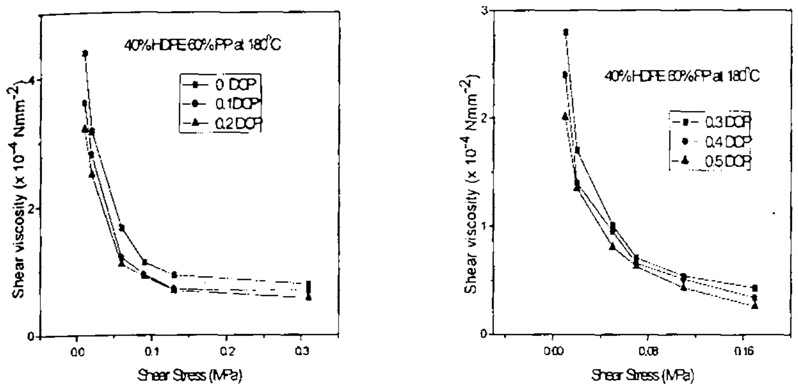
The shear viscosity measurements at 180°C of 20% HDPE/80% PP blend shows a decreasing trend with increase in concentration of DCP at all shear rates. The neat blend shows a shear viscosity of 2.39 x 10^{-4} Nmm^{-2} which decreases to 1.1 x 10^{4} Nmm^{-2} as the shear rate increases from 13.33 s^{-1} to 6667 s^{-1} [Fig 4.10 A & B]. A similar trend is observed in the case of 40% HDPE/60% PP blend. The neat blend shows a shear viscosity of 4.38 x 10^{-4} Nmm^{2} which decreases to 2.01 x 10^{-4} Nmm^{-2} as the shear rate increases from 13.33 s^{-1} to 6667 s^{-1} [Fig 4.11 A & B].



[A] [B]

Figure 4.10: *[A & B] Comparison of Shear viscosity with Shear Stress variation of 20% HDPE/80% PP blend at different concentrations of DCP at 180°C.*

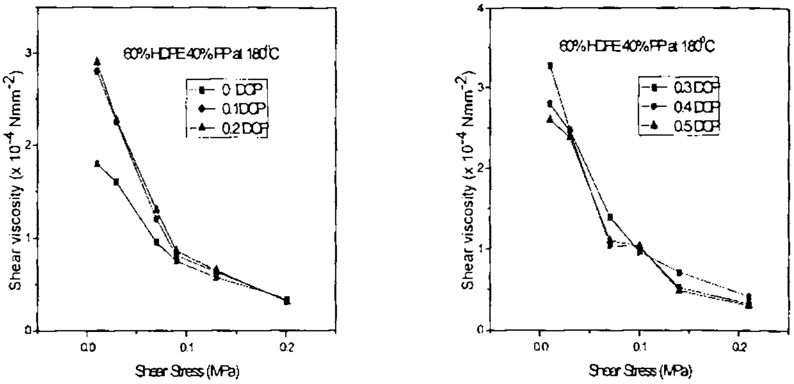
Viscosity values of 60% HDPE/40% PP blend shows a different trend. Viscosity increases to a maximum at 0.3 phr DCP and then decreases. The virgin blend has a shear viscosity of 1.8 x 10^{-4} Nmm ^{2} at 13.33 s^{-1} which increases to 3.28 x 10^{-4} Nmm ^{2} at 0.3 phr DCP and then decreases to 2.6 x 10^{-4} Nmm ^{2} at 0.5 phr DCP. The blend with 0.5 phr DCP has higher viscosity than the untreated blend. This trend is shown by the blend at shear rates 13.33s^{-1}, 133.3s^{-1}, 666.7s^{-1} and 1333s^{-1}, the shear viscosity slightly lower than untreated blend at higher shear rates [Fig 4.12 A & B].



[A] [B]

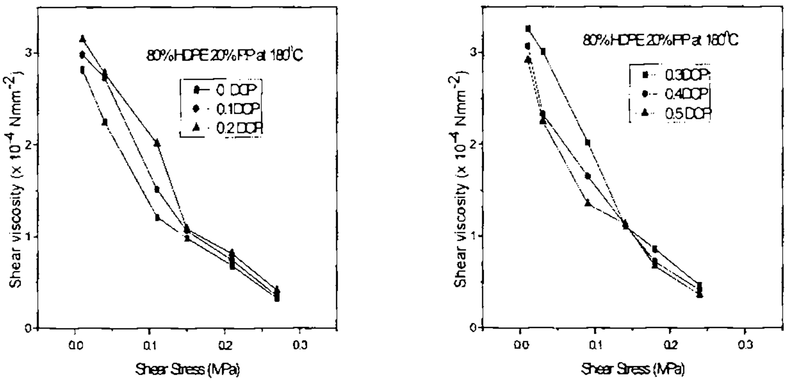
Figure 4.11: *[A & B] Comparison of Shear viscosity with Shear Stress variation of 40% HDPE/60% PP blend at different concentrations of DCP at 180°C.*

The shear viscosity of 80% HDPE/20% PP blend also shows similar trend as 60% HDPE/40% PP blend. The untreated blend has a shear viscosity of 2.82 x 10^{4} Nmm^{-2} at 13.33 s^{-1} which increases to 3.26x 10^{-4} Nmm^{-2} at 0.3 phr DCP and decreases to 2.92 x 10^{4} Nmm^{2} at 0.5 phr DCP at the same shear rate. Similar trend is observed at all shear rates [Fig 4.13 A & B].



[A] [B]

Figure 4.12: [A & B] Comparison of Shear viscosity with Shear Stress variation of 60% HDPE/40% PP blend at different concentrations of DCP at 180°C.



[A] [B]

Figure 4.13: [A & B] Comparison of Shear viscosity with Shear Stress variation of 80% HDPE/20% PP blend at different concentrations of DCP at 180°C.

The measurement of shear viscosity at 190°C for all the four blends shows a decreasing trend in viscosity with an increase in shear rates [Fig 4.14].

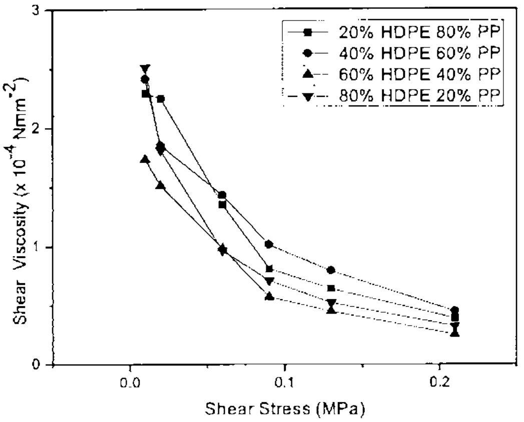
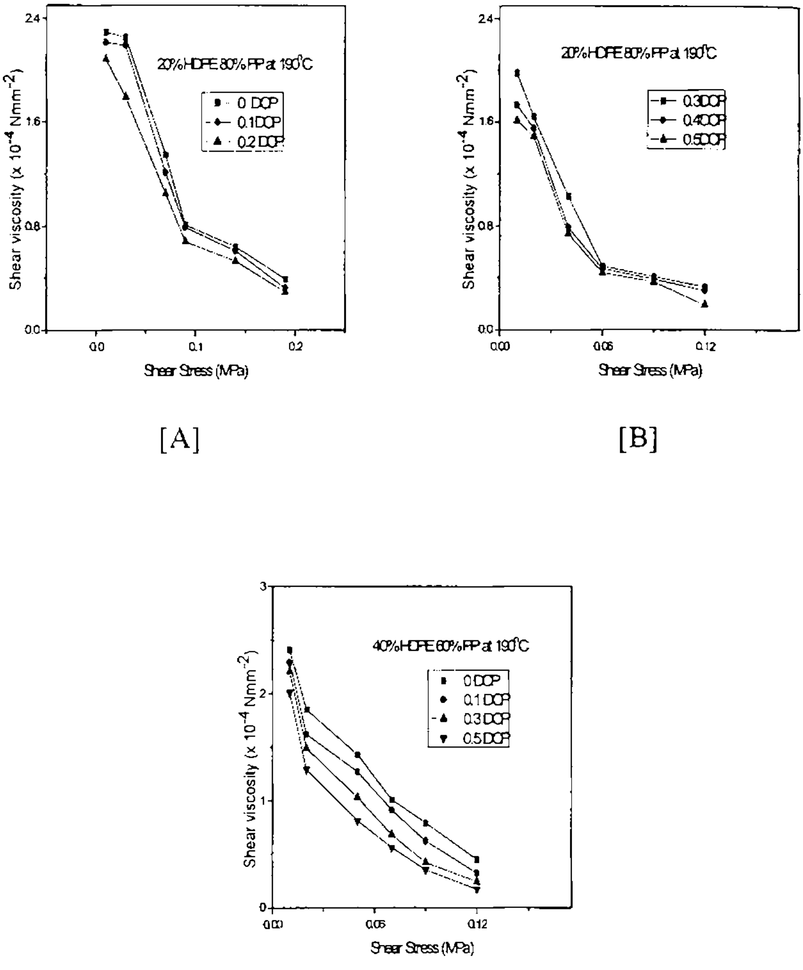


Figure 4.14: Shear viscosity with shear stress of HDPE/PP blends at 190°C

The blends of compositions 20% HDPE/80% PP as well as 40% HDPE/60% PP show a declining trend in shear viscosity as the concentration of DCP increases [Fig 4.15 A, B and C]. But for 60% HDPE/40% PP and 80% HDPE/20% PP blends, the shear viscosity increases to a maximum at 0.3 phr DCP and then declines at higher DCP concentrations [Fig 4.16 A & B].

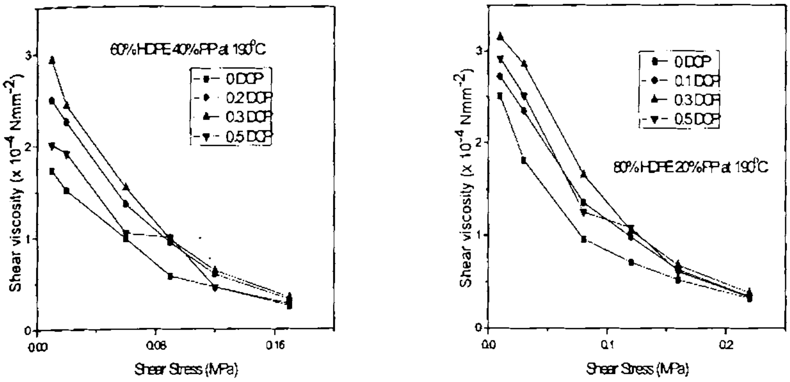


[A]

[B]

[C]

Figure 4.15: *[A, B & C] Comparison of Shear viscosity with Shear Stress variation of 20% HDPE/80% PP and 40% HDPE/60% PP blends at different concentrations of DCP at 190°C.*



[A] [B]

Figure 4.16: *[A & B] Comparison of Shear viscosity with Shear Stress variation of 60% HDPE/40% PP and 80% HDPE/20% PP blend at different concentrations of DCP at 190°C.*

The viscosity of polymer blends depends upon interfacial adhesion, interfacial thickness and the characteristics of the components forming the blend. When shear stress is applied on polymer blends, there will be interlayer slip along with orientation and disentanglement. When shear stress is applied, the blend undergoes elongational flow. If the interface is strong, the deformation of the dispersed phase will be effectively transferred to the continuous phase. If the interface is weak, interlayer slip occurs and shear viscosity decreases. The extent of negative deviation is more prominent at high shear rate region than low shear rate region [1 – 5].

The psuedoplastic behaviour of a polymer is due to the random and entangled nature of polymer chains [6]. The knowledge of rheological properties of the melt and the blend morphology are important to control the processing parameters for desired end use applications [7]. The fact that HDPE/PP blends are incompatible in nature has been established by many workers [8, 9]. The study of capillary flow properties of HDPE/PP blend melts showed that there was no correlation between the extrudate swell ratio and the entrance correction coefficient [10]. The effect of viscosity of component phases on the mechanical properties of PP – LLDPE blends showed a closer matching of component viscosities of the blend resulted in a significant improvement in tensile properties when compared to blends where the component viscosities were different [11].

The comparison of shear viscosity of HDPE/PP blends at different DCP levels shows that shear viscosity of PP rich blends decreases with increase in concentration of DCP while shear viscosity of HDPE rich blends increases with increase in concentration of DCP.

Fernando Hernandez-Sanchez *et al.* studied the effect of natural rubber (NR) as well as EPDM random copolymer as compatibilizer for PP–HDPE blends on the rheological properties of the blend. Viscosity measured in all cases was lower than predicted by linear blending rule [12]. They have shown that the viscosity of blends is more sensitive to shear stress in the case of HDPE rich blends. HDPE shows large variation in viscosity with increase in shear rate while PP shows no considerable change. This may be due to the fact that discrete domains of HDPE do not affect the pseudo plasticity of PP.

The lowering of viscosity has been explained as due to the fact that both phases in a polymer blend had an elastic response and can store a part of the elastic energy supplied to them by the viscometer. But discrete domains would dissipate less energy while flowing in the viscometer than the continuous phase that wets the walls of the viscometer. They will offer less resistance to flow and hence will lower viscosity and will be much lower if the dispersed phase gets deformed by the flow [13, 14].

In the study of effect of addition of PP to HDPE as well as LDPE, the apparent shear viscosity is increased with addition of PP to both HDPE as well as LDPE. The flow properties of PP melt is obviously improved when it is melt blended with a little HDPE or LDPE. The dependence of shear viscosity of the melted blends on temperature is in accordance with Arrhenius equation. At a fixed wall shear rate, the shear viscosity is increased with increase in PP content in both blends of HDPE as well as LDPE [15].

According to the study, the apparent shear viscosities of PP/HDPE blend melts decreases with increasing apparent shear rates and the shear dependence of apparent shear viscosity increases with increase in PP content. Same was the case with PP/LDPE blends but shear dependence of apparent shear viscosity of PP/LDPE blend melts are higher than that of PP/HDPE blend melts.

It is observed that all four unmodified blends and their modifications prepared showed lowering of shear viscosity with increase in shear stress. This observation is common for all pseudoplastics. The decrease in shear viscosity with increase in temperature is also a common observation. The increase in shear viscosity with DCP concentration in the case of 80% HDPE/20% PP and 60% HDPE/40% PP is due to the cross linking as well as compatibilization of the blends by the action of dicumyl peroxide. The increase in shear viscosity with DCP concentration in the case of 40% HDPE/60% PP and 20% HDPE/80% PP can be assigned as due to the chain scission reactins in the case of the major component PP.

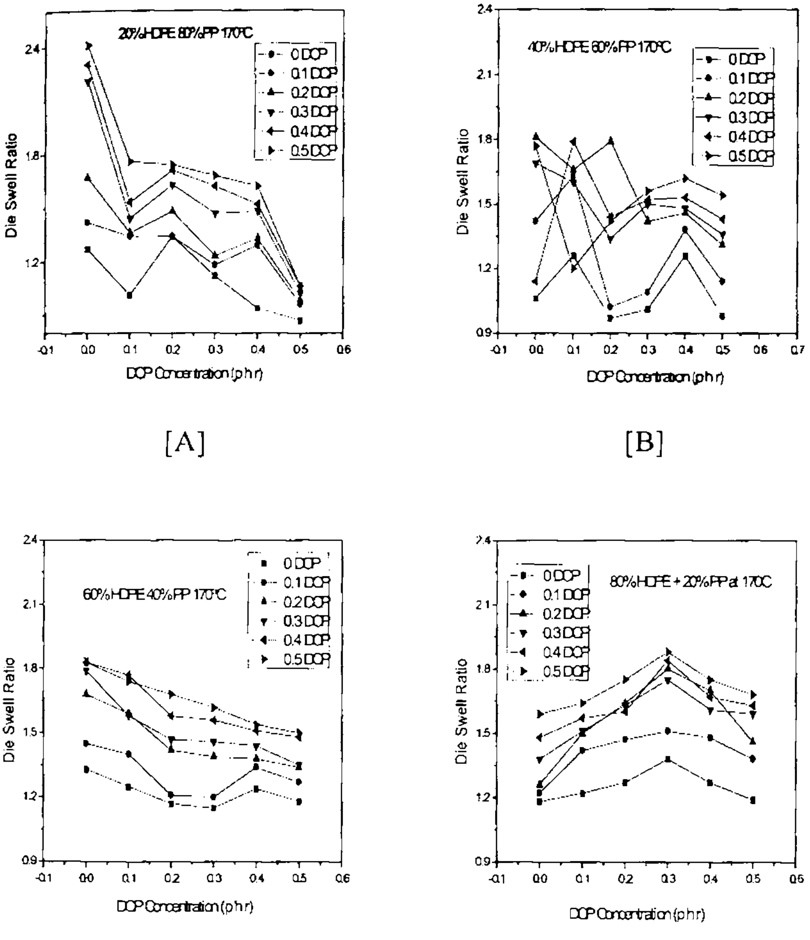
4A.3.4 Extrudate swell studies

During the rheological studies of blends and their DCP modifications, the extrudate at all six shear rates are collected and their diameter measured. From the diameter of the extrudate and diameter of the die used for extrusion, the extrudate swell ratio is determined. The study was conducted at two different temperatures – 170°C and 180°C.

The extrudate swell ratio of 20% HDPE/80% PP, 40% HDPE/60% PP and 60% HDPE/40% PP blend as well as all their DCP modifications at 170°C show an increasing trend with increase in shear rate. The extrudate swell ratio of the unmodified blend nearly doubled as shear rate increases from $13.33s^{-1}$ to $6666s^{-1}$. The ratio shows a decrement in value for the increase in DCP concentration. The 0.2phr DCP modified blend shows higher values than 0.1phr DCP modified blend. The extrudate swell ratio of 40% HDPE/60% PP blend shows lower values with increase in concentration of DCP, but the decrease is irregular. But for 80% HDPE/20% PP blend, the extrudate swell ratio shows an increasing trend with each increment of the compatibilizer (Fig. 4. 17 [A – D]).

The extrudate swell ratio at 180°C shows a more or less similar trend as at 170°C. The value increases with increase in shear rate for all the four blends as well as their modifications. The studies of 20% HDPE/80% PP blend shows that at any given shear rate, the extrudate swell ratio shows a decrement for increment in DCP, reaches a minimum at 0.4phr DCP level and a slight increment for 0.5phr DCP modification.

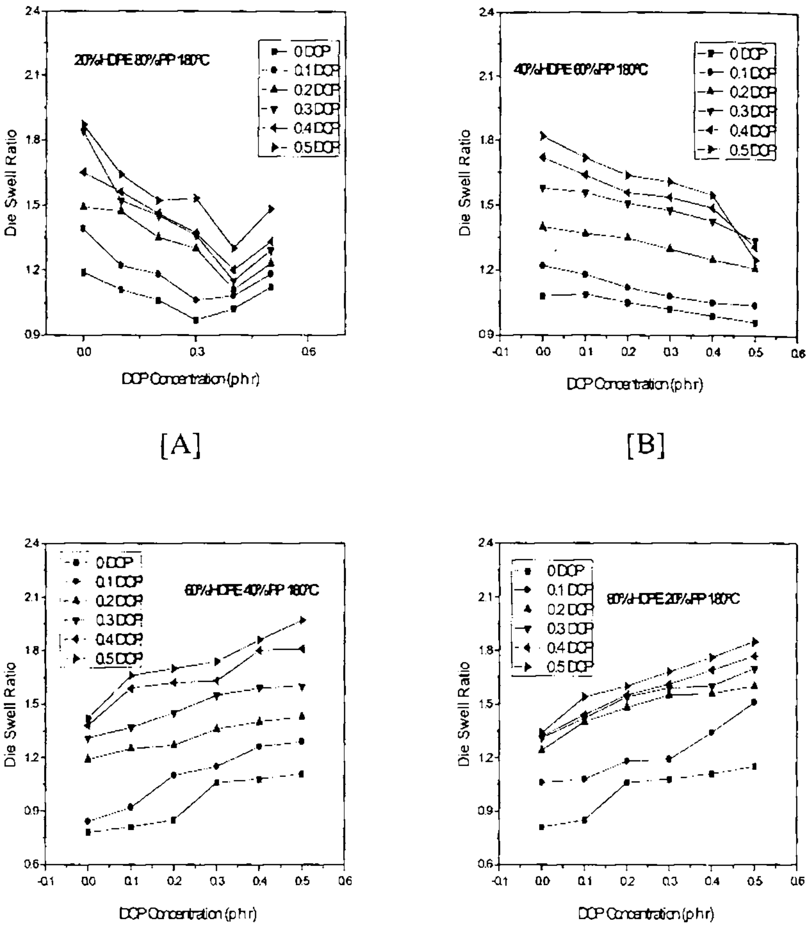
40% HDPE/60% PP blend exhibits a steady decrease in extrudate swell ratio with increase in DCP concentration. The 60% HDPE/40% PP and 80% HDPE/20% PP blends shows a steady increase in extrudate swell ratio with increase in DCP concentration (Fig. 4. 18 [A – D]).



[A] [B]

[C] [D]

Figure 4.17: [A – D] Variation of extrudate swell ratio with DCP for the HDPE/PP blends and modifications at 170°C.



[A] [B]

[C] [D]

Figure 4.18: *[A – D] Variation of extrudate swell ratio with DCP for the HDPE/PP blends and modifications at 180°C.*

On the whole, the extrudate swell ratio of PP rich blends shows a downward trend for increase in DCP concentration while the HDPE rich blends shows the reverse trend. The extrudate swell at 180°C is lesser than at 170°C.

The study of shear viscosity of HDPE / PP blends of different compositions show that shear viscosity of the blends decrease with shear rate indicating the pseudo-plastic nature of the blend. The shear viscosity decreases with increase in temperature as observed by other workers. The shear Viscosity of PP rich blends – 20% HDPE/80% PP and 40% HDPE/60% PP, decrease with increase in DCP concentration. This can be attributed to chain scission taking place in PP which lowers the molecular weight and the viscosity.

The shear viscosity of 60% HDPE/40% PP blend increases with concentration of DCP to a maximum value at 0.3phr DCP and then decreases. The shear viscosity of 80% HDPE/20% PP blend exhibits a steady increase with increase in DCP concentration. This is due to the cross linking taking place in HDPE which causes increase in viscosity. This variation in shear viscosity is shown by the blends at all three temperatures.

The extrudate swell ratios of all the four blends and their DCP modifications increases with increase in shear rate. The extrudate swell ratios of PP rich blends decrease with increase in DCP concentration. The extrudate swell ratios of HDPE rich blends increase with increase in DCP concentration. The extrudate swell is the result of orientation of long chain polymer molecules as they are sheared while passing through the capillary. As the melt is extruded out, re-orientation and recovery of the molecules occur leading to extrudate swell. Polymer molecules are said to retract by recoiling effect. The unequal retractive forces experienced by the components of the blend can lead to redistribution of polymer chains in the melt. Since the molecules on the periphery of the extrudate undergo maximum deformation, the retractive forces on these molecules will be greater.

The observation that the extrudate swell ratio increases with shear rate is in agreement with the results reported in the literature. At high shear rates, the polymer molecules cannot respond to the rapidly changing stresses and the stored elastic energy is greater. Once the material is released from the die, the excess energy is released causing extrudate swell.

The flowability or fluidity of a material could be considered to be a direct function of free volume or space in the liquid. Larger free volume is manifested in lower resistance to flow for many systems. According to free volume theory, any factor that reduces the free space increases the viscosity of the liquid. Thus external pressure applied increases viscosity of a liquid while increase in temperature decreases viscosity [1]

A liquid could be visualized as a mass of regular array of molecules with certain holes, vacant sites or free space between molecules here and there. The molecules under prevalent thermal condition normally remain confined to fixed mean positions under the influence of forces exerted by the surrounding molecules. The structure and relative position of vacant sites undergo constant change as a consequence of jumping of molecules into these sites. When a shear stress is applied, the random effect gives way to a directional effect and jumping of neighbourhood vacant sites favoured in the direction of applied stress is manifested into a resultant bulk movement or flow in that direction [2].

Eyring's theory cannot be applied to polymers since the molecules are not spherical in shape. But experiments on temperature dependence of melt viscosity have shown that the activation energy of polymer melts are not much higher than for low molecular weight liquids or melts of comparable chemical nature and composition which indicates that the flow units in the two systems are of comparable dimension. This is true since it is not the whole molecule but a short segment of the chain that moves at a given instant.

Measurement of rheological properties of fluids must take into account two points – 1. The fluid must be sheared at measurable rates and 2. The stress developed must be known. This can be accomplished using a capillary or extrusion rheometer or rotational rheometer.

Capillary or extrusion rheometers are useful in the studies of melt viscosities of thermoplastics and selected elastomer systems if selection of appropriate range of temperature and shear rates is permissible. A sample in powder, granule or other form is loaded into an extrusion cylinder or chamber and is heated to a specific temperature using thermostatic control. On attainment of temperature equilibrium, the melt is forced by a plunger through a cylinder or a capillary die attached at the bottom. The pressure on the plunger is a measure of shear stress. The plunger is allowed to move at a constant pre-set speed covering the desired range of shear rate. The amount of fluid extruded per unit time is a measure of the rate of shear.

The shear viscosity of all four blends decrease with increase in shear rate. This is due to the pseudo-plastic nature of the HDPE/PP blends. This has been reported by many workers [3 – 7].The viscosity of polymer blends depends upon interfacial adhesion, interfacial thickness and the characteristics of the components forming the blend. When shear stress is applied on polymer blends, there will be interlayer slip along with orientation and disentanglement. When shear stress is applied, the blend undergoes elongational flow. If the interface is strong, the deformation of the dispersed phase will be effectively transferred to the continuous phase. If the interface is weak, interlayer slip occurs and shear viscosity decreases. The extent of negative deviation is more prominent at high shear rate region than low shear rate region.

The psuedoplastic behaviour of a polymer is due to the random and entangled nature of polymer chains [8]. The knowledge of rheological properties of the melt and the blend morphology were important to control the processing parameters for desired end use applications [9].

Studies on the capillary flow properties of PP – HDPE blend melts and found that there was no correlation between the extrudate swell ratio and the entrance correction coefficient [10]. Fernando Hernandez-Sanchez *et al.* (1999) studied melt rheological properties of ternary blends of PP and HDPE with elaestomers like natural rubber or EPDM at several blending ratios and different shear rates. They showed that the addition of an elastomer to the polyolefin blend changed the shape of the viscosity – composition curve [11]. In a 50:50 blend, the two phases are discrete and viscosity gets closer to the linear blending rule. The viscosity of blends were more sensitive to shear stress in the case of HDPE rich blends. HDPE showed large variation in viscosity with increase in shear rate while PP showed no considerable change. This may be due to the fact that discrete domains of HDPE do not affect the pseudo plasticity of PP.

The lowering of viscosity has been explained as due to the fact that both phases in a polymer blend had an elastic response and can store a part of the elastic energy supplied to them by the viscometer. But discrete domains would dissipate less energy while flowing in the viscometer than the continuous phase that wets the walls of the viscometer. They will offer less resistance to flow and hence will lower viscosity and will be much lower if the dispersed phase gets deformed by the flow [12, 13].

The apparent shear viscosity increases with addition of PP to both HDPE as well as LDPE. The flow properties of PP melt was obviously improved when it was melt blended with a little HDPE or LDPE. The dependence of shear viscosity of the melted blends on temperature was in accordance with Arrhenius equation. At a fixed wall shear rate, the shear viscosity was increased with increase in PP content in both blends of HDPE as well as LDPE [14]. In any polymer melt, flow occurs when polymer molecules slide past each other. The ease of flow depends upon the mobility of molecular chains and the forces or entanglements holding the molecules together. The compatibility and miscibility between phases are important factors affecting the rheological characteristics of polymer melts. The dispersion and distribution of the components in the blends as well as the mixing conditions are related. Since the viscosity ratio of PP to HDPE is high, when HDPE is the continuous phase (PP < 30%), the interlayer slip is easy and as a result, viscosity is lowered.

4B. THERMAL ANALYSIS OF HDPE/PP BLENDS

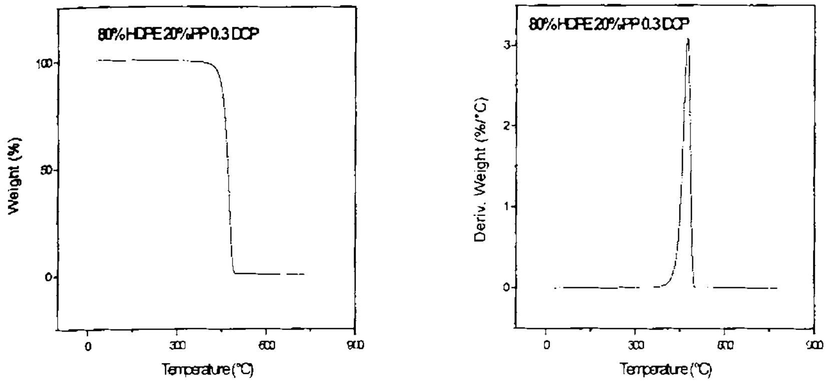
4B.1. THERMOGRAVIMETRIC ANALYSIS

4B.1.1 INTRODUCTION

Thermogravimetric Analysis or TGA is a type of testing that is performed on samples 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 materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

In a Thermogravimetric Analysis, the percent weight loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The test material is placed in the specimen holder and raised the furnace. Set The initial weight reading was set to 100%, and the heating program was initiated. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent.



[A] [B]

Figure 4.19: *[A & B] TGA and DTA curves of 80% HDPE/20% PP blend modified with 0.3 phr DCP.*

TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions. A simplified explanation of a TGA sample evaluation may be described as follows. A sample is placed into a tared TGA sample pan which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of noncombusted residue at some final temperature, and the temperatures of various sample degradation processes [ASTM E1131, ISO 11358].

4B.1.2 EXPERIMENTAL

TGA studies of polymer blends are conducted with a TGA Q50 equipment of TA Instruments. The samples in the range of 5 to 10 mg are heated in a nitrogen atmosphere. The heating Is done at a rate of 20°C per minute to a maximum temperature of 800°C. The temperature of onset of decomposition, the temperature at which 50% material had decomposed and residue left over are noted from weight loss profiles and derivative weight loss curves obtained.

4B.1.3 RESULTS AND DISCUSSION

(a) 80% HDPE/20% PP Blend

The percentage weight loss of the blend as well as its DCP modifications at three different temperatures is compared. The weight loss is below 1% at 300°C which shows the stability of the material as well as very low moisture or absorbed gases content. The weight loss is below 5% at 400°C and around 20% at 450°C. Half the initial quantity of material has volatilized around 465 - 470°C [Fig. 4. 19 A & B].

The onset temperature of decomposition increases with increase in DCP content, reaches a peak value at 0.3 phr and then decreases. Similar trend is also shown in the case of temperature at which 50% decomposition is complete. This shows the increase in thermal stability of the blend on modification with DCP [Table 4.1]. The residue level is very low indicating high volatility of the blend.

Table 4.1: Comparison of TGA of 80% HDPE/20% PP blend and its modified versions.

DCP Conc.	Weight Loss at			Temp. at 50% Decompn.	Onset Temp °C	Residue %
	300°C	400°C	450°C			
0	0.12	1.69	14.61	466.68°C	357.12	0.57
0.1	0. 14	1.33	17.82	466.88°C	374.27	0.82
0.2	0.45	2.8	20.71	468.31°C	378.31	0.22
0.3	0.37	1.45	13.57	470.29°C	388.4	0.29
0.4	0.26	1.24	13.17	470.04°C	388.4	0.38
0.5	0.35	1.54	14.91	468.60°C	367.21	0.21

(b) 60% HDPE/40% PP blend

Comparison of TGA data for the blend as well as its DCP modifications shows that the weight loss is below 1% at 300°C, below 5% at 400°C and around 30% at 450°C. The onset temperature are in the region 360–385°C, the highest value is for the untreated blend. The onset temperature shows a declining trend for increase in concentration of DCP, reaches a minimum at 0.3 phr DCP and then increases. The temperature at which 50% decomposition occurs initially increases to a maximum at 0.3 phr DCP and then a decline with increase in concentration of DCP. The DTA curve peak temperature shows a slight increase initially and a decline as DCP content increases [Table 4.2]. All modifications show very little residue (1%) which implies high volatility of the blend.

(c) 40% HDPE/60% PP blend

Comparing the TGA data of the blend and its DCP modifications,. it is found that the weight loss is below 1% at 300°C, below 5% at 400°C and around 25 - 30% at 450°C. All DCP modifications of the blend has onset temperature greater than that of untreated blend. The onset temperature increases with DCP content, reaches a maximum at 0.3 phr DCP and decreases. The temperature at which 50% decomposition of blend occurs also shows a similar trend [Table 4.3].

Table 4.2: *Comparison of TGA of 60% HDPE/40% PP blend and its modified versions.*

DCP Conc	Weight Loss at			Temp at 50% Decompn.	Onset Temp °C	Residue %
	300°C	400°C	450°C			
0	0.36	1.9	19.81	460.99°C	383.35	0.14
0.1	0.27	1.91	20.1	464.30°C	374.27	0.24
0.2	0.2	3.88	27.68	464.53°C	362.54	0.34
0.3	0.16	4.15	29.35	468.91°C	348.58	0.69
0.4	0.43	4.18	27.2	461.85°C	368.89	1.31
0.5	0.44	3.24	27.72	453.53°C	367.62	1.02

Table 4.3: *Comparison of TGA of 40% HDPE/60% PP blend and its modified versions.*

DCP Conc	Weight Loss at			Temp at 50% Decompn.	Onset Temp °C	Residue %
	300°C	400°C	450°C			
0	0.16	1.5	26.88	458.07°C	356.2	0.66
0.1	0.48	3.52	32.29	459.38°C	370.16	0.45
0.2	0.27	2.12	28.28	459.50°C	374.13	0.40
0.3	0.24	2.64	27.36	460.14°C	375.24	0.42
0.4	0.3	2.9	28.37	459.96°C	373.97	0.35
0.5	0.37	3.12	32.93	457.36°C	370.22	0.47

The DTA peak temperature increases to a maximum at 0.3 phr and then declines. The residue level is less than 1% indicating the volatile nature of the blend as well as its modifications.

(d) 20% HDPE/80% PP blend

Comparison of TGA data of the blend and its DCP modifications, it is found that the weight loss is below 1% at 300°C, around 5% at 400°C except for 0.2 phr DCP modification and around 40% at 450°C. The onset temperatures of the blend are found to increase with concentration of DCP to reach a peak value at 0.3 phr level and then decrease. The blends modified by 0.2 and 0.4 phr DCP have onset temperatures below that of unmodified blend.

The temperature for 50% decomposition is highest for 0.3 phr DCP modified blend while minimum for 0.2 phr DCP modified blend. The residue left over is below 0.5% indicating volatile nature of the blend.

Comparing the onset temperature of different blends and their DCP modifications, the 80% HDPE/20% PP blend modified with 0.3 phr DCP has the highest value. The residue is minimum for PP rich blends compared to HDPE rich blends. The temperature at which 50% weight loss occurs is also maximum for 80% HDPE/20% PP blend. Relatively low temperatures are required in the case of PP rich blends.

***Table 4.4:** Comparison of TGA of 20% HDPE/80% PP blend and its modified versions.*

DCP Conc	**Weight Loss at**			**Temp at 50% Decompn.**	**Onset Temp °C**	**Residue %**
	300°C	**400°C**	**450°C**			
0	0.09	3.8	39.58	450.17°C	360	0.29
0.1	0.46	3.79	33.83	454.47°C	370.16	0.29
0.2	0.36	9.77	49.7	450.17°C	325.72	0.18
0.3	0.34	2.87	35.05	456.24°C	373.93	0.44
0.4	0.52	5.11	39.47	454.69°C	347.31	0.12
0.5	0.39	2.99	34.18	456.69°C	367.62	0.25

Long-term properties of polymer blends under environmental stresses are strongly influenced by the co-reactivity between individual component polymers. The final effect on the life time of the blends is difficult to predict on the basis of known behaviour of individual polymers. Polymer degradation means all changes in chemical structure and physical properties of polymers due to external physical or chemical stresses leading to materials with characteristics different from the starting materials [15]. The organic polymers are vulnerable by the harmful effects of the environment. This includes attack by chemical deteriogens like dioxygen, its active forms, humidity, harmful anthropogenic emissions and atmospheric pollutants like oxides of nitrogen and physical stresses like heat, mechanical processes and radiation. Degradation processes are classified as melt degradation, long term heat ageing and weathering. On the basis of mechanisms involved, there are thermomechanical, thermal, catalytic and radiation-induced oxidations and environmental biodegradations [16].

In addition to regular polymer structure, differences in sensitivity to individual degradation processes arise from the effects of low amounts of structural polymeric inhomogeneities like unsaturation or oxygenated structures and non-polymeric impurities such as different metallic contaminants or photoreactive pigments The concentration of active impurities like catalyst and sensitizers increases during the polymer life time. The knowledge of degradation mechanisms of homopolymers and copolymers is helpful only to a small extent for the elucidation of degradation of polymer blends. Individual components of a blend may behave rather differently from their behaviour as isolated polymers [17].

According to Chiantore *et al.* (1998) degradation behaviour of the polymer blends is due to the co-reaction phenomena on interfaces of blended polymers controlled by the morphology of the blend. The processes are complicated by the reactivity of the compatibilizers. The heterogeneous character of the system, reactions in the bulk and at the boundaries of the individual phases and involvement of macromolecular and low molecular weight degradation products increase the complexity of the reactions in the blends [18]. Structural changes accounting for ageing produce an associated effect on various physical properties. The practical service life-time of blends in general and blends containing recyclates in particular is considerably affected by their resistance to degradation.

Most of the changes in the chemical structures have been accounted to the degradation due to mechanically induced thermal processes that take place during melt-processing of polymers in oxygen deficient atmosphere. This would modify the mechanical properties and weathering resistance of the final material [19, 20]. Melt-processing degradation is a short term process proceeding under severe micro environmental attacks. The effect of mechanical stress increases in melts with high viscosity, or in processes employing high mixing speeds, since high mechanical forces have to be applied for attaining mixing performance [21, 22]. Mechanical stress has a dominating effect over thermal effects. Polyolefins undergo thermo mechanical degradation in the range of temperatures where they are practically unaffected by thermal treatment alone. Trace amounts of oxygen present in the processing equipment and thermal oxidation contribute to degradation.

This study reports are supported by the literature survey. All blends show good thermal stability. Introduction of DCP increases the onset temperature for degradation to higher temperatures, reaching a maximum at 0.3phr DCP concentration. This DCP concentration was earlier found to bring in best modification of blends which also enhanced the thermal stability of the blends. A similar trend was shown for the temperature for 50% decomposition to take place.

4B.2. DYNAMIC MECHANICAL ANALYSIS

4B.2.1. INTRODUCTION

A Dynamic Mechanical Analyser measures the stiffness and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. It is frequently converted to a modulus to enable sample inter-comparisons. Damping is expressed in terms of Tan δ and is related to the amount of energy a material can store. DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed.

A force (stress) is applied to the sample through the motor. The stress is transmitted through the drive shaft onto the sample which is mounted in a clamping mechanism. As the sample deforms, the amount of displacement is measured by a positional sensor. The strain can be calculated from the displacement. The force (or stress) is applied sinusoidal with a defined frequency. The magnitude of the applied stress and the resultant strain are used to calculate the stiffness of the material under stress. The phase lag between the two (or δ) is used to determine Tan δ, the damping factor.

The sample can be mounted in the DMA in a number of ways depending on the characteristics of the sample. The 6 common geometries are Single Cantilever Bending, Dual Cantilever Bending, 3 Point Bending, Tension, Compression and Shear. When the strain is in phase with the stress, i.e. δ is 0°, the sample is classed as elastic. When the strain is 90° out of phase with the stress, i.e. δ is 90°, the sample is classed as viscous. Viscous materials such as glycerin exhibit large damping properties. Most materials are classified as viscoelastic i.e. δ is between 0° and 90°. Most polymers exhibit this behaviour and have an elastic and viscous component. For elastic materials, the modulus is simply expressed as the ratio of stress to strain. Tan δ will be negligible. For viscous materials, stress and strain are related as a function of time as there is a phase difference between the two. Tan δ will be high as the damping effect will be large.

Damping is the conversion of mechanical energy of a structure into thermal energy. A structure subject to oscillatory deformation contains a combination of kinetic and potential energy. In the case of real structures, there is also an energy dissipation element per cycle of motion. The amount of energy dissipated is a measure of the structure's damping level. Storage modulus is the ratio of the amplitude of the stress in phase with the strain to the amplitude of the strain in the forced oscillation of a material. Loss modulus is the ratio of the amplitude of the stress 90° out of phase with the strain to the amplitude of the strain in the forced oscillation of a material.

4B.2.2 EXPERIMENTAL

The dynamic mechanical measurements of 80% HDPE/20% PP as well as 20% HDPE/80% PP blends are performed on a DMA Q800 machine of TA Instruments. Polymer bars of dimension 35 mm x 12 mm x 2 mm are injection moulded using a semi-automatic injection moulding machine. The bars are subjected to dual cantilever bending test at a frequency of 1 hertz and amplitude of 15 μm. The ramp temperature is set to increase at 3°C per minute to a maximum of 160°C.

4B.2.3 RESULTS AND DISCUSSION

The molecular level changes that occur in a polymer under the application of sinusoidal stress are reflected in dynamic mechanical measurements. The variation of storage modulus E' with temperature of 80% HDPE/20% PP as well as 20% HDPE/80% PP blends as well as their DCP modifications is investigated. Three distinct regions of mechanical behaviour such as a) a glassy region, b) a glass-rubber transition region and c) a flow region are observed. In the glassy region the chain conformations are frozen into rigid networks yielding high E' value and low loss modulus. One or more secondary transitions of low magnitude are possible due to limited movement within the main chain or pendant groups. A large drop in storage modulus and a distinct peak in loss modulus are observed at glass-rubber transition. This can be attributed to long range motion of amorphous polymer chain segments. A drop in storage modulus is observed at the flow region. Here the amorphous chains undergo net translatory motion relative to each other.

(a) Variation of Storage Modulus

The variation of storage modulus as a function of temperature as well as level of dicumyl peroxide are studied (Fig. 4.20). The values in the case of 80% HDPE/20% PP blend show a declining trend with the increase in temperature for the blend as well as its DCP modifications. At any given temperature, the storage modulus increases with increase in DCP content to 0.3 phr level and then recedes.

The improvement in storage modulus indicates the superior load bearing capacity of the blend under dynamic conditions. The rate of decline is large initially in the temperature regions 35 - 90°C and then became lesser. This is true for all DCP modifications of the 80% HDPE/20% PP blend. The value is highest for 0.3 phr modification throughout the studies.

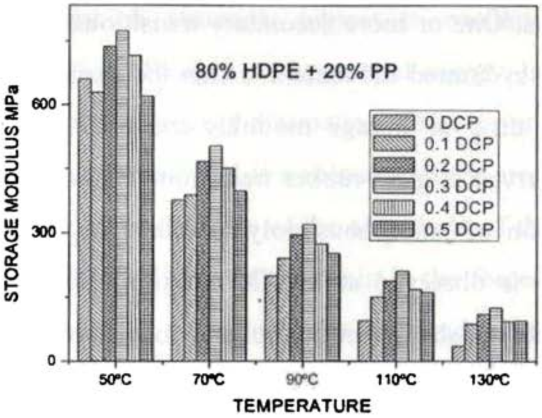


Figure 4.20: Variation of storage modulus with temperature at different DCP concentrations for 80% HDPE/20% PP blend.

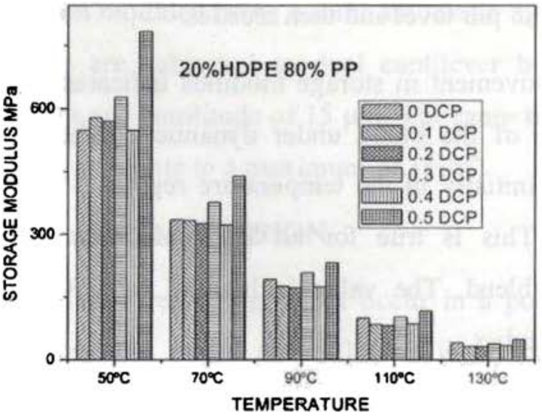


Figure 4.21: Variation of storage modulus with temperature at different DCP concentrations for 20% HDPE/80% PP blend.

Comparison of storage modulus as a function of temperature and the content of dicumyl peroxide of 20% HDPE/80% PP blend (Fig. 4. 21) shows the value to decrease with increase in temperature. At low temperature, the storage modulus of all modifications is higher than the unmodified blend, the variation being irregular at higher temperatures.

(b) Variation of Loss Modulus

Loss modulus is an indirect measure of polymer viscosity and is the product of storage modulus and tangent of loss angle. It also describes the dissipation of energy into heat when the material is deformed. The loss modulus of 80% HDPE/20% PP blends decreases with increase in temperature. At lower temperatures, the unmodified blend has higher loss modulus than the modifications.

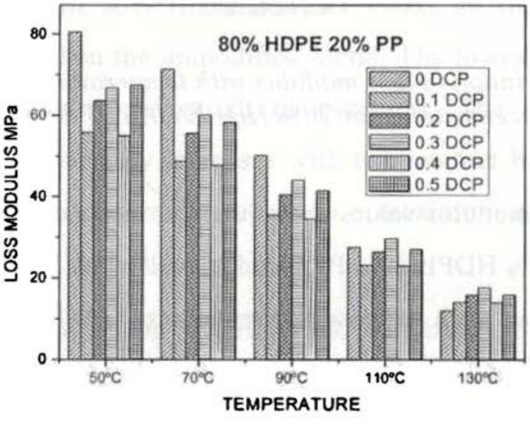


Figure 4.22: *Variation of loss modulus with temperature at different DCP concentrations for 80% HDPE/20% PP blend.*

In the case of its DCP modifications, the value shows an initial increase in value at around 45 - 55°C and then a steady decrease (Fig. 4. 22). In the case of modified blends, the modification with 0.3 phr DCP has maximum vales at all temperatures. No regular gradation is observed for increase in DCP content.

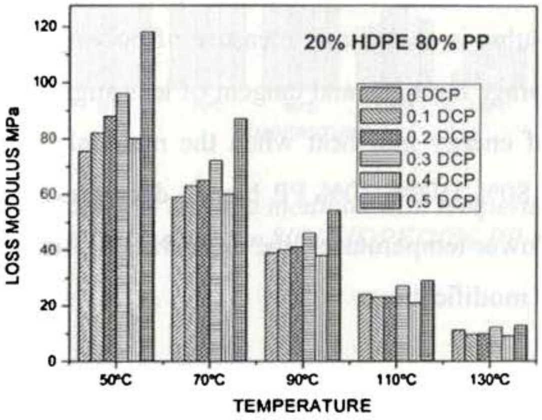


Figure 4.23: *Variation of loss modulus with temperature at different DCP concentrations for 20% HDPE/80% PP blend.*

The loss modulus values shows a slight increase around 45 - 50°C in the case of 20% HDPE/80% PP blend as well as its DCP modifications and then decreases with increase in temperature. All DCP modifications have higher loss modulus than the unmodified blend up to around 95°C. The value of loss modulus is found to increase with DCP content, reaches a peak at 0.3 phr DCP and then a slight lowering is observed. The 0.5 phr DCP modified blend shows a higher value than the other modifications (Fig. 4. 23).

(c) Variation of Tan δ

Tan δ value represents the ratio of loss modulus to storage modulus of the material and is known as damping factor. In polymers as temperature increases, damping goes through a maximum and then a minimum in the rubbery region which can be explained on a molecular basis. Damping is low below transition region since the chain segments are frozen. Below this temperature, the deformations are primarily elastic and molecular slip resulting to viscous flow is low. Above transition temperature, damping is low since molecular segments are very free to move and there is little or no resistance to their flow. Here a part of the segments are free to move about while the remainder are not so.

The tan δ values show an upward trend with increase in temperature for 80% HDPE/20% PP and 20% HDPE/80% PP blends (Fig. 4.24). In the case of 80% HDPE/20% PP blend, all DCP modifications have lower value than the unmodified blend. The lowest value is for 0.3 phr DCP modified blend at all temperatures. The tan δ value for unmodified blend steadily increases with temperature but in the case of DCP modifications, the value reaches to a maximum and then shows a decline as in Fig. 4. 24.

The tan δ values for 20% HDPE/80% PP blend show an increasing trend with increase in temperature. The value also increases with increase in DCP content, reaches a maximum at 0.3 phr levels and then a decline. But all modifications have higher values than the unmodified blend (Fig. 4. 25).

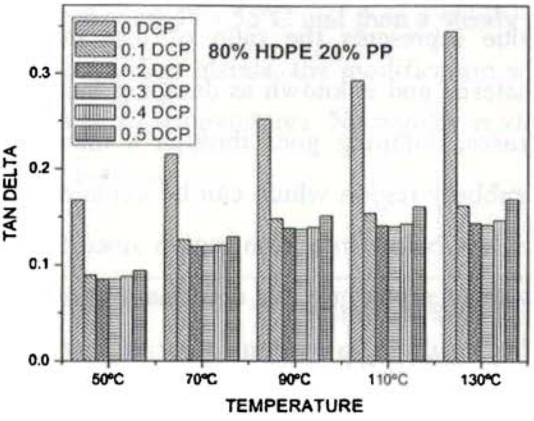


Figure 4.24: *Variation of tan δ with temperature at different DCP concentrations for 80% HDPE/20% PP blend.*

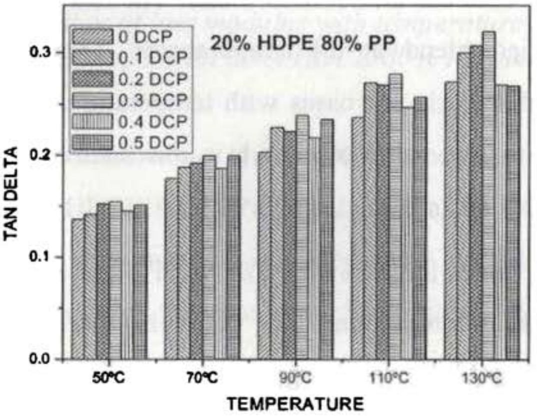


Figure 4.25: *Variation of tan δ with temperature at different DCP concentrations for 20% HDPE/80% PP blend.*

The decrease in storage modulus observed with increase in temperature is the normal observation for thermoplastics. The increase in load bearing capacity of the 80% HDPE/20% PP blend with increase in DCP concentration is due to the modifying effect of DCP on the blend. As the viscosity mismatch is lowered by incorporation of DCP, the load bearing capacity increases.

The blend with composition 20% HDPE/80% PP also showed improvement in load bearing capacity on addition of DCP. The decrease in tan δ values of the 80% HDPE/20% PP blend with increase in DCP concentration is due to the increase in viscosity by cross-linking taking place in HDPE. The increase in tan δ values of the 20% HDPE/80% PP blend with increase in DCP concentration is due to the decrease in viscosity by chain scission taking place in PP.

4B.3. DIFFERENTIAL SCANNING CALORIMETRY

4B.3.1. INTRODUCTION

Differential scanning calorimetry or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

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 to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.

4B.3.2 EXPERIMENTAL

Pure HDPE and PP are weighed out in the ratio 80% HDPE/20% PP, 60% HDPE/40% PP, 40% HDPE/60% PP and 20% HDPE/80% PP. Each blend was melted and treated with 0.1, 0.2, 0.3, 0.4 and 0.5 phr Dicumyl peroxide in a Thermo Haake Rheomix blender at 30 rpm for homogenization at 180°C. The blends were pressed into sheets on a hydraulic press. Samples weighing around 5 to 10 mg were sealed in aluminium pans and placed alongside the reference pan in DSC Q800 equipment of TA Instruments.

The sample is allowed to equilibrate at 30°C and then heated to 200°C. The ramp temperature increases at 20°C/minute to 200°C. The sample was allowed to cool to 50°C at a cooling rate of 10°C/minute. The heat flow per second was recorded and plotted. The melting point of the two components, the crystallization temperature of the blend, ΔH_{fusion} and $\Delta H_{crystallization}$ were noted.

4B.3.3 RESULTS AND DISCUSSION

(a) 80% HDPE/20% PP Blend

Differential Scanning Calorimetric analysis of the blend as well as its DCP modifications show two melting peaks corresponding to the two components and a single crystallization peak [Fig. 4. 26].

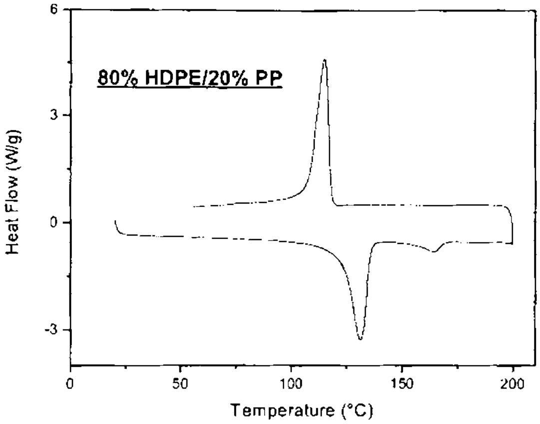


Figure 4.26: DSC Thermogram of unmodified 80% HDPE/20% PP blend.

DCP modified blends shows a decreasing trend in the melting points of the components as well as the crystallization temperature of the blend for each increment of DCP. ΔH_{fusion} values of the blend are lowered by addition of DCP and $\Delta H_{crystallization}$ values shows an irregular trend. The ratio $\Delta H_{fus}/\Delta H_{cryn}$ is found to decrease with increase in DCP content [Table 4.5].

***Table** 4.5: Tabulation of DSC data of 80% HDPE + 20% PP blend and its DCP modified versions.*

DCP	M.P$_1$ °C	M.P$_2$ °C	X'lisation Temp °C	ΔH_{fusion} J/g	ΔH_{crystn} J/g	$(\Delta H_{fus}/\Delta H_{crtn})$ x 100
0	131.45	164.7	116.44	137.3	155.2	88.4
0.1	131.41	163.0	115.12	135.5	154.8	87.5
0.2	131.15	162.6	114.52	133.7	155.2	86.1
0.3	129.96	162.2	114.51	124.0	148.7	83.4
0.4	129.76	162.0	114.21	119.8	147.5	81.2
0.5	129.49	159.7	113.79	115.0	145.0	79.3

(b) 60% HDPE/40% PP Blend

The blend and its modifications show variations in melting points of the components, crystallization temperature, ΔH_{fusion} and $\Delta H_{crystallization}$ as for 80% HDPE/20% PP blend [Table 4.6].

c) 40% HDPE/60% PP Blend

The studies on 40% HDPE/60% PP blend and its DCP modifications shows two melting peaks corresponding to the blend components and two crystallization peaks close to each other. The melting point of HDPE part increases with increase in DCP content and reaches its peak at 0.3 phr DCP level.

***Table 4.6:** Tabulation of DSC data of 60% HDPE/40% PP blend and its DCP modified versions.*

DCP	M.P$_1$ °C	M.P$_2$ °C	X'lisation Temp °C	ΔH_{fusion} J/g	ΔH_{crystn} J/g	$(\Delta H_{fus}/\Delta H_{crtn})$ x 100
0	133.97	166.61	117.76	115.5	140.7	82.0
0.1	133.71	165.50	117.31	110.3	136.5	80.7
0.2	133.54	165.08	115.72	110.0	137.2	80.2
0.3	131.98	163.91	115.26	114.0	145.6	78.3
0.4	131.34	151.42	115.10	87.85	136.5	64.4

The melting point of PP shows a steady decline with each increment in DCP. The ΔH_{fusion} and $\Delta H_{crystallization}$ values are maximum for the blend containing 0.3 phr DCP. The ratio $\Delta H_{fus}/\Delta H_{cryn}$ increases to a maximum at 0.3 phr DCP and then decreased [Table 4.7].

***Table 4.7:** Tabulation of DSC data of 40% HDPE/60% PP blend and its DCP modified versions.*

DCP	M.P$_1$ °C	M.P$_2$ °C	X'lisation Temp °C	ΔH_{fusion} J/g	ΔH_{crystn} J/g	$(\Delta H_{fus}/\Delta H_{crtn})$ x 100
0	130.33	167.44	113.86	97.32	127.7	76.2
0.1	130.68	167.07	114.26	95.37	124.3	76.7
0.2	131.35	165.68	115.52	102.5	126.7	80.9
0.3	132.85	164.77	116.07	107.8	130.9	82.3
0.4	131.23	164.22	115.03	88.95	119.8	74.1
0.5	130.81	164.20	114.46	78.79	108.4	72.6

(d) 20% HDPE/80% PP Blend

DSC examination of 20% HDPE/80% PP blend as well as its modifications with DCP shows two melting peaks as well as two crystallization peaks [Fig.4. 27]. The melting points of the components show a trend similar to 40% HDPE/60% PP blend. The ΔH_{fusion} and $\Delta H_{crystallization}$ values shows no regular variation but the ratio $\Delta H_{fus}/\Delta H_{cryn}$ increases to a maximum at 0.3 phr DCP level and then a decline [Table 4.8].

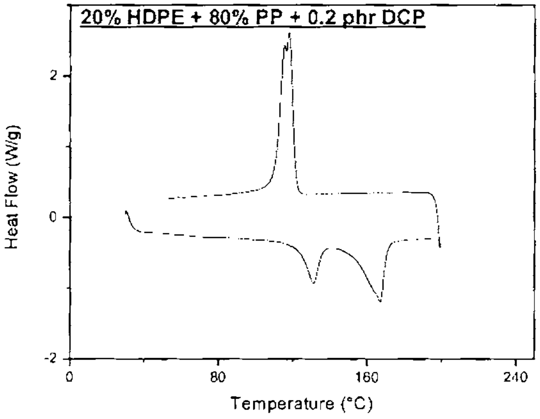


Figure 4.27: DSC Thermogram of modified 20% HDPE/80% PP blend.

DSC melting curves of the four blends and their DCP modifications shows two melting peaks at temperatures corresponding to the two components indicating separate melting in all cases. Cooling curves shows a single peak in most cases since the main crystallization peak of PP is close to that of HDPE and the peaks would overlap. 80% HDPE/20% PP and 60% HDPE/40% PP blends shows only single crystallization peak while 40% HDPE/60% PP and 20% HDPE/80% Pp blends shows separate peaks close to each other.

***Table 4.8:** Tabulation of DSC data of 20% HDPE + 80% PP blend and its DCP modified versions.*

DCP	**M.P$_1$ °C**	**M.P$_2$ °C**	**X'lisation Temp °C**	**ΔH_{fusion} J/g**	**ΔH_{crystn} J/g**	**$(\Delta H_{fus}/\Delta H_{crtn})$ x 100**
0	131.02	167.29	118.03	70.23	102.0	68.8
0.1	131.17	167.02	118.13	80.70	110.0	75.1
0.2	131.26	166.65	118.70	82.72	106.2	76.2
0.3	131.29	165.79	119.82	83.90	108.1	77.6
0.4	130.49	165.11	119.58	79.93	108.3	73.2
0.5	129.27	164.60	113.92	79.07	102.0	73.3

The DSC melting curves displayed two single melting peaks at temperatures corresponding to the pure polymers, indicating separate melting in all blends. Interpretation of cooling exotherms were complicated due to (a) the main crystallization temperature of PP was close to that of HDPE and the two peaks would overlap and (b) PP also gave rise to some lower temperature crystallization peaks. A PP-HDPE (20:80) blend showed only a single peak between crystallization temperatures of PP and HDPE.

Blom *et al.* found that HDPE was able to penetrate the PP phase sufficiently at low HDPE contents to reduce the number and size of high segment-density regions, delaying the nucleation and subsequent crystallization of the PP phase. They also claimed that there was a significant degree of interaction between PP and HDPE at low HDPE concentration below 20% [23].

Shanks *et al.* employed DSC and hot-stage optical microscopy (HSOM) techniques and found that PP was miscible with LLDPE but immiscible with LDPE and HDPE. HSOM allowed the observation of developing structures, starting from an initially crystallized droplet and in which the neighbouring droplets were observed to crystallize implying that crystallization was somehow bridging between the droplets [24].

Isothermal crystallization of PP at temperatures where PE remained molten was studied by DSC and HSOM while the resulting semi- crystalline morphology was studied by TEM. It was observed that in PP-HDPE blends, PP crystallized in phase separated droplets. The crystallization rate of PP in the blend was similar to that of pure PP. The DSC and HSOM studies indicated that PP was miscible with LLDPE at elevated temperatures at PP concentration of 20% whereas PP was immiscible with LDPE and HDPE at these temperatures [25].

4.C CONCLUSIONS

1. The shear viscosity of all blends decreases with increase in shear stress at all temperatures studied. The shear viscosity of all the four blends decrease with increase in temperature. The shear viscosity of PP rich blends – 20% HDPE/80% PP and 40% HDPE/60% PP decreases with increase in DCP concentration.
2. The shear viscosity of 60% HDPE/40% PP blend increases with concentration of DCP to a maximum value at 0.3phr DCP and then decreases. The shear viscosity of 80% HDPE/20% PP blend

exhibits a steady increase with increase in DCP concentration. This variation in shear viscosity is shown by the blends at all three temperatures.

3. The extrudate swell ratios of all the four blends and their DCP modifications increases with increase in shear rate. The extrudate swell ratios of PP rich blends decrease with increase in DCP concentration. The extrudate swell ratios of HDPE rich blends increase with increase in DCP concentration.
4. All blends and their DCP modified versions show good thermal stability. The weight loss at 400°C was less than 3% in all cases. The onset temperature for 80% HDPE/20% PP blend and its modified versions increases with increase in DCP concentration to a maximum at 0.3phr DCP and then decreases. Similar trend was observed in the case of temperature at which 50% decomposition was complete. The onset temperature for 60% HDPE/40% PP blend and its modifications decrease with increase in DCP concentration to a minimum at 0.3phr DCP and then increase. The f temperature at which 50% decomposition was complete increase with increase in DCP concentration to a maximum at 0.3phr DCP and then decrease. A trend similar to 80% HDPE/20% PP is observed in the case of 40% HDPE/60% PP blend and its modifications. The studies on 20% HDPE/80% PP blend and its modifications show the 0.3phr modification to have the highest onset temperature and the temperature at which 50% decomposition was complete
5. The .storage modulus of 80% HDPE/20% PP blend and its modifications decreases with increase in temperature. At any

given temperature the storage modulus increases with increase in DCP concentration, reached maximum at 0.3phr and then decreases. The storage modulus of 20% HDPE/80% PP blend and its modifications decreases with increase in temperature. All DCP modifications of the blend show greater storage modulus than the unmodified blend. The tan δ values increase with increase in temperature for both the blends and their modifications. All DCP modifications of 80% HDPE/20% PP blend show lower tan δ values than the unmodified blend. The tan δ values of 20% HDPE/80% PP blend increase with increase in DCP concentration, reached maximum at 0.3phr and then decreases.

6. 80% HDPE/20% PP blends – Two melting peaks corresponding to the individual polymers and a single crystallization peak are observed for the blend as well as its DCP modifications. Addition of DCP lowers the melting point of both the components as well as the crystallization temperature. The ΔH_{fusion} values shows a regular decrease for increase in DCP concentration. $\Delta H_{crystallisation}$ values show an irregular pattern. 60% HDPE/40% PP blends – they show a pattern similar to 80% HDPE/20% PP blends. 40% HDPE/60% PP blends – Two melting peaks corresponding to the individual polymers and two crystallization peaks are observed for the blend as well as its DCP modifications. Melting point of HDPE increases to a maximum at 0.3phr DCP and then decreases. Melting point of PP decreases with increase in DCP concentration. The ΔH_{fusion} and $\Delta H_{crystallisation}$ values were maximum for 0.3phr DCP modified blend. 20% HDPE/80% PP blends – Two melting peaks corresponding to the individual polymers and two

crystallization peaks are observed for the blend as well as its DCP modifications. The ΔH_{fusion} and $\Delta H_{crystallisation}$ values exhibit no regular trend but were maximum for 0.3phr DCP modified blend.

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CHAPTER 5

MECHANICAL PROPERTIES OF UNMODIFIED AND MODIFIED HDPE/PP BLEND - NYLON MAT COMPOSITES

5.1. INTRODUCTION

Human beings in order to meet the growing need for better and better materials, has been in pursuit of new materials. He has been combining two or more existing materials in order to bring out the better properties of the materials mixed. The Holy Bible refers mixing of mud with hay to produce reinforced bricks for building purposes. Man in pursuit of new cost effective materials is trying to combine the existing materials for a cost effective replacement for engineering materials. The polymer matrix composites are reliable and more efficient than the components, light weight, durable and possess properties like easy mouldability, non corrosiveness, adequate strength, stiffness and load bearing qualities. Thermoplastic based composites have received more attention as their processing is easy compared to thermosetting polymers.

Polypropylene and high density polyethylene are two of the most versatile polymers used. They have many properties that make them the choice for various applications [1 – 4]. Many ways are available to modify their properties to suit the end user. One of the most efficient methods is to add fillers to them in order to attain cost effective composite mechanical properties. Fibrous materials have been shown to increase both the mechanical as well as thermal properties like tensile strength, flexural strength, flexural modulus, thermal stability etc [5 – 8]. Nylon is one of the important industrial fibres due to its high performance and low cost.

5.2. EXPERIMENTAL

HDPE and PP granules are placed in an air oven set at 100°C for 4 hours to remove any moisture present and allowed to cool to room temperature in a desicator. Two blend compositions are selected namely 80%HDPE/20% PP and 20%HDPE/80%PP and the granules are weighed out. The individual polymers as well as the two blends are melted in a Thermo Haake Rheomix 600P blender set at 180°C at a rotor speed of 30 rpm. The blends and the pure polymers are modified with 0.3phr DCP as well as 5phr maleic anhydride along with 0.3phr DCP. The molten polymers are pressed into sheets in a hydraulic press. Three grades of nylon mats namely A, B and C of fibre diameters 0.2, 0.4 and 0.6mm respectively are sandwiched between two polymer sheets and compression moulded in a hydraulic press at 180°C using a 2mm mould and allowed to cool in a cold press. The composites so prepared were subjected to tensile, flexural and impact testing.

The composites prepared by compression moulding of blend matrix with nylon mats as reinforcement are chopped and fed to the barrel of a semi automatic injection moulding machine. The materials are injection moulded into dumb-bell shapes for tensile testing and bars for flexural and impact testing.

5.3. RESULTS AND DISCUSSION

5.3.1 TENSILE PROPERTIES

(a) Tensile Properties of unmodified and modified HDPE composites

The tensile strength of HDPE – nylon mat composites with mats A and B are higher than the matrix while that with mat C has lower value (Fig. 5.1). The tensile modulus of all composites are higher than that the matrix.

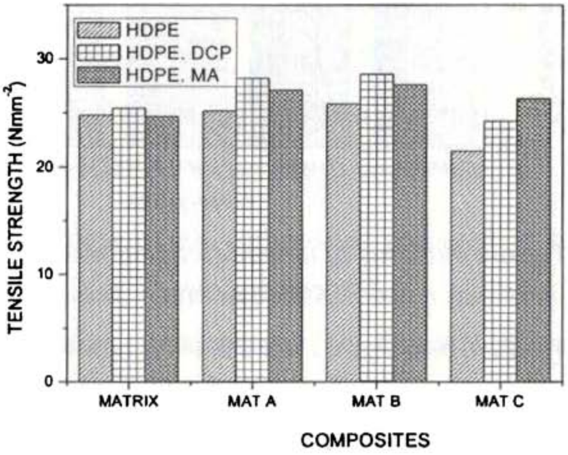

Figure 5.1: *Tensile strength of HDPE, modified HDPE and their composites*

Modification of HDPE with 0.3 phr DCP improves the tensile strength of matrix. The composites with mats A and B show higher tensile strength while that with mat C shows lower value. The tensile modulus of all the composites are higher than the matrix. Modification of HDPE with maleic anhydride along with DCP produces a matrix with same strength as unmodified HDPE while its composites are found to have higher tensile strength than the composites of unmodified HDPE. The tensile modulus of maleic anhydride modified HDPE composites show the highest values (Fig. 5.2).

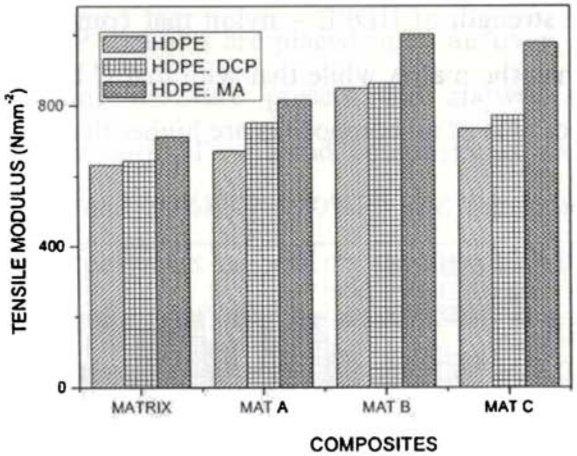

Figure 5.2: *Tensile modulus of unmodified and modified HDPE and their composites.*

The tensile strength of compression moulded HDPE matrix is measured to be 24.75 N/mm^2. The tensile strength of HDPE – nylon composites with nylon mats A and B show improved tensile strength while the composite with nylon mat C has lower tensile strength. The improvement in tensile strength for composites with nylon mats A and B are 1.6 and 4.2% respectively while the decrement for composite with nylon mat C is 13.3%.

Addition of 0.3phr DCP to HDPE improved the tensile strength of the matrix by 2.5%. The composites with nylon mats A and B show improvement in tensile strength by 11 and 13% respectively while the composite with nylon mat C shows lower tensile strength by 5% than the matrix. Comparing of tensile strength of composites with untreated HDPE matrix composites, an overall improvement in tensile strength by 12% for all three types of composites are observed.

Introduction of 5phr maleic anhydride and 0.3phr DCP to HDPE is found to bring out only slightly lesser improvements in tensile strength of the composites. The improvement in tensile strength is 10, 12 and 6.7% for composites with nylon mats A, B and C respectively. Even though the DCP – MA modified matrix has 0.5% lesser tensile strength than HDPE matrix, all composites have better tensile strength than composites of untreated HDPE matrix, the enhancement being by 8, 7 and 22% for composites with nylon mats A, B and C respectively. The highest tensile strength of 28.57 N/mm^2 is shown by DCP modified HDPE - nylon mat B composite.

The tensile modulus of all composites prepared is higher than the corresponding matrices used. Untreated HDPE has a modulus of 630 N/mm^2 which increases by 6, 34 and 16% for the composites with nylon mats A, B and C respectively.

Addition of 0.3phr DCP to HDPE increases the modulus of the matrix by 2% over that of untreated HDPE. The composites of this matrix has improved modulus by 16, 34 and 20% over the matrix with nylon mats A, B and C respectively. These values are an improvement from the untreated HDPE composites by 12, 2 and 5% for nylon mats A, B and C respectively.

Addition of 5phr maleic anhydride and 0.3phr DCP to HDPE increases the modulus of the matrix by 13%. All its composites show improved modulus by 15, 41 and 37% for nylon mats A, B and C respectively. Comparison with the tensile modulus of untreated HDPE composites, these composites have enhanced modulus by 21, 18 and 33% for nylon mats A, B and C respectively.

When HDPE is treated with low molecular weight coupling agents like dicumyl peroxide, the polymer chains undergo cross-linking and as a result the molecular weight increases. The increased molecular weight and cross linking causes increase in tensile strength of the material. This also increases the tensile modulus of the material.

The increase is tensile properties of the matrix causes the increase in tensile properties of the composites also. Its observed that composites of DCP modified HDPE matrix has higher tensile strength than the unmodified HDPE. The lowering of tensile properties of nylon mat C reinforced HDPE can be attributed to poor fibre adhesion and fibre pull out as shown by the SEM pictures [Fig 5.3].

Incorporation of maleic anhydride into HDPE is found to cause increments in tensile properties. Here maleic anhydride units get linked to polyethylene chains which hold the nylon fibres more firmly by hydrogen bonding.

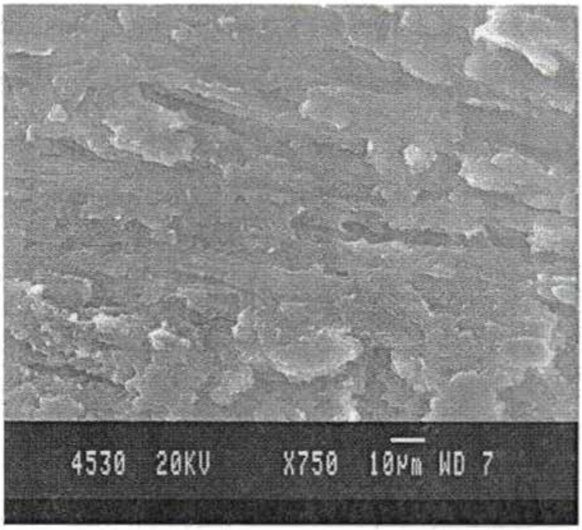

***Figure 5.3:** SEM of HDPE – Nylon mat C composite.*

(b) Tensile Properties of unmodified and modified PP composites

PP – Nylon composites show slightly higher tensile strength than the composites of HDPE. The reinforcement by nylon mats A and B enhance the tensile strength over the matrix while reinforcement by mat C reduces the tensile strength. As in the case of HDPE the tensile modulus of the matrix as well as the composites are higher than those for HDPE composites. The tensile modulus of all composites is greater than that of the matrix. Modification of PP with 0.3 phr DCP lowers the tensile strength of the matrix as well as the composites. Nylon mats A and B as reinforcement improve the tensile strength while mat C lower the tensile strength (Fig. 5.4).

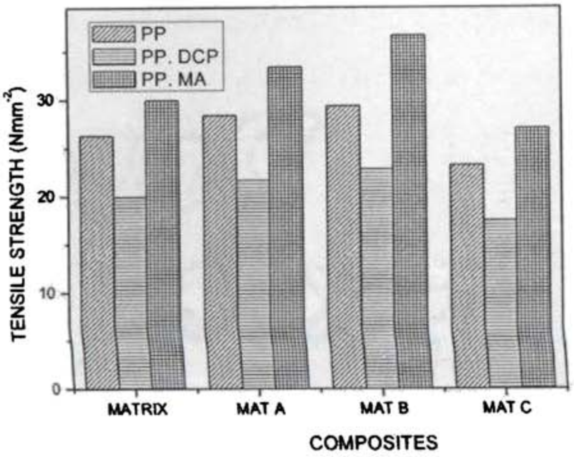

Figure 5.4: Tensile strength of PP, modified PP and their composites.

Tensile modulus of DCP modified PP matrix as well as the composites is lower than the unmodified PP matrix and composites. The reinforcements increase the tensile modulus of DCP modified PP matrix. Incorporation of maleic anhydride enhances the tensile strength of the matrix while the tensile modulus show the opposite trend over unmodified PP matrix and composites (Fig. 5.5).

The pure PP matrix is found to have a tensile strength of 26.8N/mm^2. Introduction of nylon mats A and B increase the tensile strength by 8 and 12% respectively while mat C decreases the tensile strength by 12%. Modification of PP with 0.3phr DCP causes depreciation in tensile strength of the matrix by 25%. Introduction of nylon mats A and B in composites increases the tensile strength by 8.5 and 14% respectively while mat C causes a decrement by 13%. Comparison of tensile strengths of unmodified and

CP modified PP matrix composites, its found that the DCP modified matrix s well as composites showed 25% depreciation in tensile strength.

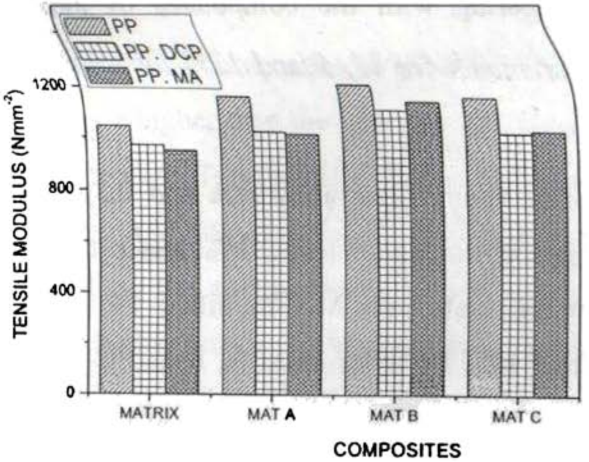

Figure 5.5: *Tensile modulus of PP, modified PP and their composites.*

Introduction of 5phr maleic anhydride and 0.3phr DCP to PP is found to produce better performance by the matrix as well as the composites. The tensile strength of the matrix is improved by 14% over unmodified PP. The composites with nylon mats A and B show improvement in tensile strength by 12 and 22% respectively while composite with mat C shows lowering in tensile strength by 10% than the matrix. Comparison of tensile strengths of PP and maleic anhydride treated PP composites the composites with maleic anhydride treated PP as matrix shows improved tensile strengths of 18, 25 and 16% for nylon mats A, B and C respectively.

The tensile modulus of compression moulded PP is found to be 1044 N/mm^2. Introduction of nylon mats improves the modulus by 12, 16 and 12%

for nylon mats A, B and C respectively. Addition of 0.3phr DCP to PP lowers the modulus of the matrix by 7%. The composites have higher modulus than the matrix, the increments being 6, 15 and 6% for nylon mats A, B and C respectively. Comparing with the composites of unmodified PP matrix composites, the increments are 12, 9 and 12% for nylon mats A, B and C respectively.

Introduction of 5phr maleic anhydride and 0.3phr DCP lowers the modulus of the matrix, the value being 9% lesser than the PP matrix. Incorporation of nylon mats into MA modified PP matrix improvs the modulus by 7, 21 and 10% for nylon mats A, B and C respectively. But all values are lower than untreated PP matrix composites by 12.5, 5 and 11% for nylon mats A, B and C respectively.

The lowering of tensile properties of DCP modified PP can be due to the chain scission caused by incorporation of DCP in to PP matrix. chain scission lowers the molecular weight which in turn lowers the tensile properties. This trend is observed in the composites of DCP modified PP matrix for all reinforcements.The nylon mat reinforcements improve the tensile properties of the DCP modified matrix which is due to the reinforcement of the nylon mat present.

Maleic anhydride is known to graft onto polymer chains and these units attach to nylon fibres by hydrogen bonding increasing the tensile properties. The lowering in tensile strength of nylon mat C reinforced composites can be the inability of the matrix to match the higher tensile strength of the fibre with larger diameter which causes the matrix to crumble under tension.

(c) Tensile Properties of unmodified and modified 80% HDPE/20% PP blend-composites

The tensile strength of composites of 80% HDPE/20% PP blend with nylon mats A and B are higher than the matrix while the composite with mat C has lower tensile strength. The tensile modulus of all composites is greater than that of the matrix. Addition of 0.3 phr DCP improves the tensile strength of the matrix as well as the composites (Fig. 5.6). Composites with nylon mats A and B shows higher tensile modulus than the matrix. Incorporation of maleic anhydride along with DCP further enhances the tensile strength of the matrix and composites with reinforcements of nylon mats A and B. The tensile modulus of maleic anhydride modified matrix is higher than the unmodified matrix which was further enhanced by all three types of reinforcement (Fig. 5.7).

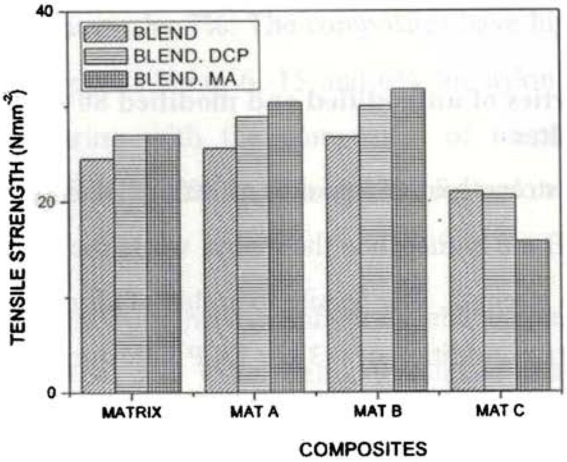

Figure 5.6: *Tensile strength of 80% HDPE/20% PP blend matrix, modified versions and their composites.*

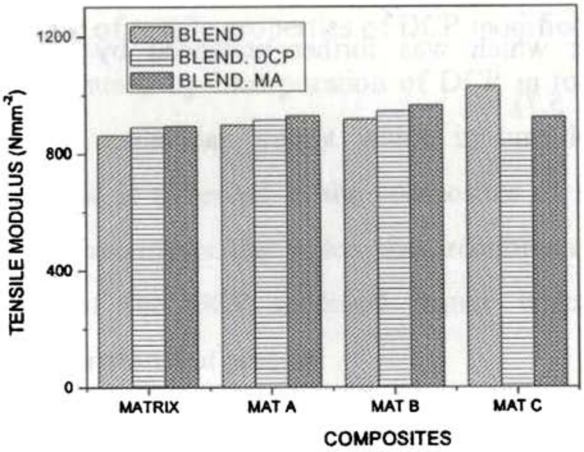

Figure 5.7: *Tensile modulus of 80%HDPE/20%PP blend matrix, modified versions and their composites.*

The matrix of 80% HDPE/20% PP blend prepared by compression moulding shows a tensile strength of 25 N/mm^2 which improves upon introduction of nylon mats A and B while mat C shows lowering of tensile strength. The enhancement shown by nylon mats A and B is 4.5 and 9% respectively while the decrement for mat C is 14%.

Blending of the polymer melt with 0.3phr DCP is found to enhance the tensile strength of the matrix by 10% than the untreated matrix. Composites with nylon mats A and B are stronger than the matrix by 7 and 11% respectively while mat C composite shows a value lesser by 23%. On comparison with the composites of untreated blend as matrix, the DCP treated matrix composites with nylon mats A and B has better tensile strength by 12.6 and 12% respectively while composite with mat C has a 2% lesser value.

Introduction of 5phr maleic anhydride and 0.3phr DCP into the polymer blend improves the tensile strength of the matrix by 10% over the untreated blend. The composites of nylon mats A and B reinforcements show enhancement by 13 and 17% respectively while the composite with nylon mat C shows a 41% lesser value than the matrix. On comparison with tensile strengths of composites with untreated blend matrix, the composites of the treated blend having nylon mats A and B as reinforcement are stronger by 18% while that with mat C is weaker by 25%. The highest tensile strength is observed in the case of composite with nylon mat B with the blend modified by 5phr maleic anhydride and 0.3phr DCP.

The matrix of 80% HDPE/20% PP blend is found to have a tensile modulus of 862 N/mm^2 and the modulus is found to be higher for its composites. The enhancements are 4, 7 and 19% with the introduction of nylon mats A, B and C respectively.

Blending the polymer melt with 0.3phr DCP improves the tensile modulus of the matrix by 4%. The composites prepared with nylon mats A and B show enhancement by 3 and 6% respectively while nylon mat C lowers the modulus by 5% than the matrix. Comparison with untreated blend matrix shows the treated matrix to have higher tensile modulus by 3% and the composites with nylon mats A and B reinforcements for treated blend enhances the value by 2 and 3% respectively while mat C lowered the tensile modulus by 18% than the unmodified matrix.

Introduction of 5phr maleic anhydride and 0.3phr DCP into the blend enhances the modulus of the matrix by 4%. The composites of this matrix has greater tensile modulus than the matrix by 4, 8 and 30% for nylon mats A, B and C respectively. On comparison with the composites of untreated blend as matrix, composites of maleic anhydride treated blend with nylon mats A and B has greater tensile modulus by 3 and 5% respectively while the composite with mat C shows a decrement by 10%. The composite of untreated blend containing nylon mat C as reinforcement has the highest modulus followed by composite of maleic anhydride treated blend with mat C as reinforcement.

(d) Comparison with HDPE – Nylon Composites

Addition of 20% PP to HDPE lowers the tensile strength of the matrix by 1%. The composites of the blend with nylon mats A and B has higher tensile strengths of 2 and 4% respectively than HDPE composites of the same reinforcements. The composite of the blend with nylon mat C is inferior by 2% than the composite of HDPE. Comparing the tensile strengths of DCP modified HDPE as well as 80% HDPE/20% PP blend shows the composites of the modified blend with nylon mats A and B to be stronger than the HDPE composites. The enhancement observed is 2.5 and 5% for nylon mats A and B respectively. But the composite with nylon mat C reinforcement of DCP modified blend is 15% inferior than the DCP modified HDPE composite of nylon mat C. Modification of the blend with 5phr maleic anhydride and 0.3phr DCP enhances the tensile strength of the blend matrix as well as composites with nylon mats A and B over 5phr maleic anhydride and 0.3phr DCP treated HDPE, the enhancement being 9, 12 and 15% for the matrix and composites of nylon mats A and B respectively. But introduction of mat C into maleic anhydride modified blend lowers the tensile strength by 40%.

Comparison of tensile modulus of the 80% HDPE/20% PP blend with HDPE, the blend as the matrix as well as its composites has higher tensile modulus than the HDPE matrix and composites. The enhancement observed is 36, 34, 8 and 40% for the matrix and composites with nylon mats A, B and C respectively. Similar enhancement is observed for 0.3phr DCP modified blend and its composites over 0.3phr DCP modified HDPE matrix. The enhancement is 39, 22, 10 and 10% for the matrix and composites with nylon mats A, B and C respectively. On comparison of the modulus of the matrix and composites of HDPE and 80% HDPE/20% PP blend both modified with 5phr maleic anhydride and 0.3phr DCP shows that the maleic anhydride modified blend matrix and composite with nylon mat A shows enhancement of 26 and 14% respectively over maleic anhydride treated HDPE while the composites of maleic anhydride modified HDPE has better tensile modulus, the depreciation for blend composites being 4 and 5% for nylon mats B and C respectively.

The tensile properties of the unmodified as well as modified blend matrix and composites show the modified blend matrix and composites to have greater values. Addition of DCP during blending causes branching and cross-linking in HDPE and chain scission in PP. These processes lower the mismatch in viscosities of HDPE and PP and compatibilization of the blend takes place. This increases the tensile properties of the modified blend over the unmodified blend. Introduction of nylon mats as reinforcement further improves the tensile properties.

Introduction of nylon mat C into the matrix lowers the tensile properties due to poor adhesion leading to fibre pull out as indicated by SEM pictures [Fig 5.8 & 5.9].

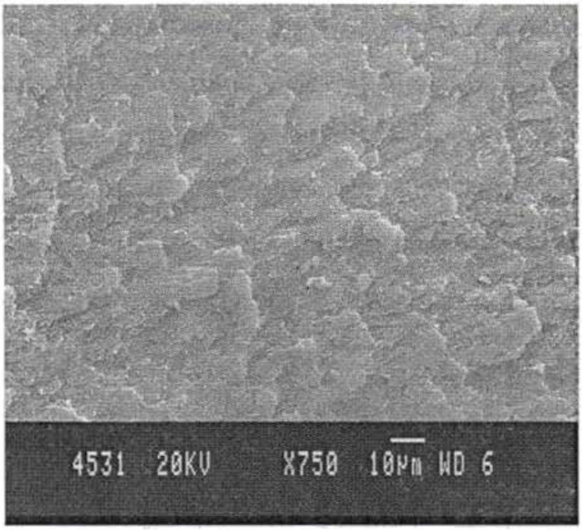

Figure 5.8: *SEM micrograph of unmodified 80% HDPE/20% PP blend reinforced with nylon mat A.*

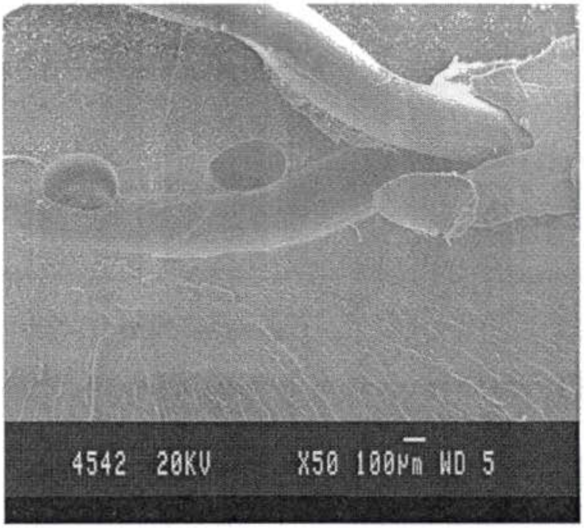

Figure 5.9: *SEM micrograph of DCP modified 80% HDPE/20% PP blend with nylon mat C as reinforcement.*

(e) Tensile Properties of unmodified and modified 20% HDPE/80% PP blend-composites

Composites of 20% HDPE/80% PP blend with nylon mats A and B as reinforcements has higher tensile strength than the matrix. A similar trend is observed in the case of tensile modulus. The composites with reinforcement of nylon mat C has lower tensile strength as well as tensile modulus. Modification of the blend with 0.3 phr DCP lowers the tensile strength of the matrix as well as the composites when compared to the unmodified blend (Fig. 5.10).

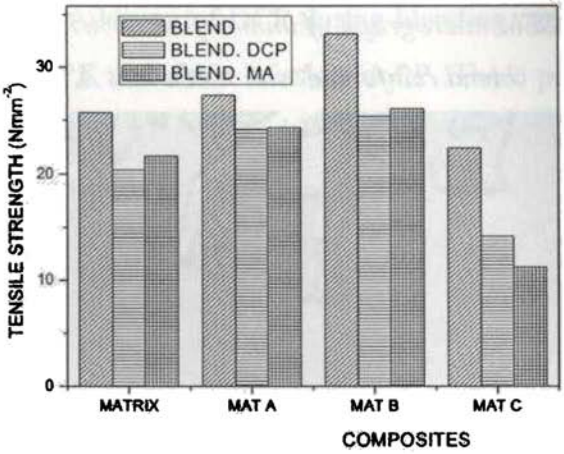

Figure 5.10: Tensile strength of 20% HDPE/80% PP blend matrix, modifications and their composites.

Similar trend is observed for tensile modulus with an exception of mat C composite. All composites has higher tensile modulus than the matrix. Addition of maleic anhydride into the blend makes slight improvement in the tensile strength of the matrix as well as the composites with nylon mats A and B over the DCP modified blend. This is true for the tensile modulus also, all composites having higher tensile modulus than the matrix (Fig. 5.11).

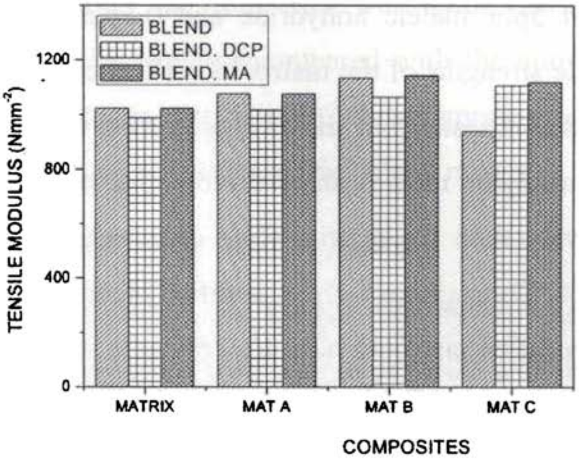

Figure 5.11: *Tensile modulus of 20%HDPE/80% PP blend matrix, modifications and their composites.*

The matrix of 20% HDPE / 80% PP blend is found to be 25.7 N/mm^2. The composites of nylon mats A and B with blend matrix has enhanced tensile strength by 6 and 29% respectively where as the composite with nylon mat C is weak by 12% than the matrix.

Modification of the blend by 0.3phr DCP lowers the tensile strength of the matrix by 20% than the unmodified matrix. The tensile strength is enhanced when nylon mats A and B are used as reinforcement by 19 and 25% respectively over the matrix. The composite with nylon mat C has tensile strength lower by 30% than the matrix. The composites with DCP modified blend shows depreciation in tensile strength by 12, 23 and 37% over composites of unmodified blend matrix for nylon mats A, B and C respectively.

Addition of 5phr maleic anhydride and 0.3phr DCP to the blend improves the tensile strengths of the matrix as well as composites over DCP modified blend and composites but shows depreciation with untreated blend. The composites with nylon mats A and B have higher tensile strength by 12 and 20% respectively than the matrix while composite with mat C has a lower value by 48%. Comparison with unmodified blend as matrix shows the composites with modified matrix to have lesser tensile strength by 15, 11, 21 and 50% for the matrix and composites with nylon mats A, B and C respectively.

The tensile modulus of the blend matrix is measured at 1020 N/mm^2. Introduction of nylon mats A and B to the matrix as reinforcement improves the tensile modulus by 5 and 11% respectively while mat C caused a depreciation of 8%.

Addition of 0.3phr DCP to the blend lowers the tensile modulus of the matrix by 3.5%. All composites shows enhancement of tensile modulus, the value being 3, 8 and 12% higher than the matrix for nylon mats A, B and C respectively. The tensile modulus of the treated matrix composites with nylon mats A and B are weaker by 5 and 6% respectively while composite with mat C is stronger by 19%.

Addition of 5phr maleic anhydride and 0.3phr DCP to the blend did not change the tensile modulus of the matrix. The composites have improved tensile modulus to the tune of 5, 12 and 9% for nylon mats A, B and C respectively. The matrix and composite with nylon mat A show negligible improvement in tensile modulus compared with the unmodified blend. But the composites with nylon mats B and C shows improvement to the tune of 7 and 19% respectively over the unmodified blend matrix.

(f) Comparison with PP – Nylon Composites

Comparison of tensile strength of PP – Nylon and 20% HDPE/80% PP blend – Nylon composites, the composites of PP with nylon mats A and C are stronger than blend composites by 3.5% while composites of the blend with nylon mat B is 13% stronger than the corresponding PP composite. DCP modification of the blend shows improvement in tensile strength in the case of nylon mats A and B by 12% over DCP modified PP composites while the composite with nylon mat C is inferior by 19%. 5phr maleic anhydride and 0.3phr DCP added to the blend as well as PP showed the PP composites to have better tensile strength.

The tensile modulus of the PP matrix as well as the composites is higher than that of the blend as well as the composites. The depreciations for the blend are 2, 8, 7 and 20% for the matrix and composites with nylon mats A, B and C respectively. The tensile modulus of the DCP modified PP matrix and composite with nylon mat C are lower by 2 and 8% than the blend while composites with nylon mats A and B has higher tensile modulus by 1 and 5% respectively. 5phr maleic anhydride and 0.3phr DCP modification of PP and the blend shows the modified blend composites with mats A and C to have higher tensile modulus than modified PP matrix composites while maleic anhydride modified PP matrix composite with mat C has 1% greater value than the blend composite.

The tensile properties of composites of unmodified 20% HDPE/80% PP blend are greater than the matrix due to the reinforcements. The tensile properties of the DCP modified blend are lower than the unmodified blend due to the deteriorating effect of peroxides on PP rich blends. Slight improvements are observed for the composites due to the reinforcing effect of the fibres.

The increase observed in the case of maleic anhydride modified blend matrix composites are due to hydrogen bonding interactions between the matrix and the fibre. The inferior nature of the DCP modified blend matrix is clear from its scanning electron micrograph which shows fibre pull out as well as matrix cracking (Fig 5.12).

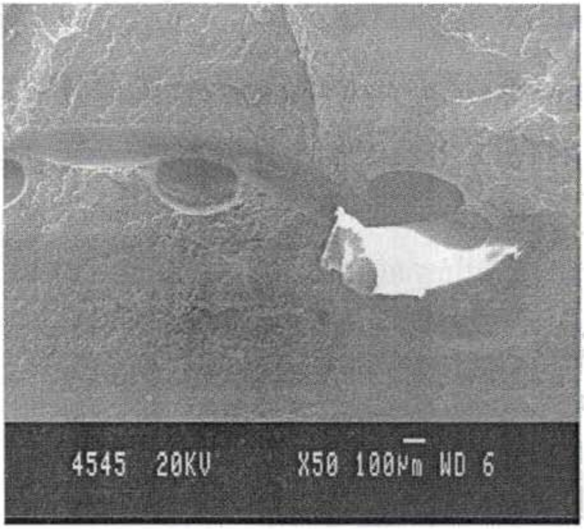

Figure 5.12: *SEM micrograph of DCP modified 20% HDPE/80% PP blend matrix reinforced by nylon mat C.*

Chun *et. al.* examined unidirectional composites composed of continuous fibers with sinusoidal waviness in the matrix. Specimens with various degrees of fiber waviness were fabricated. The tensile and compressive tests were conducted on the specimen to obtain elastic properties and behaviour of the composite materials [9].

Joseph *et. al.* (1999) compared the tensile properties of melt mixed and solution mixed composites. They found treatment with chemicals such as sodium hydroxide, maleic anhydride and permanganate were carried out to improve the bonding at the fiber / polymer interface and all the treatments enhanced the tensile properties of the composites considerably to varying degrees [10].

5.3.2 FLEXURAL PROPERTIES

(a) Flexural Properties of unmodified and modified HDPE composites

The flexural strength and flexural modulus of HDPE composites are higher than the HDPE matrix. 0.3phr DCP modification of HDPE improves the flexural strength and modulus of the matrix as well as the composites. This is further enhanced by addition of maleic anhydride to HDPE (Figs 5.13 & 5.14).

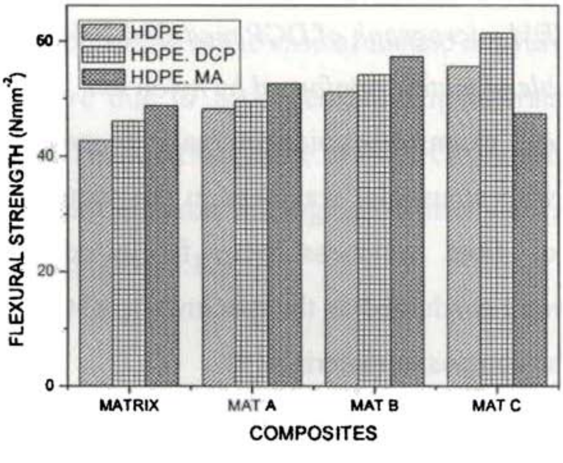

Figure 5.13: Flexural strength of HDPE matrix, modified versions and their composites.

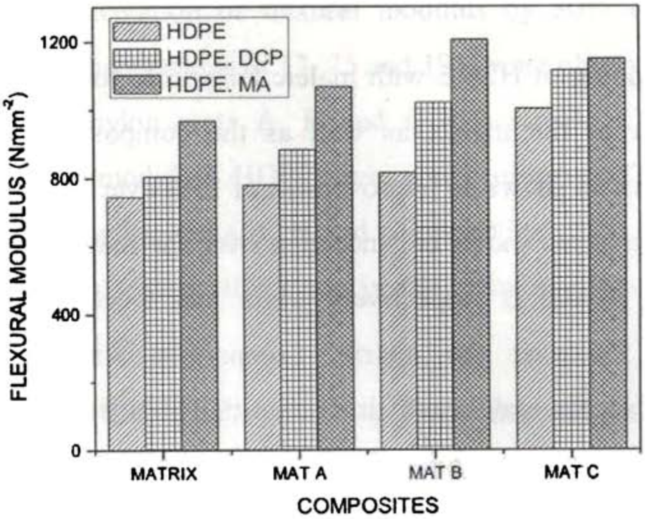

Figure 5.14: *Flexural modulus of HDPE matrix, modified versions and their composites.*

The flexural strength of HDPE matrix is measured at 42.58 N/mm^2. All composites with HDPE matrix and nylon mats as reinforcements has enhanced flexural strength, the enhancement being 13, 20 and 30% for nylon mats A, B and C respectively.

Introduction of 0.3phr DCP into the matrix by melt mixing has positive results on the flexural strength of the matrix as well as its composites. The flexural strength of the matrix gains 8% over the unmodified matrix while the composites with DCP modified matrix has 8, 17 and 33% enhancement for nylon mats A, B and C respectively over the matrix. Comparison with composites of unmodified matrix shows the DCP modified matrix composites to be stronger by 3, 6 and 11% for nylon mats A, B and C respectively.

Melt blending of HDPE with maleic anhydride further improves the flexural strength of the matrix as well as the composites. The flexural strength of the matrix shows an improvement of 15% over unmodified HDPE matrix. The composites shows enhancement over the matrix by 8 and 18% for nylon mats A and B respectively while mat C composite shows a curtailment of 3% over the matrix. Comparison with HDPE matrix composites indicate the maleic anhydride modified HDPE matrix composites of mats A and B to be more stronger by 9 and 12% while composite with mat C to be weaker by 15%. The composite with maleic anhydride modified HDPE matrix and nylon mat B reinforcement has the highest flexural strength.

The HDPE matrix has a flexural modulus of 744 N/mm^2. All composites show improvement in flexural modulus irrespective of the reinforcement used. The enhancements were 5, 10 and 35% for composites with nylon mats A, B and C respectively.

0.3phr DCP modification of HDPE produces composites with improved flexural modulus. The flexural modulus of the matrix is found to be 8% higher than the unmodified HDPE. Further increments of 10, 27 and 39% are made by the introduction of nylon mats A, B and C respectively as reinforcements. Comparing with the composites of unmodified HDPE, the enhancements made are 13, 25 and 11% for nylon mats A, B and C respectively.

Modification of HDPE with 0.3phr DCP and 1phr maleic anhydride brought out augmentation of flexural modulus by 30% over unmodified HDPE. Further enhancements of 13, 25 and 19% were observed in the case of composites with nylon mats A, B and C respectively. Comparison with composites of unmodified HDPE, we could observe 37, 48 and 15% augmentation for nylon mats A, B and C respectively. The composite with maleic anhydride modified HDPE matrix and nylon mat B reinforcement had the highest flexural modulus.

When HDPE is treated with low molecular weight coupling agents like dicumyl peroxide, the polymer chains undergo cross-linking and as a result the molecular weight increases. The increased molecular weight and cross linking causes increase in flexural properties of the matrix material. Further improvements in flexural properties of nylon mat A, B & C reinforcements are due to the effect of the nylon fibres. The flexural strength increases with fibre diameter.

(b) Flexural Properties of unmodified and modified PP composites

All composites with PP matrix has higher flexural strength and modulus compared to the matrix. Addition of 0.3 phr DCP to PP lowers the flexural strength and modulus of the matrix and composites. However all composites have enhanced flexural strength and modulus when compared to the DCP modified matrix. Addition of maleic anhydride along with DCP enhances the flexural strength and modulus of the matrix and composites over PP matrix and composites. The matrix has lower flexural strength and modulus when compared to the composites (Figures 5.15 & 5.16).

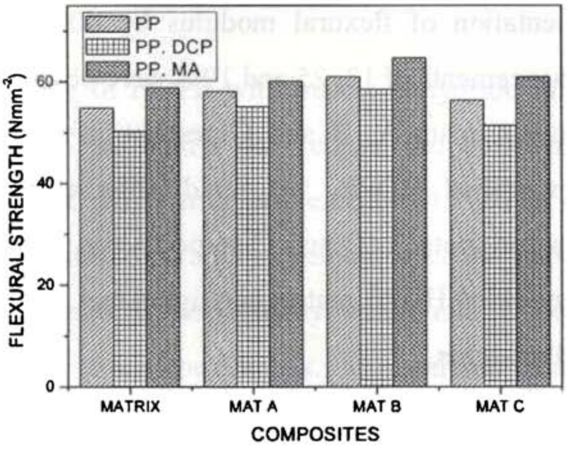

Figure 5.15: *Flexural strength of PP matrix, modified versions and their composites.*

The PP matrix shows a flexural strength of 54.8 N/mm^2 which is greater than that of HDPE matrix. All its composites show greater flexural strength than the matrix. The improvements induced are 6, 11 and 3% for nylon mats A, B and C respectively.

Modification of PP using 0.3phr DCP brings out decrease in flexural strength of the matrix as well as its composites. The curtailment in the case of matrix is of the order of 8%. The introduction of reinforcements induces increments in flexural strength, the increments being 10, 16 and 2% for nylon mats A, B and C respectively over the matrix. These composites are inferior to the unmodified PP composites by 5, 4 and 9% for nylon mats A, B and C respectively.

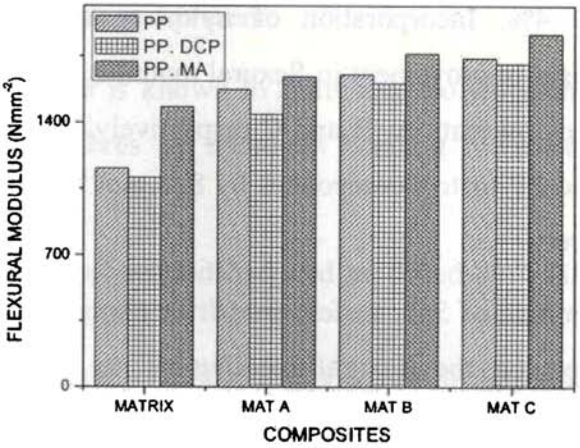

Figure 5.16: *Flexural modulus of PP matrix, modified versions and their composites*

Modification of PP by 5phr maleic anhydride and 0.3phr DCP shows enhancement of flexural strength of the matrix as well as composites. The flexural strength of the matrix shows an enhancement of 7% over unmodified PP matrix. Further enhancement to the tune of 2, 10 and 4% are produced on incorporation of nylon mats A, B and C respectively. These composites are superior in flexural strength to unmodified PP matrix composites by 4, 6 and 8% for nylon mats A, B and C respectively. The highest flexural strength is observed in the case of maleic anhydride modified PP – nylon mat B composite.

The flexural modulus for PP matrix is measured at 1157 N/mm^2 which is augmented by the incorporation of nylon mats as reinforcements. The augmentations caused are 36, 43 and 50% than the matrix for nylon mats A, B and C respectively.

Modification of PP with 0.3phr DCP curtails the flexural modulus of the matrix by 4%. Incorporation of nylon mats as reinforcements in composites causes improvement in flexural modulus by 39, 45 and 54% than the matrix for nylon mats A, B and C respectively. These results are lesser than unmodified PP matrix composites by 8, 3 and 2% for nylon mats A, B and C respectively.

Incorporation of 5phr maleic anhydride along with 0.3phr DCP has a greatening effect on the flexural modulus of the matrix as well as the composites. The matrix shows a greatening by 28% than unmodified PP matrix and the composites shows further greatening than the matrix by 10, 19 and 26% for nylon mats A, B and C respectively. Comparing with PP matrix composites, the flexural modulus shows improvement by 4% for nylon mat A and 7% each for mat B and C respectively. The highest flexural modulus is observed in the case of maleic anhydride modified PP – nylon mat B composite.

The flexural properties of composites are greater than the matrix due to the reinforcements. The composites of nylon mat C reinforcements show slightly lower values due to the inability of the matrix to withstand high load as done by the strong fibres

The lowering of flexural properties of DCP modified PP can be due to the chain scission caused by incorporation of DCP in to PP matrix. chain scission lowers the molecular weight which in turn lowers the flexuralproperties. This trend is observed in the composites of DCP modified PP matrix for all reinforcements.The nylon mat reinforcements improve the tensile properties of the DCP modified matrix which is due to the reinforcement of the nylon mat present.

Maleic anhydride is known to graft onto polymer chains and these units attach to nylon fibres by hydrogen bonding increasing the flexural properties.

(c) Flexural Properties of unmodified and modified 80% HDPE/20% PP blend-composites

The flexural strength of HDPE is lowered on introduction of PP by melt blending. The 80% HDPE 20% PP blend studied shows lower flexural strength but higher flexural modulus when compared to HDPE (Fig. 5.17 & 18). All three types of composites have higher flexural strength and modulus than the matrix. Addition of 0.3 phr DCP to the blend enhances the flexural strength and modulus of the matrix as well as the composites, the composites having higher values than the matrix. Incorporation of maleic anhydride along with DCP further improves the flexural properties of the matrix and composites.

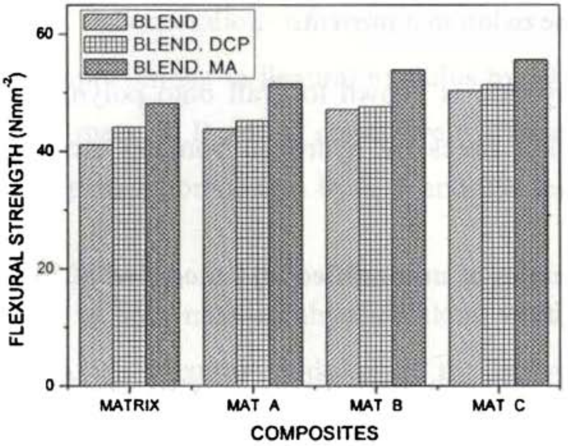

Figure 5.17: *Flexural strength of 80% HDPE/20% PP blend matrix, modifications and their composites.*

The flexural strength of the blend matrix is measured at 41 N/mm^2 which improved with the incorporation of nylon mats as reinforcements. The augmentations caused are 7, 15 and 23% for nylon mats A, B and C respectively.

Modification of the blend with 0.3phr DCP causes a 7% enhancement in the flexural strength of the matrix over the unmodified blend matrix. The flexural strength of the composites is further enhanced over the matrix by 3, 8 and 16% for nylon mats A, B and C respectively. These results are also a slight improvement from the composites of unmodified blend by 3, 1 and 2% for nylon mats A, B and C respectively.

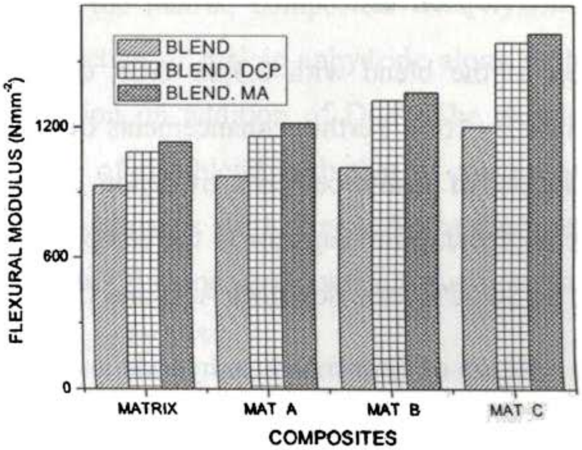

Figure 5.18: Flexural modulus of 80% HDPE/20% PP blend matrix, modifications and their composites.

The addition of 5phr maleic anhydride along with 0.3phr DCP to the blend augments the flexural strength of the matrix by 17% over the unmodified blend matrix. All composites prepared have improved flexural strength over the matrix by 7, 12 and 16% for nylon mats A, B and C respectively. The enhancements over the composites of unmodified blend are 8, 14 and 11% for nylon mats A, B and C respectively. The highest flexural strength is observed in the case of maleic anhydride modified mat C composite.

The blend matrix shows a flexural modulus of 931 N/mm^2. All its composites are stronger in terms of flexural modulus by 5, 9 and 29% for nylon mats A, B and C respectively.

Modification of the blend with 0.3phr DCP enlarges the flexural modulus of the matrix by 16%. Further enhancements of 7, 22 and 46% are noted on incorporation of reinforcements of nylon mats A, B and C respectively. These composites are superior to the composites of unmodified blend as matrix by 19, 30 32% for nylon mats A, B and C respectively.

The addition of 5phr maleic anhydride and 0.3phr DCP to the blend augments the flexural modulus of the matrix as well as its composites. The matrix is 21% stronger than the unmodified matrix. The nylon mats A, B and C causes further improvement by 8, 20 and 44% respectively. Comparison with composites of unmodified matrix, these show an enhancement by 25, 34 and 36% for nylon mats A, B and C respectively. The highest flexural modulus is observed in the case of maleic anhydride modified mat C composite.

(d) Comparison to HDPE – Nylon Composites

The flexural strength of HDPE and its DCP as well as maleic anhydride modifications used as matrix show greater values than the corresponding blend matrix. Comparison of the unmodified blend to HDPE, the matrix and the composites of the blend are weaker than the unmodified HDPE matrix and the composites. The depreciations are 4% for the matrix, 9% each for composites with nylon mats A and C and 8% for composites with nylon mat B. A similar trend is observed in the case of DCP modification of the blend as well as HDPE. The depreciations observed are 4, 9, 12 and 16% for the matrix, composites with nylon mats A, B and C respectively. Introduction of maleic anhydride along with DCP is found to check the deterioration on addition of DCP. The deterioration of flexural strength in the case of the blend with that of maleic anhydride modified HDPE matrix and composites are 1, 2 and 6% for the matrix and composites with nylon mats A and B respectively while the composite of the blend with nylon mat C is stronger by 18%.

Comparison of flexural modulus of composites of the blend and its modifications as matrix to HDPE and its modifications as matrix, the blend and its modifications produces composites with higher modulus. The augmentation over HDPE in the case of unmodified blend is 25% each for the matrix and composites with nylon mats A and B while composite with mat C show an augmentation of 20%. Considering the DCP modification of the blend, the matrix as well as the composites have higher flexural modulus than DCP modified HDPE and composites. The increments are 34, 31, 29 and 42% for the matrix, composites with nylon mats A, B and C respectively. Similar is the observation in the case of maleic anhydride modification of the blend. The improvements are 17, 14, 12 and 42% for the matrix, composites with nylon mats A, B and C respectively.

Unmodified HDPE has greater flexural strength than the blend due to formation of an immiscible polymer blend of HDPE and PP on melt blending. The composites show improved properties due to the reinforcements.

The flexural properties of the unmodified as well as modified blend matrix and composites show the modified blend matrix and composites to have greater values. Addition of DCP causes compatibilization of the blend. This increases the flexural properties of the modified blend over the unmodified blend. Introduction of nylon mats as reinforcement further improves the tensile properties.

(e) Flexural Properties of unmodified and modified 20% HDPE/80% PP blend-composites

Studies on 20% HDPE/80% PP blend and its composites reveal that the incorporation of nylon mat C as reinforcement has a diminishing effect on the flexural strength in the case of the blend matrix as well as its modifications.

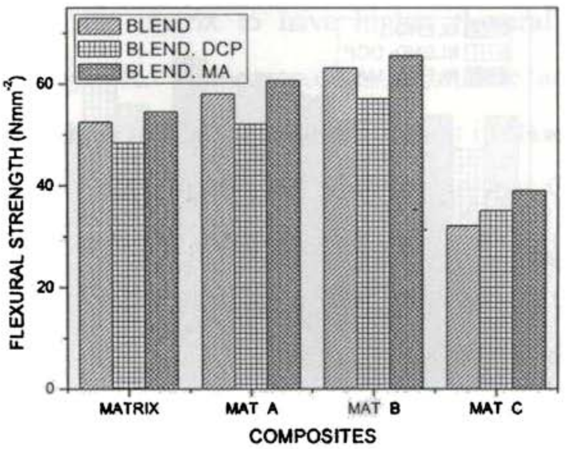

Figure 5.19: *Flexural strength of 20% HDPE/80% PP blend matrix, modified versions and their composites.*

Introduction of nylon mats A and B as reinforcement improves the flexural strength of the matrix in all cases (Fig. 5.19). The flexural modulus of the composites is higher than the matrix for the blend as well as its DCP modification. When maleic anhydride is introduced, the flexural modulus of nylon mat C composite is lower than that of the matrix (Fig. 5.20).

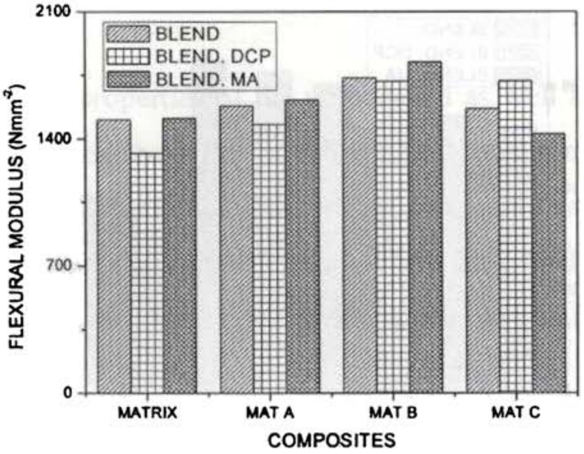

Figure 5.20: *Flexural modulus of 20% HDPE/80% PP blend matrix, modified versions and their composites.*

The flexural strength of the blend matrix is observed to be 52.5 N/mm^2 which improved by 10 and 20% respectively when nylon mats A and B are introduced. But introduction of nylon mat C lowers the flexural strength of the composite by 38%.

DCP modification of the blend causes deterioration of the flexural strength of the blend matrix by 8%. The composites prepared by the introduction of nylon mats A and B as reinforcements show enhanced flexural strength by 8 and 18% respectively over the matrix while nylon mat C introduces a curtailment by 27%. The DCP modified blend matrix and its composites are weaker than the unmodified blend matrix and its composites by 8, 10, 10 and 9% for the matrix and composites with nylon mats A, B and C respectively.

Introduction of maleic anhydride along with DCP into the blend by melt mixing causes the matrix to have higher flexural strength than the unmodified blend by 4%. The composites of maleic anhydride modified blend with nylon mats A and B show augmentation in flexural strength by 11 and 20% respectively over the matrix while nylon mat C as reinforcement causes a curtailment by 28%. Overall, the composites of maleic anhydride modified blend are stronger in terms of flexural strength than composites of unmodified blend by 5, 4 and 21% for nylon mats A, B and C respectively. The composite of maleic anhydride modified blend with nylon mat B has the highest flexural strength.

The 20% HDPE 80% PP blend matrix shows a flexural modulus of 1504 N/mm^2 which is augmented by the nylon mats introduced as reinforcement. The augmentation brought out is 5, 15 and 17% for nylon mats A, B and C respectively.

DCP modification of the blend causes a fall in flexural modulus of the matrix by 13%. The reinforcement by nylon mat A causes an augmentation of 12% while nylon mats B and C cause augmentation by 30% each over that of the matrix. Overall, the DCP modified matrix and its composites with nylon mats A and B are weaker than unmodified blend matrix and composites by 13, 6 and 1% respectively while composite with mat C was stronger by 10%.

Incorporation of maleic anhydride along with DCP slightly improves the flexural modulus of the matrix over the unmodified blend matrix. Introduction of nylon mats A and B cause augmentation by 7 and 20% respectively while mat C causes curtailment by 6%. The composites with nylon mats A and B are stronger than the untreated blend matrix by 2 and 5% respectively while its mat C composite was weak by 9%.

(f) Comparison with PP – Nylon Composites

The blend as well as its modifications is weaker in flexural strength than the corresponding PP matrix. Introduction of nylon mat A into PP as well as the 20% HDPE 80% PP blend matrices produce composites of same flexural strength. Introduction of nylon mat B into the blend show a 3% enhancement than the PP composite while mat C composite produce a 40% weaker composite. DCP modification of the blend show a weaker matrix than DCP modified PP, all composites of the blend also weaker than the corresponding PP composites. The curtailment shown is 4, 5, 2 and 32% for the matrix, composites with nylon mat A, B and C respectively. Maleic anhydride modification of the blend causes a curtailment of 7% in flexural strength of the matrix and 36% in the case of composite with nylon mat C. The composites of the modified blend with nylon mats A and B are slightly better than the corresponding modified PP composites.

The flexural modulus of the blend as well as the modifications has better values than the corresponding PP matrices. The unmodified blend has a 30% greater modulus than PP. Composites with mat A of both PP and the blend have same flexural modulus. The composite of the blend with mat B is stronger by 5% and with mat C is weaker by 10%. The DCP modification of the blend is stronger than DCP modification of PP by 19%. The composites of the modified blend with mats A and B are stronger by 3 and 7% respectively while the composite with mat C is only slightly stronger. Maleic anhydride modification of the blend is 2% stronger than maleic anhydride modification of PP. The composites of the modified blend with nylon mats A and C have lesser flexural modulus by 2 and 24% respectively while mat B reinforcement to the modified blend improved the flexural modulus by 3%.

The flexural strength of the composites were higher than their matrix due to the reinforcing nature of the nylon mats. The DCP modification has loer values due to the deteriorating effect of DCP on the larger component PP. Slight improvements are observed for the composites due to the reinforcing effect of the fibres.

The increase observed in the case of maleic anhydride modified blend matrix composites are due to hydrogen bonding interactions between the matrix and the fibre.

The lower flexural properties of the blend composites than PP is due to the formation of immiscible blend with HDPE.

5.3.3 IMPACT STRENGTH

(a) Impact Strength of unmodified and modified HDPE composites

Studies of the HDPE composites with nylon mat reinforcements reveals higher impact strength for composites than the matrix in the case of HDPE, its DCP modification and maleic anhydride modification. DCP modification of HDPE improved the impact strength of the matrix as well as composites over unmodified HDPE while maleic anhydride modification deteriorated the impact strength of matrix as well as composites (Fig. 5.21).

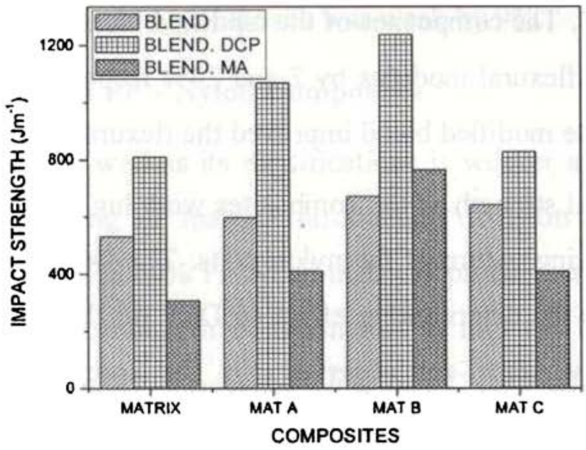

Figure 5.21: *Impact strength of HDPE matrix, modified versions and their composites.*

HDPE has impact strength of 530 J/mm^2 which improved on nylon reinforcement. The augmentation caused was 13, 27 and 21% over the matrix for nylon mats A, B and C respectively.

DCP modification of HDPE is found to enhance the impact strength of 809 J/mm^2, a 52% increase over unmodified HDPE. All composites had enhancement in impact strength to the tune of 32, 53 and 2% for nylon mats A, B and C respectively. These observations were an improvement over composites of unmodified HDPE matrix by 79, 84 and 29% for nylon mats A, B and C respectively.

Addition of maleic anhydride along with DCP to HDPE lowered the impact strength of the matrix by 42%. All its composites had higher impact strength than the matrix. The augmentations observed were34, 150 and 33%

for nylon mats A, B and C respectively. But the impact strength in the case of composites with nylon mats A and C were lower than the respective HDPE composites by 31 and 36% respectively while nylon B composite was stronger by 14%. The highest impact strength was observed in the case of DCP modified HDPE – nylon mat B composite.

The higher impact strength of HDPE – nylon composites are due to the reinforcements introduced. DCP modification of HDPE formed a tougher material which had higher impact resistance than the unmodified HDPE. The composites had greater impact strength due to the reinforcements.

(b) Impact Strength of unmodified and modified PP composites

Nylon mats A and B as reinforcements to PP matrix show the composites to have higher impact strength than the matrix while mat C composite has lower impact strength. This is also observed in the case of its DCP and maleic anhydride modifications. DCP modification lowers the impact strength of the matrix and its composites when compared with unmodified PP matrix and composites while maleic anhydride modification improves the impact strength of matrix as well as composites (Fig. 5.22).

The impact strength of PP matrix is measured at 200 J/mm^2 which improves on introduction of nylon mats A and B while mat C brings out lower impact strength. The increments made are 15 and 80% for nylon mats A and B while a 28% decrement is observed for nylon mat C reinforcement.

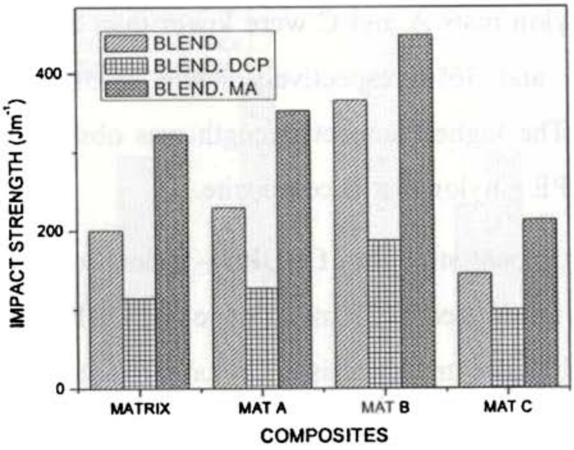

Figure 5.22: *Impact strength of PP matrix, modified versions and their composites*

Blending PP with 0.3 phr DCP lowers the impact strength of the matrix by 43 %. Slight improvement is observed on introduction of nylon mat A while a 7% improvement is observed for mat B reinforcement. The impact strength is lowered by mat C to an extent of 13 %. The DCP modified PP matrix composites are weaker than unmodified PP matrix composites, the curtailments being 44, 49 and 32% for nylon mats A, B and C respectively.

Introduction of maleic anhydride along with DCP to PP improves the impact strength of the matrix as well as the composites. The matrix is stronger by 60% than unmodified PP. The composites with nylon mats A and B as reinforcement show improvement in impact strength by 9 and 39% respectively while mat C lowers the impact strength by 34%. All the three composites of maleic anhydride modified PP are stronger than unmodified PP composites by 53, 23 and 47% for nylon mats A, B and C respectively. The highest impact strength is observed in the case of maleic anhydride modified PP matrix with nylon mat B as reinforcement.

The higher impact strength of PP – nylon composites are due to the reinforcements introduced. DCP modification of PP formed a weaker material which had lower impact resistance than the unmodified HDPE. The composites had greater impact strength due to the reinforcements. Maleic anhydride modification produces better results due to the interactions between the matrix and reinforcements.

Flaris and Stachurski focused an improvement of poly propylene's poor impact strength at low temperatures by blending with PE. The addition of LLDPE alone is ineffective in improving the impact strength of PP to acceptable levels for applications at low temperatures. This may be due to the fact that the dispersed LLDPE particles are present as a minor percentage and cannot initiate plastic deformations crazes nor arrest crack growth to the extent of the EP copolymer. Adhesion between these two components is improved by the presence of ethylene–propylene block copolymer as each segment anchors firmly in the phase it is trying to compatibilizer.

To maximize the impact strength of a blend, a ternary component was considered which actually improved the adhesion of the two components but also reinforced the matrix [11].

(c) Impact Properties of unmodified and modified 80% HDPE/20% PP blend-composites

Introduction of nylon mat reinforcements improves the impact strength of composites with 80% HDPE 20% PP blend matrix. This is true for its DCP as well as maleic anhydride modifications. The impact strength measured is higher for maleic anhydride modification than DCP modification (Fig. 5.23).

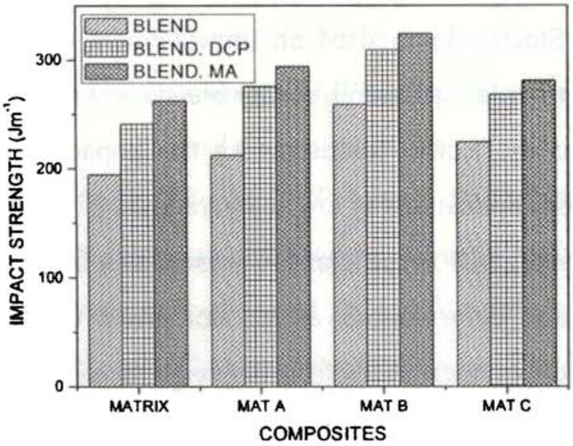

Figure 5.23: *Impact strength of 80% HDPE/20% PP blend matrix, modified versions and their composites.*

Incorporation of PP to an extend of 20% to HDPE is found to lower the impact strength of the matrix by nearly 40%. The impact strength is augmented by the introduction of nylon mats to an extent of 9, 34 and 15% for nylon mats A, B and C respectively over the matrix. But these composites show impact strength of about 40% when compared with HDPE composites.

Modification of the blend by 0.3phr DCP improves the impact strength of the matrix by 24% over the unmodified blend matrix. All its composites have improved impact strength than the matrix as well as the corresponding unmodified blend composites. The augmentations over the matrix are 14, 28 and 11% for nylon mats A, B and C respectively. The augmentations over the corresponding unmodified blend composites are 30, 19 and 20% for nylon mats A, B and C respectively.

Addition of maleic anhydride along with DCP further improves the impact strength of the matrix as well as the composites over DCP modified blend matrix and its composites. The matrix shows an improvement of 35% over the unmodified blend matrix. A further enhancement of 12, 24 and 75 are observed for reinforcements of nylon mats A, B and C respectively. When compared to unmodified blend composites, enhancement of 39% for nylon mat A and 25% for nylon mats B and C are observed in the case of maleic anhydride modified blend composites. The highest impact strength is shown by the composite of nylon mat B with maleic anhydride modified blend matrix. But all composites with blend matrix are inferior to HDPE composites.

The composites of the unmodified blend had greater impact strength due to the reinforcements introduced. DCP modification caused the improvement of the blend matrix and hence better impact resistance observed. Introduction of DCP into the matrix improved the adhesion between the fibres and matrix which further improved the impact strength.

(d) Impact Properties of unmodified and modified 20% HDPE/80% PP blend-composites

Improvement in impact strength is observed on introduction of nylon mats as reinforcements for composites of 20% HDPE/80% PP blend and its modifications as matrix. The DCP modification lower the impact strength of the matrix which is improved by addition of reinforcements. But maleic anhydride modification improved the impact strength of the matrix as well as its composites over the unmodified blend and its composites (Fig 5.24).

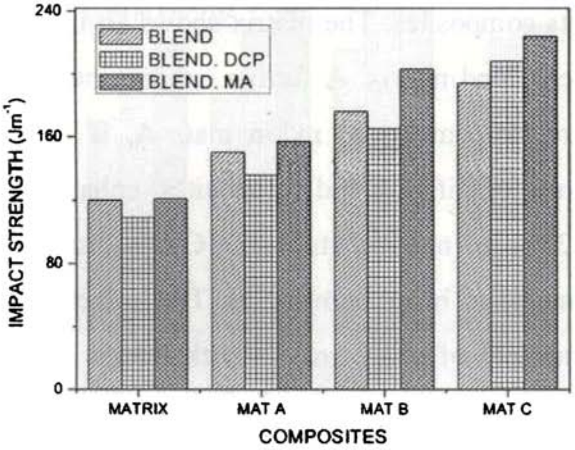

Figure 5.24: *Impact strength of 20% HDPE/80% PP blend matrix, modified versions and their composites.*

Addition of HDPE to an extent of 20% to PP is found to lower the impact strength of the matrix by 40%. Incorporation of nylon mat reinforcements shows the composites to have greater impact strength. The enhancements observed are 25, 46 and 62% for nylon mats A, B and C respectively.

Blending with 0.3 phr DCP is found to lower the impact strength of the matrix by 10%. The composites of the modified blend are stronger than the matrix by 25, 50 and 83% for nylon mats A, B and C respectively. Comparison with composites of the unmodified blend show that the composites with nylon mats A and B are weaker by 10 and 6% respectively while that with nylon mat C is stronger by 7%.

Addition of maleic anhydride along with DCP gave a matrix as strong as unmodified blend matrix. The composites are stronger than the matrix by 30, 68 and 85% for nylon mats A, B and C respectively. The composite with nylon mat A is 5% stronger than the unmodified blend composite while nylon mats B and C improves the impact strength by 15% each over the unmodified blend composite. The highest impact strength is shown by maleic anhydride modified blend – nylon mat C composite. But all these composites are weaker than PP composites.

The impact strength of the composites of the unmodified blend are greater than the matrix due to the reinforcing effect of nylon mats used as reinforcements. The lowering of impact resistance observed in the case of its DCP modification is due to the chain scission of PP component which is the major component in the blend. Incorporation of maleic anhydride increases interaction between the matrix and fibre causing augmentation in impact strength.

Hsiao and Daniel investigated the effect of fiber waviness on stiffness and strength reduction of unidirectional composites under compressive loading. They observed that in unidirectional composites both major

Young's modulus and compressive strength are degraded seriously with increasing fibre waviness. Material anistropy is also shown to influence the degree of stiffness and strength reduction [12].

In a study of the flexural creep behaviour of poly propylene and glass giber commingled woven composite sheets obtaining the test samples in a compression moulding apparatus at different plate temperatures. Greco *et. al.* observed higher temperatures of the plates lead to a composite with a low creep compliance, which was related to the crystalline structure developed in the polymer matrix during cooling and to a better fibre impregnations. An increase in the temperature of the mould resulted in higher degree of crystallinity of the polymer matrix and lower final void fraction of the composite. Higher crystalline fraction and lamellar thickness of crystallization were found to decrease the ductility of the composite as evidenced from Charpy impact tests [13].

Kugler *et. al.* conducted a detailed survey of the localized fiber waviness which develops in unidirectional thermoplastic laminates (T300/P 1700) in order to determine how part length effects the distribution of fiber waviness. They observed that waviness severity increases slightly with increasing part length [14].

Lammerant and Verpoest, during their investigation of the transverse impact of plate like composite specimen showed an accurate prediction of the development of matrix cracks and delaminations during impact requires the use of energy criteria taking into account the appropriate fracture toughness values depending on the interface and the mixed mode of loading [15].

Hsuch in a study of the Young's modulus of a unidirectional discontinous fiber composite predicted stress distribution along the fiber length during uniaxial loading of the composite in an excellent agreement with that obtained form a finite element analysis [16].

Beckert and Lauke investigated the interface failure process of a single fibre pull out test for the measurement of fiber / matrix adhesion on the basis of a fracture mechanics debonding criterion. They observed that the actual adhesion failure was closely connected with the interface local normal load while local shear load induces sub microscopic friction and matrix inelasticity which strongly reduce the interface sensitivity [17].

5.3.4 MECHANICAL PROPERTIES OF RECYCLED COMPOSITES

(a) Effect of recycling on the tensile strength of 80% HDPE/20% PP blend matrix and composites

The tensile strength of 80% HDPE/20% PP blend matrix and composites on recycling showed a trend similar to that of the composites – reinforcements with nylon mat A & B showing greater tensile strength than the matrix. The tensile strength of the composite with nylon mat A & B as reinforcements were greater than that of the matrix by 2 & 3.5%. The recycled material using nylon mat C as reinforcement exhibited lower tensile strength than the matrix by 5%. The recycled material had lower tensile strength than the composites.

The DCP modified blend and composites on recycling exhibited trends similar to unmodified blend and composites. The tensile strengths of nylon mat A & B reinforced composites on recycling had greater values by 4

& 8% than the recycled matrix. The composite with nylon mat C as reinforcement showed a decrement by 24%. The recycled material of DCP modifications had greater tensile strength than those of the unmodified blend.

The maleic anhydride grafted blend and its composites also showed a similar trend. The increments observed were 10 & 15% for nylon mat A & B as reinforcements and a decrement of 25% was observed for nylon mat C as reinforcement [Fig. 5.25].

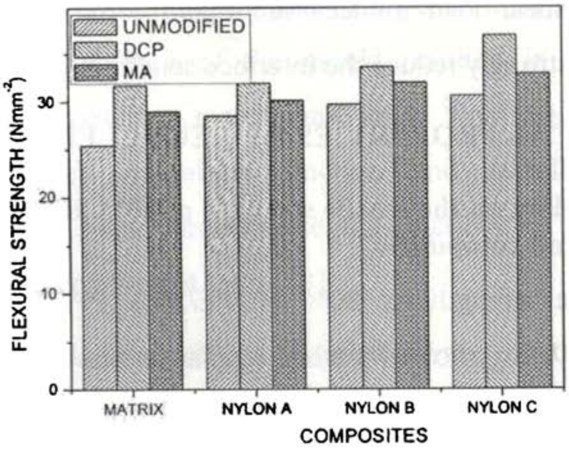

***Figure 5.25:** Comparison of tensile strength of recycled matrix and composites of unmodified and modified 80% HDPE/20% PP blend.*

(b) Effect of recycling on the tensile strength of 20% HDPE / 80% PP blend matrix and composites

All recycled samples had greater tensile strength than their respective matrix materials. The tensile strengths of the matrix and composites with nylon mat A & B as reinforcements were higher than those of the composites itself.

The recycled matrix possessed lower tensile strength than the recycled composites. The increments observed were 1.7 & 9.2% for composite with nylon mats A & B as reinforcements and a decrement of 50% in the case of nylon mat C reinforcement.

The recycled composites of DCP modified blend possessed higher tensile strength than the matrix material for nylon mats A & B used as reinforcement. The increments over the matrix materials were 20 & 23% and a decrement of 30% for nylon mat C reinforcement.

Increments of 1 & 1.5% were observed when composites with nylon mats A & B were used as reinforcements for maleic anhydride grafted blend as matrix were recycled. The nylon mat C reinforcement exhibited a decrement of 40% over the matrix [Fig 5.26].

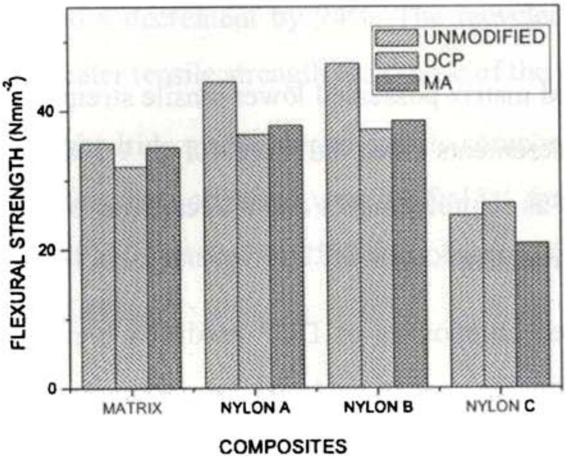

Figure 5.26: *Comparison of tensile strength of recycled matrix and composites of unmodified and modified 20% HDPE/80% PP blend.*

(c) Effect of recycling on the flexural strength of 80% HDPE/20% PP blend matrix and composites

The flexural strength of unmodified blend matrix composites was higher than that of the matrix. The increments observed were 12, 17 & 20% for nylon mat A, B & C as reinforcements respectively. A similar trend was observed when DCP modified blend was used as matrix. The increments observed were a, 6 & 16% respectively. The maleic anhydride grafted blend also showed the same trend, the increments in flexural strength over the matrix being 4, 10 & 14% respectively (Fig. 5.27).

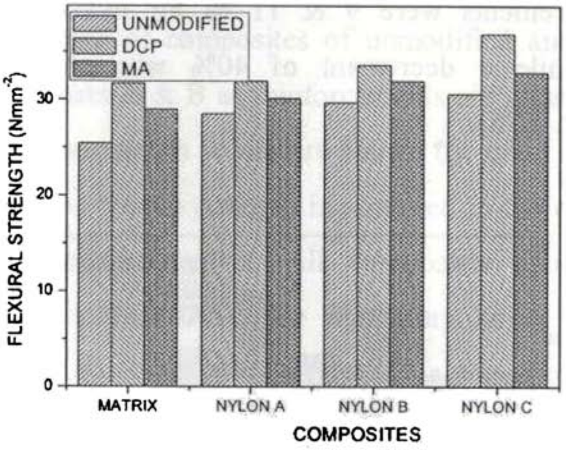

Figure 5.27: *Comparison of tensile strength of recycled matrix and composites of unmodified and modified 80% HDPE / 20% PP blend.*

(d) Effect of recycling on the flexural strength of 20% HDPE/80% PP blend matrix and composites

The recycled composites with nylon mat A & B as reinforcement had greater flexural strength than the recycles matrix, the increments being 25 x 33% over the matrix respectively. The composite with mat C reinforcement was inferior than the matrix by 29%.

The composites of DCP modified blend on recycle produced materials with lower flex strength than the unmodified blend samples. However the composite with nylon mats A & B as reinforcement had higher flexural strength than the matrix, the increments observed were 14 & 16.5% each. The composites with mat C as reinforcement exhibited a decrement of 17% over the matrix.

A similar trend was observed in matrix anhydride grafted blend matrix. The increments were 9 & 11 % for nylon mats A & B as reinforcements while a decrement of 40% was observed for mat C reinforcement (Fig. 5.28).

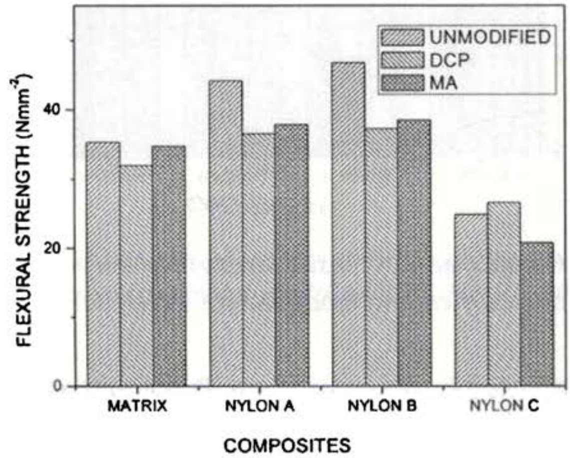

Figure 5.28: *Comparison of tensile strength of recycled matrix and composites of unmodified and modified 20% HDPE / 80% PP blend.*

(e) Comparison of recycled composites with composites

It is observed that the composites have higher tensile strength than then recycled samples. The lowering in tensile strength caused by recycling is less than 10% in almost all cases when 80% HDPE/20% PP blend is used. When the 20% HDPE/80% PP blend is used, the tensile strengths are slightly higher for the recycled samples. The flexural strengths of all recycled samples are found to be lower than that of the composites.

5.4 CONCLUSIONS

1. Tensile strength of composites of unmodified and modified HDPE with nylon mats A & B as reinforcements are greater than that of the matrix. The maximum values are shown by nylon mat B composites. The maximum tensile strength is observed in the case of composites of DCP modified matrix. All composites show greater tensile modulus than the matrix, the maximum being for nylon mat B reinforced composites. The highest value was shown by composites of maleic anhydride modified matrix.
2. Tensile strength of composites of unmodified and modified PP with nylon mats A & B as reinforcements are greater than that of the matrix. The highest value is observed in the case of composites of maleic anhydride modified matrix. The tensile modulus of composites of unmodified and modified matrix is greater than the matrix, the maximum being for nylon mat B reinforced composites.
3. Maleic anhydride modified matrix and composites of 80% HDPE/20% PP blend with nylon mats A & B as reinforcements had greater tensile strength than those of unmodified and DCP modified matrix and composites. Lower tensile strength than the matrix is observed for nylon mat C reinforced composites for unmodified and modified blends. The tensile modulus of the matrix and composites are found to increase in the order unmodified < DCP modified < maleic anhydride modified matrix. Nylon mat C composites are

observed to have lower tensile modulus than the matrix fo unmodified and DCP modified blends.

4. Tensile strength of composites of unmodified and modified 20% HDPE/80% PP blend with nylon mats A & B as reinforcements are greater than that of the matrix for unmodified and modified blends. Highest values are observed in the case of unmodified blend matrix. All composites of modified 20% HDPE/80% PP blend blend possess greater tensile modulus than those of unmodified blend. The largest value is observed for mat B composite of maleic anhydride modified matrix. Mat C composite of unmodified blend has lower tensile modulus than the matrix.
5. The flexural strength of all composites of unmodified and modified HDPE are greater than their matrix except for the nylon mat C reinforced composite of maleic anhydride modified HDPE matrix. The flexural modulus of all composites are greater than their matrix, the maximum being for mat B reinforced maleic anhydride modified HDPE matrix.
6. The flexural strength of all composites of unmodified and modified PP are greater than their matrix, the maximum values observed for nylon mat B reinforced composites. The flexural modulus of all composites of unmodified and modified are greater than their matrix, the maximum being for mat B reinforced composites. The flexural modulus increases with fibre diameter.

7. The flexural strength of all composites of unmodified and modified 80%HDPE/20%PP blend are greater than their matrix, the maximum values being for maleic anhydride modified matrix. The flexural strength increases with fibre diameter. Similar trend is observed for flexural modulus.
8. The flexural strength of nylon mats A & B composites are greater than their matrix for unmodified and modified 20% HDPE/80% PP blends, the highest values are for nylon mat B reinforcements. The flexural modulus of all composites are greater than their matrix, the maximum being for mat B reinforced composites.
9. The impact strength of all composites of unmodified and modified HDPE are greater than their matrix, the maximum values being observed for DCP modified HDPE composites. In each case, mat B composites had greater impact strength.
10. The impact strength of nylon mat A & B composites of unmodified and modified PP is greater than that of the matrix. The modification with DCP lowers the impact strength while maleic anhydride modification improves it.
11. The impact strength of all composites of unmodified and modified 80% HDPE/20% PP blend is greater than that of the matrix, both unmodified and modified. Both modifications are found to improve impact strength, maximum observed in the case of maleic anhydride modification.

12. The impact strength of all composites of unmodified and modified 20%HDPE/80%PP blend are greater than their matrix. The modification with DCP slightly lowers the impact strength while maleic anhydride modification improves it.
13. Recycled Composites of unmodified and modified 80% HDPE/20% PP blend with reinforcements of nylon mat A & B show greater tensile strength than the matrix even on recycling. The best results are observed for maleic anhydride modified version. The flexural strength of all composites are greater than those of their respective matrix.
14. Recycled Composites of unmodified and modified 20% HDPE/80% PP blend with reinforcements of nylon mat A & B show greater tensile strength than the matrix even on recycling. Similar trends are observed in the case of flexural strength also.

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CHAPTER 6

THERMAL PROPERTIES OF UNMODIFIED AND MODIFIED HDPE/PP BLEND - NYLON MAT COMPOSITES

6.1 INTRODUCTION

Thermogravimetric Analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, blends and their composites in order to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials and solvent residues. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. It also indicates the number of stages of thermal breakdown, weight loss at each stage, onset temperature etc [1]. Many fillers have been incorporated into polymer matrix for cost reduction and it was later discovered that they improved the stiffness and mechanical properties [2 – 8]. Both TGA and DTG provide information about the nature and extent of degradation of the material.

Dynamic Mechanical Analyser measures the stiffness and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. It is frequently converted to a modulus to enable sample inter-comparisons. Damping is expressed in terms of Tan δ values and is related to the amount of energy a material can store. DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behaviour is observed.

6.2 EXPERIMENTAL

HDPE and PP granules are placed in an air oven set at 100°C for 4 hours to remove any moisture present and allowed to cool to room temperature in a desicator. Two blend compositions are selected namely 80% HDPE/20% PP and 20% HDPE/80% PP and the granules are weighed out. The individual polymers as well as the two blends are melted in a Thermo Haake Rheomix 600P blender set at 180°C at a rotor speed of 30 rpm. The blends as well as the pure polymers are modified with 0.3phr DCP as well as 5phr maleic anhydride in presence of 0.3phr DCP. The molten polymers are pressed into sheets in a hydraulic press. Three grades of nylon mats namely A, B and C with fibre diameter 0.2, 0.4 and 0.6mm respectively are sandwiched between two polymer sheets and compression moulded in a hydraulic press at 180°C and allowed to cool in a cold press. The composites so prepared are subjected to dynamic mechanical analysis and thermo gravimetric analysis.

TGA studies of HDPE, PP and their blend matrix and composites are conducted with a TGA Q50 equipment of TA Instruments. The samples in the range of 5 to 10 mg are heated in a nitrogen atmosphere. The heating is done at a rate of 20°C per minute to a maximum temperature of 800°C. The temperature of onset of decomposition, the temperature at which 50% material had decomposed and residue left over are noted from weight loss profiles and derivative weight loss curves obtained.

The dynamic mechanical measurements of HDPE, PP and their blend matrix and composites are performed on a DMA Q800 machine of TA Instruments. Bars of dimension 35 mm x 12 mm x 2 mm are cut from the composites prepared. The bars are subjected to dual cantilever bending test at a frequency of 1 hertz and amplitude of 15 μm. The ramp temperature is set to increase at 3°C per minute to a maximum of 160°C.

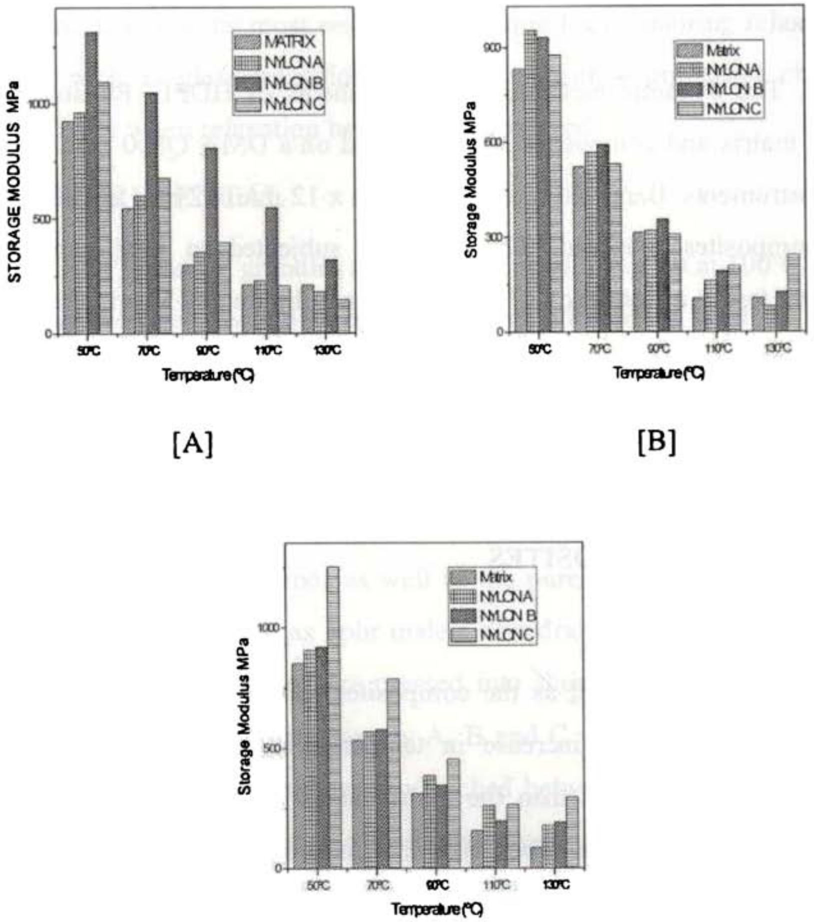
6.3. RESULTS AND DISCUSSION

6.3.1. DYNAMIC MECHANICAL ANALYSIS

6.3.1.1. HDPE COMPOSITES

(a) Storage modulus

The matrix as well as the composites show a decreasing trend in storage modulus with increase in temperature. The composites have higher storage modulus than the matrix at all temperatures studied. A similar trend is observed when HDPE is modified with DCP as well as maleic anhydride grafted to HDPE (Fig 6.1 A – C).



[A] [B]

[C]

***Figure 6.1:** [A – C] Storage modulus of HDPE matrix and its composites with nylon mats.*

The storage modulus of the composites with HDPE as matrix with nylon mat reinforcement is higher than the matrix at almost all temperatures at which studies are conducted. The highest storage modulus is observed in the case of composite with nylon mat B as reinforcement.

The matrix as well as composites show a declining trend in storage modulus with increase in temperature. At 50°C, the composites show an increase in storage modulus by 4, 42 and 18% for nylon mats A, B and C as reinforcements over the matrix which increase to 10, 92 and 24% at 70°C and 18, 170 and 30% at 90°C. The composite with nylon mat C as reinforcement show lower storage modulus than the matrix at 110° and 130°C while the composite with mat A as reinforcement shows lower value at 130°C.

The storage modulus of DCP modified HDPE matrix as well as the composites show a trend similar with unmodified HDPE matrix and composites. The storage modulus decrease with increase in temperature except for nylon mat C reinforcement which shows a higher value at 130°C than at 110°C. The storage modulus is higher by 14, 12 and 5% than the matrix for nylon mats A, B and C as reinforcements at 50°C and 9, 13 and 2% at 70°C. At 90°C, the composites with nylon mats A and B as reinforcement show increments of 2 and 14% while mat C composite shows a decline of 1.5%. The maximum increments shown are 51 and 80% at 110°C for nylon mat A and B as reinforcements.

The storage modulus of maleic anhydride grafted HDPE matrix and composites also show a decreasing trend on increasing the temperature. Here the composites with nylon mat C as reinforcement has the highest storage modulus at all temperatures. The increments over the matrix are 7, 8 and 47% at 50° and 70°C while at 90°C are 23, 11 and 45% for nylon mats A, B and C respectively. The storage modulus of mat A and C composites at 110°C are nearly equal, 67 and 69% higher than the matrix while mat B composite recorded an increment of 27% only. At

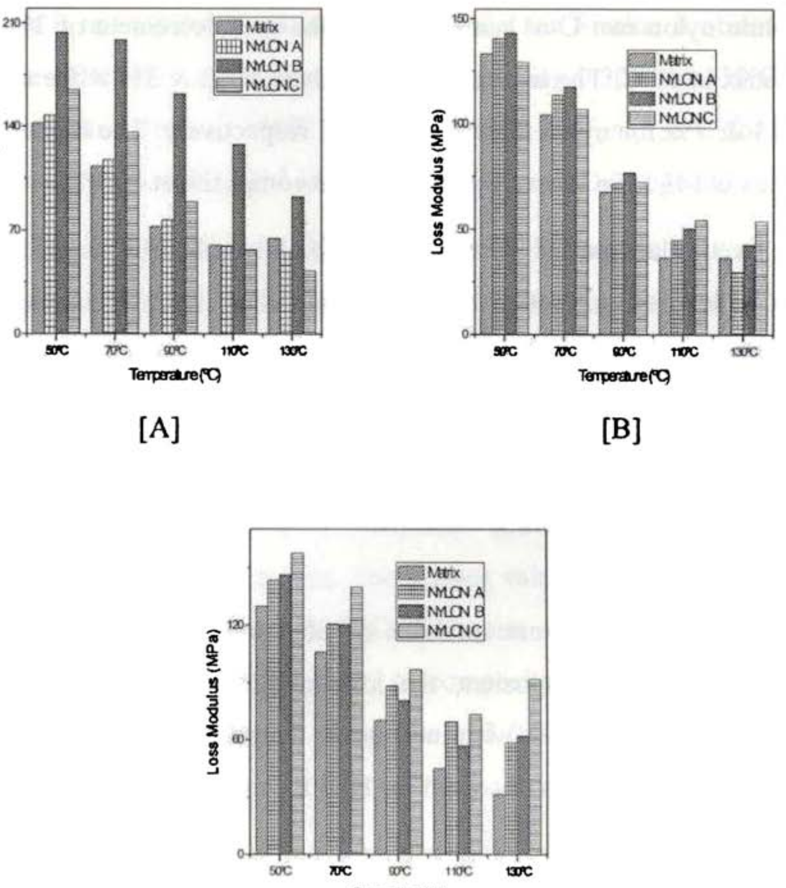
130°C, composites of mat A and B show 100% higher storage modulus than the matrix while mat C composite a 250% increment over the matrix.

Overall comparison between HDPE and its modifications as matrix for composites, it is found that HDPE matrix has the highest storage modulus compared to its modifications at 50°C. The highest storage modulus is shown by the composite with nylon mat B as reinforcement to DCP modified HDPE matrix.

(b) Loss modulus

The loss modulus of the matrix decreases to a minimum and increase as temperature is increased. A regular decreasing trend is observed for the composites. The composites have higher loss modulus than the matrix at most temperatures. A regular decreasing trend is shown by the DCP modified HDPE, but when maleic anhydride is grafted to HDPE, the loss modulus show an increase at higher temperatures for certain composites (Fig 6.2 [A – C]).

The loss modulus of the HDPE matrix and its composites decreases with increase in temperature. The composites have higher loss modulus than the matrix. The increments for the composites are 4, 43 and 16% for nylon mats A, B and C respectively at 50°C. The values show increments of 4, 75 and 20% over the matrix at 70°C while at 90°C, it is 6, 124 and 23% for nylon mats A, B and C respectively. Composites with nylon mats A and C had lower loss modulus than the matrix at 110° and 130°C.



[A] [B]

[C]

Figure 6.2: *[A – C] Loss modulus of HDPE matrix and its composites with nylon mats.*

The loss modulus of the matrix and the composites show decrements when HDPE is modified with DCP. The matrix shows a decrement of 6%. The composites have higher loss modulus than the matrix at all temperatures except in the case of composite with nylon mat C as reinforcement at 50°C and nylon mat A at 130°C. The composites with nylon mats A and B as reinforcement show an increment of 5 and 7% while nylon mat C as reinforcement shows a decrement of 3% over the matrix at 50°C. The increments at 70°C are 9, 12 & 3% while at 90°C is 8, 13 & 7% for nylon mats A, B and C respectively. The highest loss modulus is 143 MPa shown by nylon mat B composite at 49.8°C.

A similar trend is observed when maleic anhydride is grafted on HDPE. The composites had higher loss modulus than the matrix at all temperatures. The increments at 50°C are 10, 13 & 21%; at 70°C are 13.6, 13.5 & 32%; at 90°C are 26, 15 & 38%; at 110°C are 54, 26 & 63% and at 130°C are 86, 97 & 191% for nylon mats A, B and C respectively. The highest loss modulus is observed is 158 MPa for the composite with nylon mat C as reinforcement.

Comparing the loss modulus of both unmodified and modified HDPE matrix and composites, the loss modulus is found to increase slightly and then decrease with increase in temperature. The highest loss modulus of 207.3 MPa is observed for HDPE - nylon mat B composite.

(c) Tan δ values

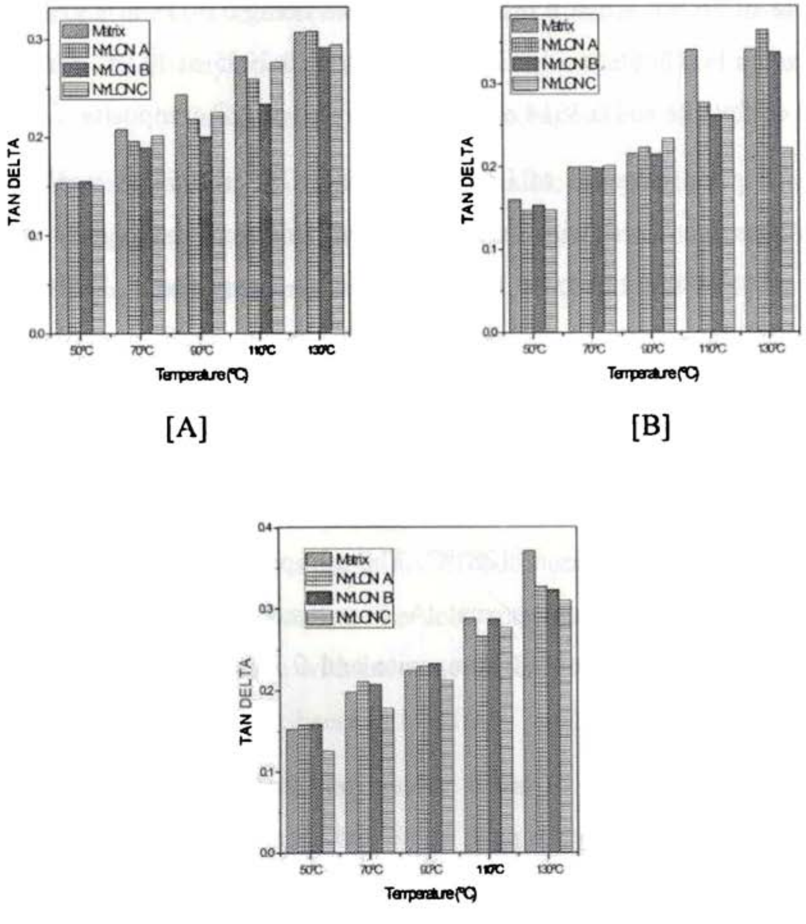
Tan δ values of HDPE as well as the composites with HDPE as matrix increased with increase in temperature. The composites had lower tan δ values than the matrix under experimental conditions. A similar trend is observed in the DCP modified HDPE as well as maleic anhydride grafted HDPE used as matrix (Fig 6.3 [A – C]).

The tan δ values shows an increasing trend with increase in temperature in the case of all matrix and composites of HDPE and its modifications. The tan δ values of HDPE matrix and its composites are nearly equal at 50°C and then increased with increase in temperature. The increase is not regular in all cases. The highest tan δ value is observed in the case of HDPE - nylon mat A composite being 0.3077 at 130°C. The peak value is 0.3066 at 130°C for the matrix, 0.2955 at 131°C for nylon mat B composite and 0.3014 at 124°C for nylon mat C composite.

The tan δ values of DCP modified HDPE matrix as well as its composites increased with increase in temperature. The highest tan δ value of 0.3678 is observed for nylon mat A composite at 128°C. The peak value for the matrix is 0.3409 at 130°C. nylon mat B composite had 0.3377 at 130°C and nylon mat C composite had 0.264 at 106°C.

The studies on maleic anhydride grafted HDPE matrix and composites show similar results. The highest value of 0.3732 is observed in the case of the matrix at 128 °C. The composites had peak tan δ of 0.3271 at 130°C for nylon mat A composite, 0.3231 at the same temperature for nylon mat B composite and 0.3208 at 133°C for nylon mat C composite.

The comparison of tan δ values indicated the value to increase with temperature to reach a peak value and then a decline slightly. This trend is observed in almost all cases of HDPE matrix and composites.



[A] [B]

[C]

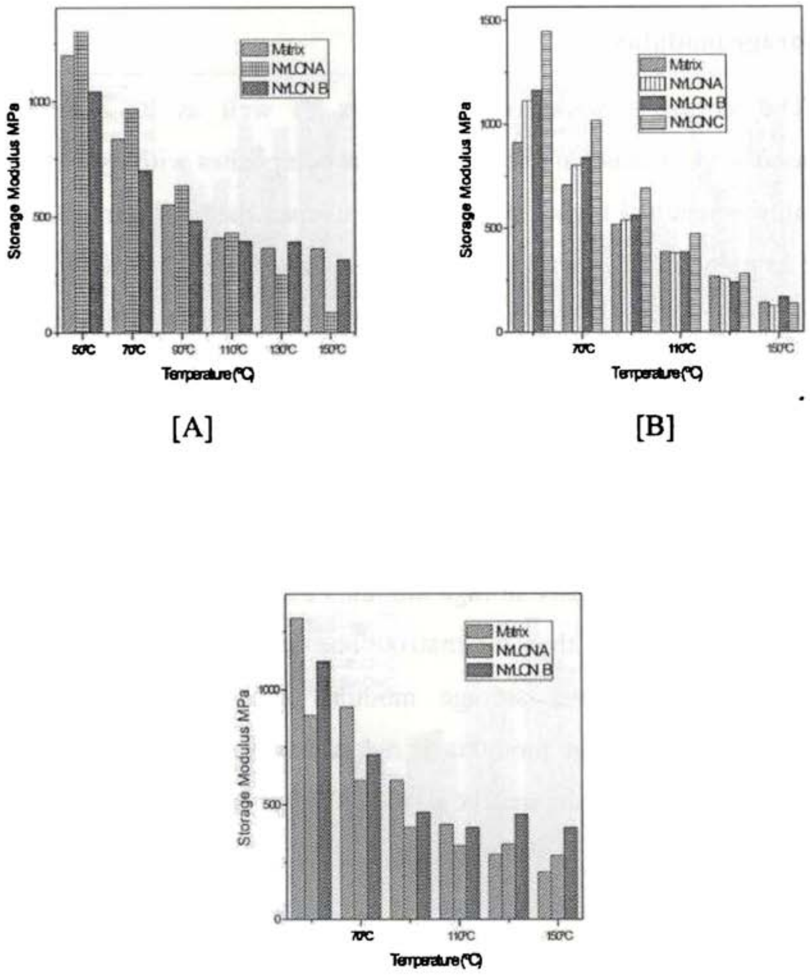
Figure 6.3: *[A – C]Tan Delta values of HDPE matrix and its composites with nylon mats.*

6.3.1.2. PP COMPOSITES

(a) Storage modulus

The storage modulus of PP matrix as well as its composites decreased with increase in temperature. The composites with nylon mat A as reinforcement had higher storage modulus than the matrix up to 110°C where as nylon mat B as reinforcement had lower storage modulus at all temperatures. A similar decreasing trend with increase in temperature is shown by the DCP modification as well as maleic anhydride grafted version of PP used as matrix (Fig 6.4 [A – C]).

The storage modulus of PP matrix as well as the composites decreased with increase in temperature. The composite with nylon mat A as reinforcement had higher storage modulus than the matrix up to 110°C and then became lesser than the matrix. The composite nylon mat B as reinforcement had lower storage modulus than the matrix at all temperatures. The storage modulus of nylon mat A composite is 8.5, 15, 15 and 5% higher than the matrix at 50°, 70°, 90° & 110°C respectively. At the same time the increments are 13, 16, 12 & 4% at the same temperatures. At 130°C, the decrements are 75 and 13% for nylon mat A and B composites.



[A] [B]

[C]

Figure 6.4: *[A – C] Storage modulus of PP matrix and its composites with nylon mats.*

The modification of the matrix with 0.3phr DCP is found to lower the storage modulus of the matrix by 23% than pure PP. All its composites had higher storage modulus than the matrix up to 90°C and then decreased. The composite with nylon mat A as reinforcement shows increments of 22, 13 & 4% at 50°, 70° and 90°C respectively where as the composite with nylon mat B as reinforcement had 27, 18 and 8% as increments at the same temperatures while the nylon mat C composite shows increments of 58, 43 and 33%. Slight decrements are shown by all composites at higher temperatures when compared with the matrix.

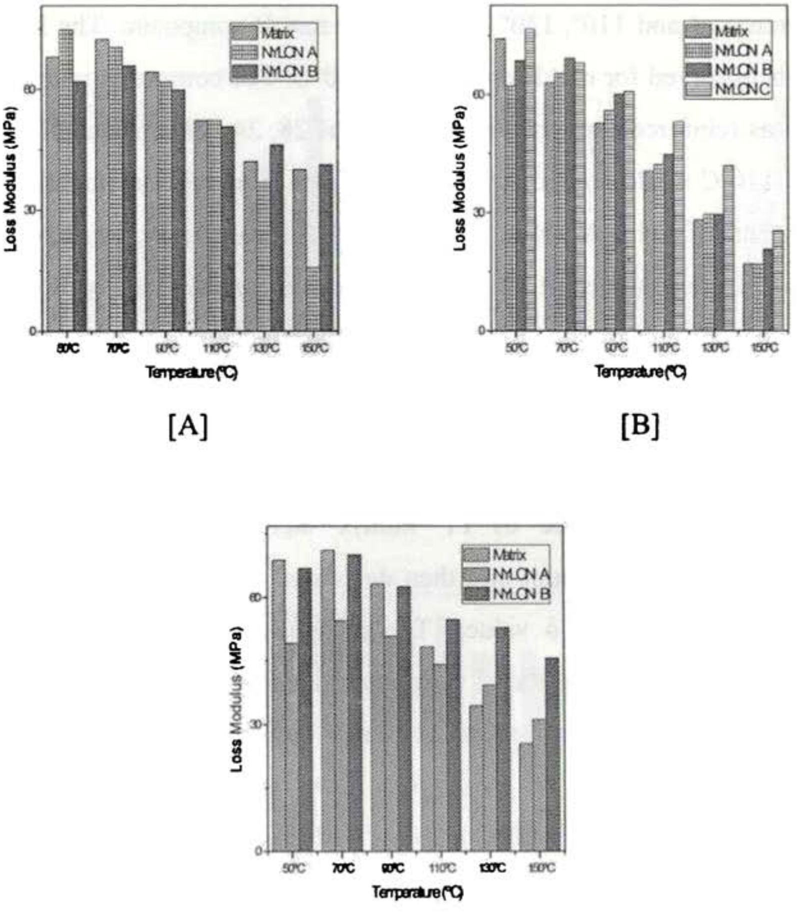
Grafting of PP with maleic anhydride improved the storage modulus of the matrix. The values are higher than those for unmodified matrix up to 110°C and then a decrement is observed. The composites with nylon mats A and B as reinforcement had lower storage modulus than the matrix up to 110°C. Increments are observed in the case of composites at higher temperatures. The decrements observed are 32, 34, 33 & 22% for mat A as reinforcement and 14, 22, 23 & 3% for mat B reinforcement at 50°, 70°, 90° and 110°C respectively. Large increments are observed in the case of mat B reinforcement at higher temperatures.

(b) Loss modulus

The loss modulus of PP matrix as well as the composites show a slight increasing trend up to 70°C and then decreased with increase in temperature. On DCP modification, the matrix as well as the composite with nylon mat C as reinforcement show a regular decrease in value with increase in temperature while the composites with nylon mat A & B as reinforcement show a trend similar to that of unmodified PP. The composites had a slightly higher loss modulus than the DCP modified matrix. Grafting of maleic anhydride into PP produced a result similar to unmodified PP matrix (Fig 6.5 [A – C]).

The loss modulus of PP matrix as well as its composites show an increase followed by decrease with increase in temperature. The maximum values are observed at 70°C. The matrix had higher values than the composites except at 130° & 150°C for composites with nylon mat B as reinforcement. The loss modulus of composites with nylon mat A as reinforcement are lower by 4, 3, 4, 0.1, 12 & 13% at 50°, 70°, 90°, 110°, 130° & 150°C respectively. The decrements in the case of composites with nylon mat B as reinforcement are 9, 9, 7 and 3% at 50°, 70°, 90° & 110°C respectively while increments of 10 & 3% are observed at 130° & 150°C.

The loss modulus of DCP modified PP matrix and the composite with nylon mat C as reinforcement decreases with increase in temperature where as an initial increase followed by decrease is observed for composites with nylon mats A & B as reinforcement. All composites exhibited higher loss modulus than the matrix at all temperatures except composites with nylon mats A & B as reinforcement at 50°C. The highest loss modulus is observed for composite with nylon mat C as reinforcement at 50°C. Nylon mat A & B as reinforcement for composites show decrements of 16 & 8% at 50°C while composite with nylon mat C as reinforcement show an increment of 3% at the same temperature. At all other temperatures the matrix had higher loss modulus than composites, the decrements being 4, 6, 4, 5 & 4% for mat A composite, 10, 14, 11, 5 & 22% for mat B composite and 8, 15, 31, 48 & 48% for mat C composite at 50°, 70°, 90°, 110°, 130° & 150°C respectively.



[A] [B]

[C]

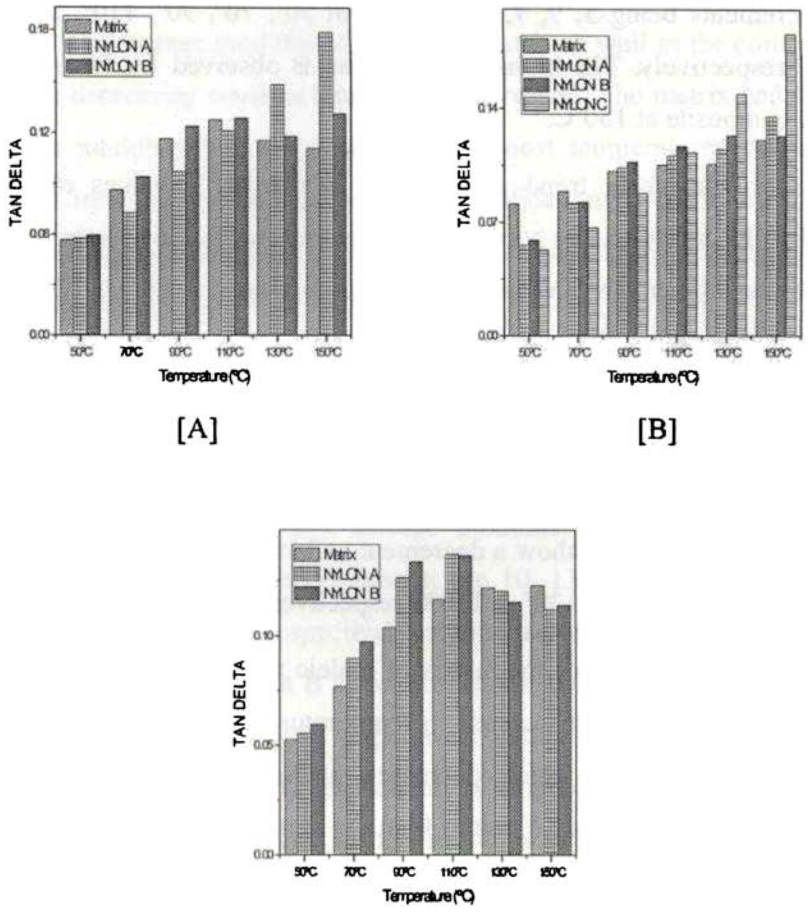
Figure 6.5: *[A - C] Loss modulus of PP matrix and its composites with nylon mats.*

Loss modulus of maleic anhydride grafted PP matrix as well as its composites is found to show an increase initially and further decrease with increase in temperature. The peak values are observed around 70°C. In most cases the loss modulus of composites are lower than that of matrix except at 130° and 150°C for composite with nylon mat A reinforcement and 110°, 130° & 150°C for mat B composite. The highest value is observed for mat B composite at 70°C. The composite with nylon mat A as reinforcement shows decrement of 28, 24, 19 & 9% at 50°, 70°, 90° & 110°C while composite with nylon mat B as reinforcement shows decrements of 3, 1.5 & 1% at 50°, 70° & 90°C respectively. Increments of 14 & 22% are observed at 130° & 150°C for composite with nylon mat A as reinforcement while 13, 53 & 79% are observed at 110°, 130° & 150°C for composite with nylon mat B as reinforcement.

(c) Tan δ values

The tan δ value of PP matrix increased with increase in temperature to a maximum and then decreased. The composites show a regular increase in tan δ values. The composite with nylon mat A as reinforcement had lower tan δ value than the matrix while nylon mat B reinforcement had higher values. The tan δ values of the DCP modified PP matrix as well as its composites show an increasing trend with temperature. The matrix had higher tan δ value at low temperatures while the composites had higher value at high temperatures. Maleic anhydride grafted PP matrix shows a steady increase in tan δ with increase in temperature. The composites show a maximum at 110°C (Fig 6.6 [A – C]).

The tan δ values of PP matrix is found to increase with increase in temperature, reached a peak value at 110°C and then declined. The composite with nylon mat A as reinforcement is found to show an increasing trend while composite with nylon mat B as reinforcement behaved similar to the matrix.



[A] [B]

[C]

Figure 6.6: *[A – C] Tan Delta values of PP matrix and its composites with nylon mats.*

The composites had higher tan δ values than the matrix at 50°C. At 70°, 90° & 110°C, composite with nylon mat A as reinforcement had lower tan δ values while composite with nylon mat B as reinforcement had higher values. At 130° and 150°C, the composite with nylon mat A as reinforcement had the highest tan δ values. The composite with nylon mat B as reinforcement had higher values than the matrix at all temperatures, the increments being 5, 9, 7, 12 & 18% at 50°, 70°, 90°, 110°, 130° & 150°C respectively. The highest tan δ value is observed for PP – nylon mat A composite at 150°C.

An increasing trend is observed in the tan δ values of DCP modified PP as well as its composites on increasing the temperature. The matrix had higher tan δ values than the composites at 50° & 70°C. At higher temperatures, the composites had higher tan δ values. Composites with nylon mat A as reinforcement had increments of 2, 6, 9 & 12% while that with mat b as reinforcement had 6, 11, 17 & 2% increments over the matrix at 90°, 110°, 130° & 150°C respectively. The composite with nylon mat C as reinforcement show a decrement of 14% at 90°C and increments of 7, 40 & 54% at 110°, 130° & 150°C respectively.

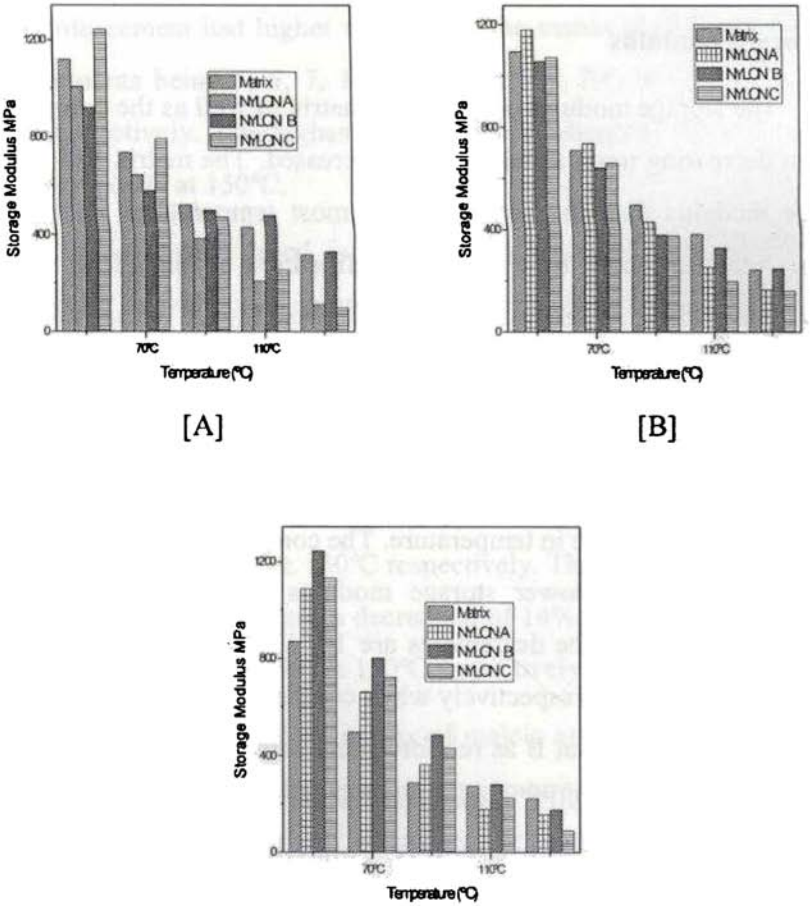
The tan δ value of the matrix of maleic anhydride grafted PP had an increasing trend with increase in temperature. The composites had a peak value at 110°C which decreased at higher temperatures. The composites had higher tan δ values than the matrix up to 110°C and then became lower. The composite with nylon mat A as reinforcement exhibited increments of 5, 17, 21 & 18%: mat B as reinforcement exhibited 13, 26, 28 & 17% increments at 50°, 70°, 90° & 110°C respectively. The decrements observed are 1 & 9% for mat A as reinforcement and 5 & 7% for mat B as reinforcement at 130° & 150°C.

6.3.1.3 80% HDPE/20% PP BLEND AND COMPOSITES

(a) Storage modulus

The storage modulus of the blend matrix as well as the composites show a decreasing trend as temperature increased. The matrix had higher storage modulus than the composites at most temperatures studied. A similar trend is shown by the DCP modification of the blend. When maleic anhydride is grafted in, the composites had higher storage modulus than the matrix (Fig 6.7 [A – C]).

A regular decrement is observed in the case of the storage modulus of the 80% HDPE + 20% PP blend matrix as well as the composites with increase in temperature. The composite with nylon mat A as reinforcement had lower storage modulus than the matrix at all temperatures studied. The decrements are 10, 13, 26, 52 & 64% at 50°, 70°, 90°, 110° & 130°C respectively when compared with the matrix. The composite with nylon mat B as reinforcement shows values lesser by 18, 22 & 4% at 50°, 70° & 90°C respectively while 11 & 4% increments are observed at 110° & 130°C respectively. Composite with nylon mat C as reinforcement shows greater storage modulus by 11 & 8% at 50°& 70°C but at higher temperatures the storage modulus is lowered to large extents.



[A]

[B]

[C]

Figure 6.7: *[A – C] Storage modulus of 80% HDPE + 20% PP blend matrix and its composites with nylon mats.*

The storage modulus of the blend modified with 0.3phr DCP shows a trend similar to the unmodified blend. The storage modulus of the matrix as well as the composites decreased with increase in temperature. The DCP modified matrix is observed to possess greater storage modulus than the composites except for composite with nylon mat A as reinforcement at 50° & 70°C, the increments being 8 & 4% respectively. The composite with nylon mat A as reinforcement shows decrements of 14, 34 & 32% over the matrix at 90°, 110° & 130°C respectively. Decrements of 4, 10, 24 & 14% are observed at 50°, 70°, 90° & 110°C respectively while an increment of 2% is observed at 130°C for the composite with nylon mat B as reinforcement. The composite with nylon mat C as reinforcement shows decrements of 2, 7, 24, 48 & 33% at 50°, 70°, 90°, 110°& 130°C respectively.

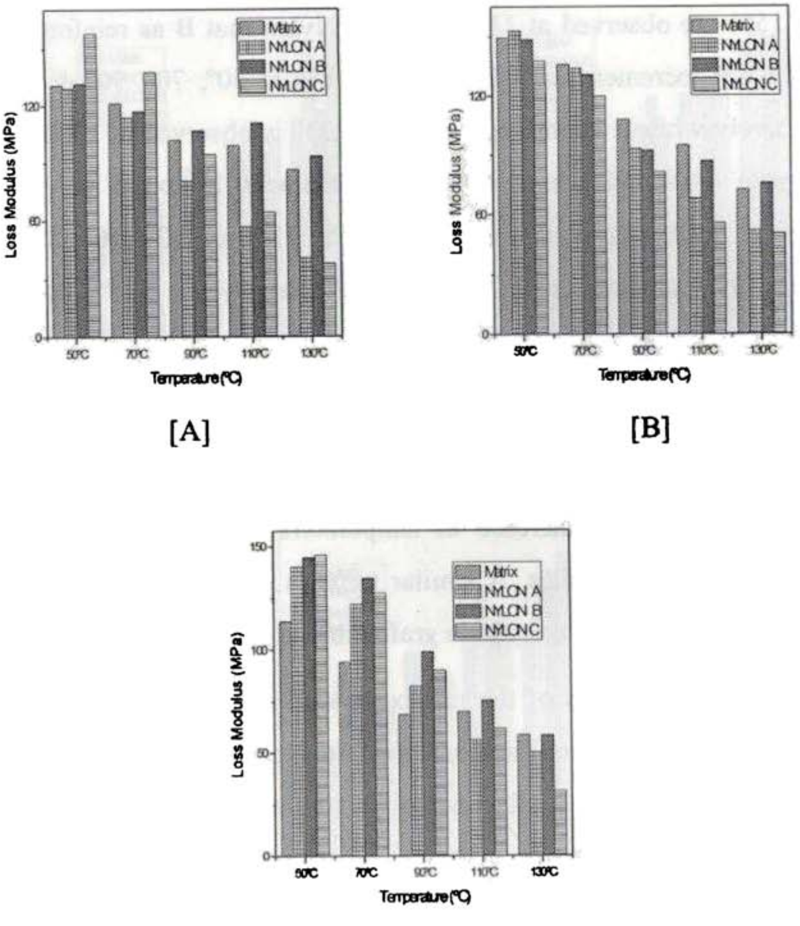
Introduction of maleic anhydride into the blend did not change the decreasing trend of storage modulus with increase in temperature. The composites had greater storage modulus than the matrix up to 90°C which then decreased. The increments are 25, 33 & 26% for nylon mat A; 43, 61 & 67% for nylon mat B and 30, 45 & 49% for nylon mat C reinforcement at 50°, 70° & 90°C respectively. The decrements observed are 35 & 30% for nylon mat A and 18 & 60% for nylon mat C reinforcements at 110° &130° C respectively. The composite with nylon mat B shows an increment of 3% at 110°C while at 130°C, a decrement of 21% is observed.

(b) Loss modulus

The loss modulus of the blend matrix as well as its composites decreased with increase in temperature. A similar trend is observed when the DCP modification and maleic anhydride grafted blend are used to prepare the composites. In most cases, the matrix had higher loss modulus than the composites (Fig 6.8 [A – C]).

A decreasing trend is observed in the loss modulus of the blend as matrix and as well as composites with increase in temperature. A higher loss modulus is observed in the case of the matrix except for nylon mat B as reinforcement at 110° & 130°C and for nylon mat C as reinforcement at 50° & 70°C. The composite with nylon mat A as reinforcement shows decrements of 10, 13, 26, 52 & 64% at 50°, 70°, 90°, 110°& 130°C respectively while composite with nylon mat B as reinforcement shows decrements of 18, 22 & 4% at 50°, 70° & 90°C and increments of 11 & 4% at 110°& 130°C. At the same time composite with nylon mat C as reinforcement shows increments of 11 & 8% at 50° & 70°C while decrements of 10, 40 & 68% are observed at 90°, 110° & 130°C respectively.

DCP modification of the blend also shows the loss modulus of the matrix to be higher than the composites prepared except for nylon mat A as reinforcement at 50°C and nylon mat B as reinforcement at 130°C. The nylon mat A as reinforcement shows higher loss modulus by 3% at 50°C while nylon mat B as reinforcement shows an increase by 5% at 130°C. The decrements observed are 2, 14, 29 & 28% at 70°, 90°, 110° & 130°C respectively for composite with nylon mat A as reinforcement; 1,4, 15 & 9% at 50°, 70°, 90° & 110°C respectively for composite with nylon mat B as reinforcement and 8, 12, 25, 42 & 31% at 50°, 70°, 90°, 110° & 130°C respectively for composite with nylon mat C as reinforcement.



[A]

[B]

[C]

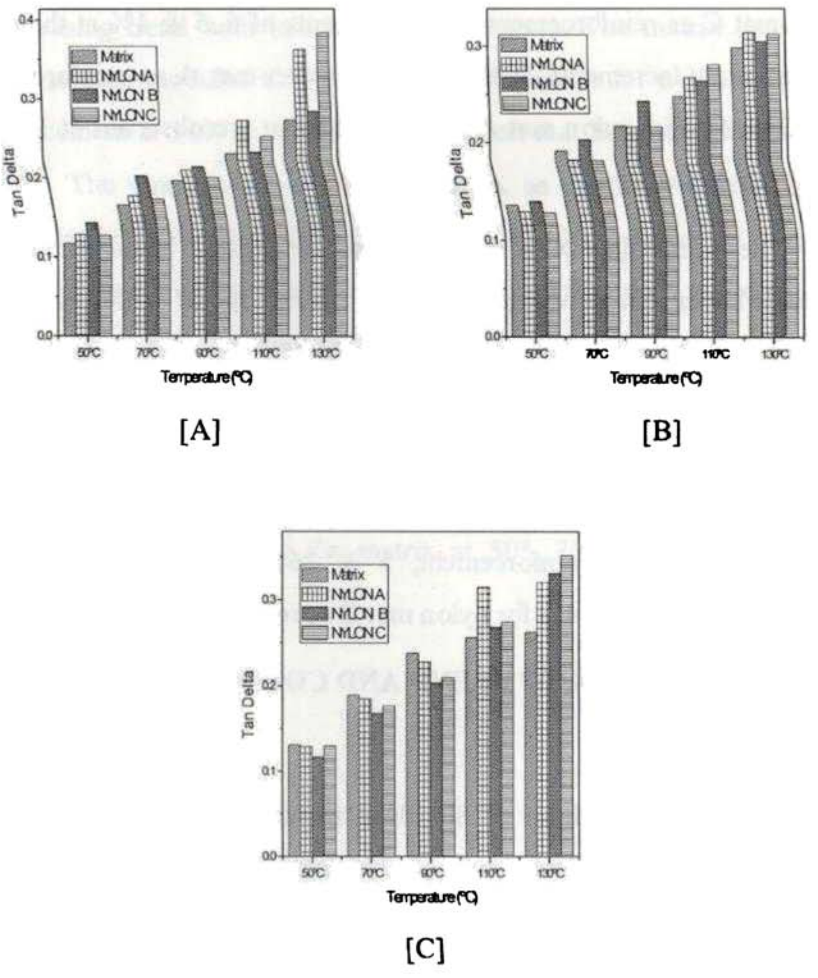
Figure 6.8: [A – C] Loss modulus of 80% HDPE + 20% PP blend matrix and its composites with nylon mats.

Grafting of maleic anhydride onto the blend did not change the trend in loss modulus of the matrix and composites prepared. The composites exhibited greater loss modulus than the matrix except at 110°C for nylon mat A & C as reinforcement and at 130°C for all composites. The increments for composite with nylon mat A as reinforcement are 23, 30 & 20% at 50°, 70° & 90°C while decrements of 20 & 15% are observed at 110°& 130°C. Nylon mat B as reinforcement brought out increments of 27, 43, 44 & 8% at 50°, 70°, 90° & 110°C respectively while a slight decrement of 0.2% is observed at 130°C. The composite with nylon mat C as reinforcement is found to possess increment in loss modulus by 28, 35 & 31% at 50°, 70° & 90°C respectively and decrements of 12 & 46% at 110°& 130°C over the matrix.

(c) Tan δ values

The tan δ values of the blend as well as its composites show an increasing trend with increase in temperature. The matrix had lower values than the composites. A similar trend is observed when the DCP modification and maleic anhydride grafted blend (Fig 6.9 [A – C]).

The tan δ values of the matrix as well as the composites of the blend as well as its modifications exhibited an increasing trend with increase in temperature. All composites of the unmodified blend had higher tan δ values than the matrix at all temperatures. The increments observed are 10, 8, 7, 18 & 33% for nylon mat A as reinforcement, 22, 23, 9, 1 & 4% for nylon mat B as reinforcement and 9, 5, 2, 9 & 40% for nylon mat C as reinforcement at 50°, 70°, 90°, 110° & 130°C respectively.



[A] [B]

[C]

Figure 6.9: [A – C] Tan Delta values of 80% HDPE + 20% PP blend matrix and its composites with nylon mats.

The composite with DCP modified blend and nylon mat B as reinforcement exhibited higher tan δ values than the matrix at all temperatures, the increments being 3, 6, 11, 7 & 2% at 50°, 70°, 90°, 110° & 130°C respectively. Decrements of 5, 5 & 1% are observed for nylon mat A as reinforcement at 50°, 70° & 90°C where as the composites with nylon mat C as reinforcement had decrements of 6, 5 & 1% at the same temperatures. Increments of 8 & 5% for nylon mat A as reinforcement and 13 & 5% for nylon mat A as reinforcement are observed at 110° & 130°C respectively.

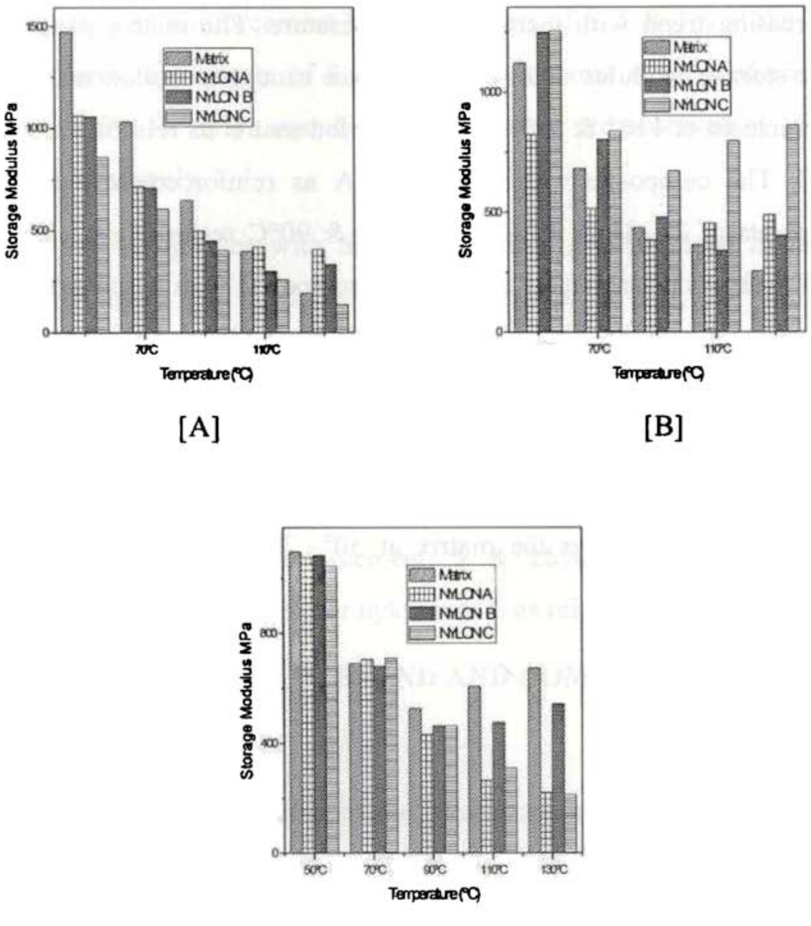
The composites with maleic anhydride grafted blend as matrix exhibited lower tan δ values than the matrix at 50°, 70° & 90°C respectively. The decrements are 2, 3 & 4% for nylon mat A as reinforcement, 11, 12 & 14% for nylon mat B as reinforcement and 2, 7 & 12% for nylon mat C as reinforcement. All composites had higher tan δ values than the matrix at 110° & 130°C, the increments being 23 & 22% for nylon mat A as reinforcement, 5 & 26% for nylon mat B as reinforcement and 7 & 34% for nylon mat C as reinforcement.

6.3.1.4 20% HDPE/80% PP BLEND AND COMPOSITES

(a) Storage modulus

The storage modulus of the blend matrix as well as composites decreased when temperature increased. The matrix had higher values than the composites prepared. The storage modulus of the DCP modified blend matrix show a regular decreasing trend with increase in temperature but the composites show a minimum value which then increase. The storage modulus of maleic anhydride grafted blend matrix decreased to a minimum and then increased with increase in temperature. The composites prepared show a regular decrease in storage modulus (Fig 6.10).

The storage modulus of the blend matrix and composites exhibited a decreasing trend with increase in temperature. The matrix possessed higher storage modulus than the composites except for nylon mat A as reinforcement at 110° & 130°C and for nylon mat B as reinforcement at 130°C. The composite with nylon mat A as reinforcement exhibited decrements of 28, 31 & 23% at 50°, 70° & 90°C respectively while at 110°C it shows an increment of 6%. The composite with nylon mat B as reinforcement exhibits decrements of 28, 31, 30 & 24% at 50°, 70°, 90° & 110°C respectively while at 130°C, it shows an increment of 74%. In fact the storage modulus at 130°C is greater than at 110°C by 11%. The composites with nylon mat C as reinforcement exhibits decrements of 42, 41, 38, 35 & 30% over the matrix at 50°, 70°, 90°, 110° & 130°C respectively.



[A] [B]

[C]

***Figure 6.10:** [A – C] Storage modulus of 20% HDPE + 80% PP blend matrix and its composites with nylon mats.*

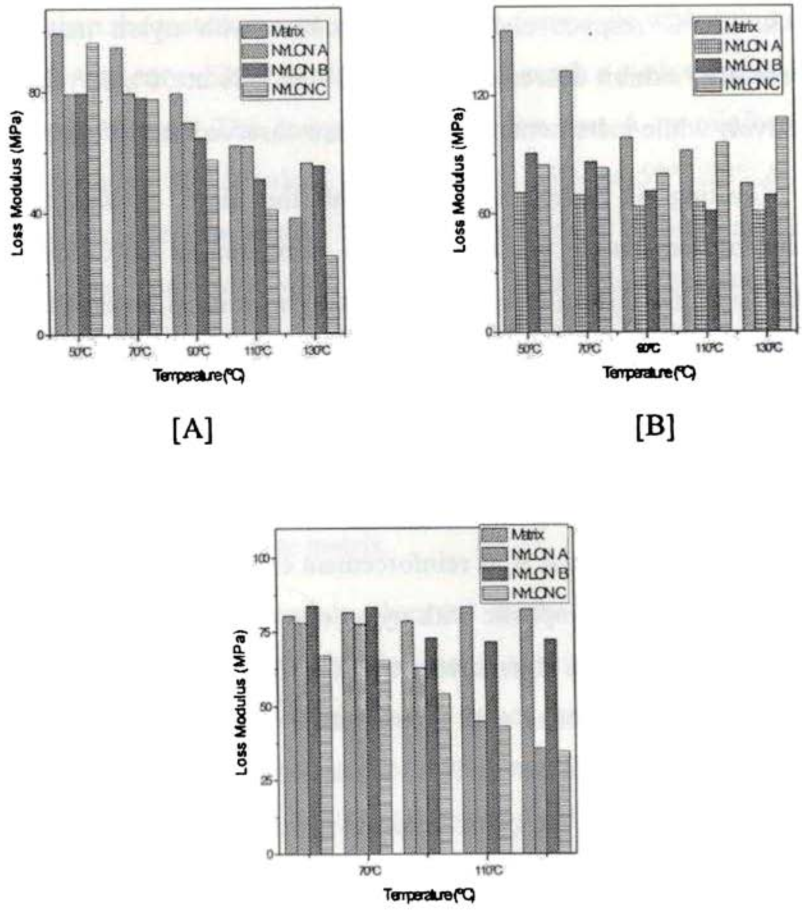
Modification of the blend with 0.3phr DCP shows the matrix to behave in the same pattern as the unmodified blend. The composites exhibit a decreasing trend, reaching a minimum at 90°C for nylon mat A & C as reinforcements and 110°C for nylon mat B as reinforcement. Composites with nylon mat A as reinforcement possess lower storage modulus than the matrix at 50°, 70° & 90°C, the decrements being 27, 25 & 12% and at higher temperatures, the composite has larger storage modulus by 25 & 90% at 110° & 130°C respectively. Composites with nylon mat B & C as reinforcement possess higher storage modulus than the matrix, the increments being11, 18, 10, 7 & 58% at 50°, 70°, 90°, 110° & 130°C respectively for nylon mat B as reinforcement and 12, 23, 54, 120 & 240% at 50°, 70°, 90°, 110° & 130°C respectively for nylon mat C as reinforcement.

Grafting the blend with maleic anhydride along with DCP, storage modulus of the matrix decreases to a minimum at 110°C and then increases slightly with increase in temperature. The composites with nylon mat A & C as reinforcement exhibit a decreasing trend with increase in temperature while composite with nylon mat B as reinforcement shows a trend similar to the matrix. The matrix possess higher storage modulus than the composites at all temperatures except for composites with nylon mat A & C as reinforcement at 70°C, the increments being 2 & 3% respectively for the composites. The composite with nylon mat A as reinforcement exhibits decrements of 2, 18, 56 & 67% at 50°, 90°, 110° & 130°C respectively while composite with nylon mat C as reinforcement exhibit decrements of 5, 12, 49 & 68% at the same temperatures. The decrements observed for nylon mat B as reinforcement are 1, 1, 12, 22 & 19% at 50°, 70°, 90°, 110° & 130°C respectively.

(b) Loss modulus

The loss modulus of the blend as well as the composites decreases with increase in temperature. The matrix has higher loss modulus than the composites prepared. DCP modified blend matrix shows a similar trend while the composites show a minimum followed by increase. Similar trend is shown by maleic anhydride grafted blend (Fig 6.11 [A – C]).

The loss modulus of the blend matrix and composites exhibit a trend similar to its storage modulus. The loss modulus decreases with increase in temperature. The matrix has higher loss modulus than the composites except at 130°C for nylon mat A & B as reinforcements. The decrements found are 20, 16, 12 & 1% for nylon mat A as reinforcement and 20, 18, 19 & 18% for nylon mat B as reinforcement at 50°, 70°, 90°& 110°C respectively. The composites with nylon mat C as reinforcement exhibits decrements of 3, 18, 27, 34 & 33% at 50°, 70°, 90°, 110° & 130°C respectively.



[A] [B]

[C]

***Figure 6.11:** [A – C] Loss modulus of 20% HDPE + 80% PP blend matrix and its composites with nylon mats.*

The loss modulus of DCP modified blend decreases with increase in temperature, but for composites, it reaches a minimum and then increase. All composites have lower loss modulus than the matrix except for composite with nylon mat C as reinforcement at 110° & 130°C. The depreciations are 54, 47, 36, 28 & 19% for nylon mat A as reinforcement,;

41, 35, 28, 33 & 8% for nylon mat B as reinforcement at 50°, 70°, 90°, 110° & 130°C respectively. The composites with nylon mat C as reinforcement exhibit decrements of 45, 37 & 19% at 50°, 70° & 90°C respectively while increments of 4 & 44% are observed at 110° & 130°C.

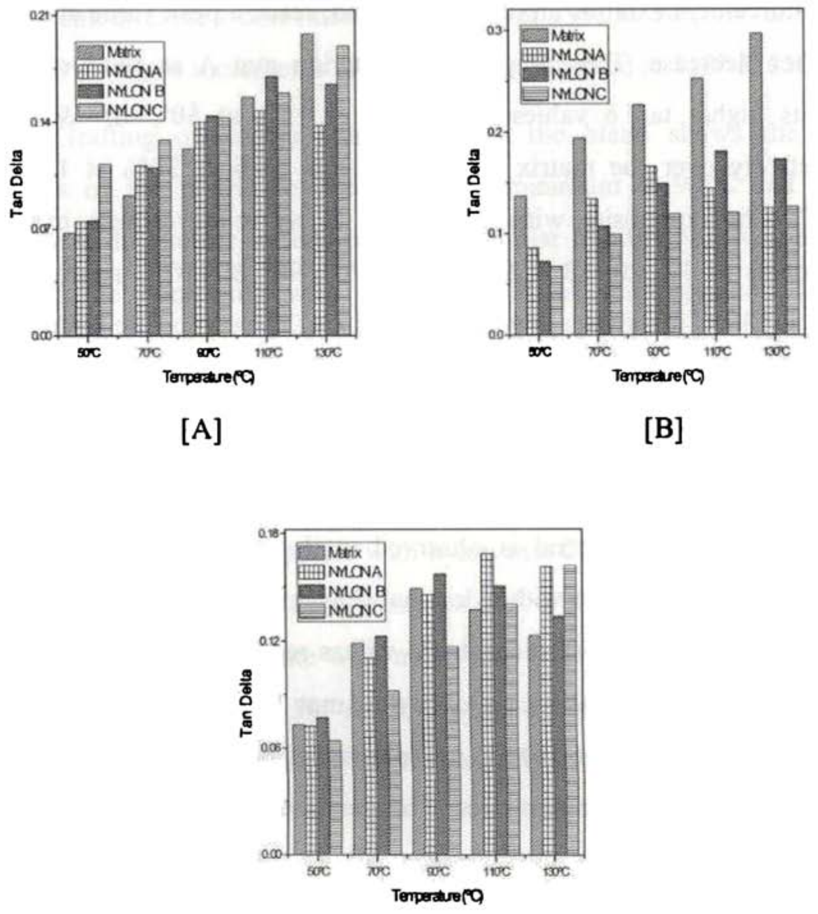
Grafting of maleic anhydride with the blend shows the loss modulus of the matrix to decrease to a minimum at 90°C and then increase with increase in temperature. A similar trend is observed in the case of the composite with nylon mat B as reinforcement. Other composites exhibit a regular decrease in loss modulus with increase in temperature. The matrix has greater loss modulus than the composites except that with nylon mat B as reinforcement at 50°& 70°C. The composites with nylon mat A as reinforcement exhibit decrements of 3, 2, 20, 46 & 57% while composite with nylon mat C as reinforcement show 17, 15, 31, 48 & 58% decrements at 50°, 70°, 90°, 110° & 130°C respectively. The composite with nylon mat B as reinforcement showed increments of 4 & 5% at 50° & 70°C while decrements of 7, 14 & 13% are observed at 90°, 110° & 130°C respectively over the grafted matrix.

(c) Tan δ values

The tan δ values of the blend matrix as well as its composites increases with increase in temperature. The composites have higher value than the matrix. Similar trend is observed in the case of DCP modified blend and its composites. Maleic anhydride grafting of the blend shows the values to increase to a maximum and then decrease as temperature is increased (Fig 6.12 [A – C]).

The tan δ values of the blend matrix increases with increase in temperature. A similar trend is observed in the case of composites with nylon mat B & C as reinforcements. All composites have higher tan δ values than the matrix except at 130°C. The composite with nylon mat A as reinforcement exhibits an increasing trend, reach a peak value at 110°C and then decrease. The composite with nylon mat A as reinforcement exhibits higher tan δ values by 11, 21 & 15% at 50°, 70° & 90°C respectively over the matrix and decrements of 6 & 30% at 110° & 130°C. The composite with nylon mat B as reinforcement exhibits increments of 12, 20, 18 & 9% at 50°, 70°, 90° & 110°C respectively while at 130°C it shows a lower value by 17%. The composite with nylon mat C as reinforcement has higher tan δ values by 66, 40, 17 & 2% at 50°, 70°, 90° & 110°C respectively while at 130°C the composite exhibits a decrement of 17% over the matrix.

An increasing trend is observed in the case of DCP modified matrix and the composite with nylon mat C as reinforcement. When nylon mat A is used as reinforcement, tan δ values reach a maximum at 90°C and then decrease. In the case of nylon mat B as reinforcement, the maximum is observed at 110°C. All composites have lower tan δ values than the matrix at all temperatures. The decrements are 37, 31, 27, 43 & 58% for nylon mat A as reinforcement; 47, 45, 34, 28 & 42% for nylon mat B as reinforcement and 51, 49, 47, 52 & 58% for nylon mat C as reinforcement at 50°, 70°, 90°, 110° & 130°C respectively.



[A] [B]

[C]

Figure 6.12: *[A – C] Tan Delta values of 20% HDPE + 80% PP blend matrix and its composites with nylon mats.*

Grafting of maleic anhydride along with DCP with the blend shows tan δ values to increase with temperature, reach a maximum at 90°C and then decrease for the matrix as well as composites with nylon mat A & B as reinforcements. The composite with nylon mat C as reinforcement exhibited an increasing trend with temperature. The nylon mat B composite as reinforcement have increments of 6, 3, 5, 10 & 9% over the matrix at 50°, 70°, 90°, 110° & 130°C respectively. The composites with nylon mat A & C as reinforcements have lower tan δ values than the matrix at 50°, 70° & 90°C. The decrements are 1, 7 & 3% for mat A and 12, 23 & 22% for nylon mat C as reinforcement at 50°, 70° & 90°C respectively. At 110° & 130°C, mat A reinforced composites show increments of 23 & 31% while mat C reinforced had 2 & 32% increments.

DMA studies have been conducted at a constant frequency and in a wide temperature region on epoxy glass fibre composites. The tensile testing are conducted at three different strain rates at different temperatures in order to study the strain rate as well as the temperature effect. The strong material dependence on temperature and strain rate which is mainly attributed to the inelastic response of the polymer matrix is modeled with empirical scaling rules for material elastic constants, valid in viscoelasticity. They also observed a satisfactory agreement between simulated and experimental results for different temperatures and strain rates and various types of off-axis specimens using the same set of parameter values.

It was observed the storage modulus of the composite decrease with increase in temperature in all cases studied. The tan δ values showed a maxmima and then diminished with increase in temperature [9]. The dependence of the thermo mechanical behaviour of the composite on the distribution of fibers in the cross section of a unidirectional composite has been investigated by Bulsara *et.al.* The importance of non – Uniformity of fiber spatial distribution with regard to the transverse failure of composites was highlighted. It was observed that by the use of an actual radial distribution function obtained for a ceramic matrix composite by quantitative stereology in conjunction with a simulation technique. The RVE size is investigated with respect to the initiation of debonding and radial matrix cracking. Tensile loading transverse to the fiber and residual stresses induced by thermal cool down are considered separately as loading modes for transverse failures [10 -13].

6.3.2 THERMOGRAVIMETRIC ANALYSIS

6.3.2.1 HDPE COMPOSITES

The TGA studies of the matrix and composites of HDPE with nylon mat reinforcements show the following observations. The decomposition started around 400°C for the matrix as well as the composites with nylon mats A and B as reinforcement. The onset temperature is only 360°C for the composite with nylon mat C as reinforcement. 50% of the material decompose around 475°C for the matrix as well as composites with nylon mats A and B while it is 468°C for composite with mat C. The residue left over is less than 0.5% indicating the volatile nature of the polymer used (Fig 6.12).

Modification of HDPE with 0.3phr DCP lowers the onset temperature of the matrix as well as the composites prepared. Composites with mat C as reinforcement has the lowest onset temperature of 340°C. 50% of the material decomposed around 475°C for the matrix and composites with nylon mats A and B as reinforcements while mat C composite has 461°C for 50% decomposition. The residue left over is around 0.35%.

Grafting of maleic anhydride onto HDPE increases the onset temperature of the matrix as well as its composites over the DCP modification. The lowest onset temperature is for the composite with nylon mat C as reinforcement. The temperature at which 50% decomposition takes place is lowest for the composite. The residue left over is around 0.5%.

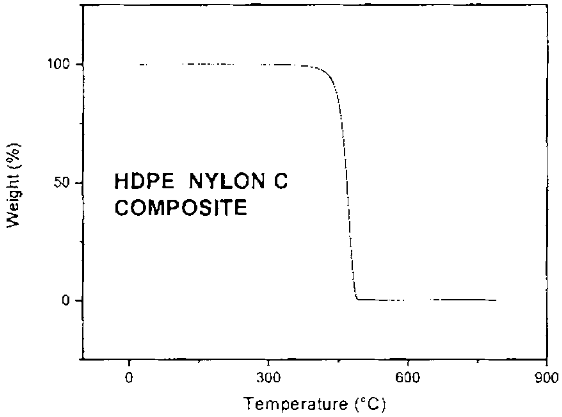


Figure 6.12: TGA curve of HDPE - Nylon C composite.

The TGA analysis of HDPE matrix and the composites indicate less than 0.35% weight loss at 300°C. This indicates the presence of very low quantity of volatile matter involved in the composites. The weight loss is around 1.5% at 400°C for all composites while at 450°C, the matrix and composites with nylon mats A & B as reinforcements recorded a weight loss of around 10% while composite with mat C recorded a weight loss of 16%. These results indicate the thermal stability of the matrix and composites.

The onset temperature for the decomposition of the matrix and composites with nylon mats A & B as reinforcements are nearly same at around 400°C while the composite with nylon mat C as reinforcement recorded a lower value of 360°C. The temperature for 50% decomposition is around 476°C for the matrix and composites with nylon mats A & B as reinforcements while the composite with nylon mat C as reinforcements has a lower value. The residue left over is below 0.5% indicating the volatile nature of the composites (Table 6.1).

Table 6.1: *Comparison of TGA scans of HDPE matrix composites*

Material studied	Weight Loss at			50% Decompos-ition at	Onset Temper-ture °C	Residue %
	300°C	400°C	450°C			
HDPE	0.24%	1.05%	9.14%	476.18°C	398.49	0.38%
NYLON A	0.34%	1.11%	8.83%	475.73°C	399.50	0.16%
NYLON B	0.08%	0.96%	8.42%	476.20°C	392.43	0.43%
NYLON C	0.16%	1.51%	15.96%	468.02°C	360	0.17%
HDPE/DCP	0.2%	0.98%	10.42%	473.72°C	380.32	0.18%
NYLON A	0.33%	1.2%	9.72%	475°C	377.78	0.001%
NYLON B	0.37%	0.93%	7.35%	477.05°C	384.13	0.18%
NYLON C	0.11%	4.88%	29.15%	461.1°C	339.69	0.04%
HDPE/MA	1.82%	6.41%	43.04%	454.26°C	391.42	0.37%
NYLON A	1.6%	2.83%	11.15%	477.78°C	399.50	0.34%
NYLON B	1.42%	2.50%	10.02%	477.45°C	391.42	0.04%
NYLON C	1.38%	8.41%	34.70%	461.63°C	384.4	0.40%

A similar trend is observed in the DCP as well as maleic anhydride modifications of HDPE used as matrix. The weight loss at

300°C is below 0.5%, around 1% at 400°C and 10% at 450°C. The nylon mat C reinforced composites showed higher weight loss, 5% at 400°C and 29% at 450°C. The onset temperature of DCP modified HDPE composites are around 377 - 385°C which is lower than that for unmodified composites. The composite with nylon mat C reinforcement had onset temperature of 340°C. The temperature for 50% decomposition is 473 – 477°C while the composite with nylon mat C reinforcement recorded 454°C. The residue left over is below 0.2%.

6.3.2.2 PP COMPOSITES

Introduction of nylon mats as reinforcements to PP matrix lowers the onset temperature as well as the temperature for 50% decomposition. The matrix has an onset temperature of 366.2°C. The lowest onset temperature is for the composite with nylon mat B as reinforcement. Residue left over is nearly 0.6% (Fig 6.13).

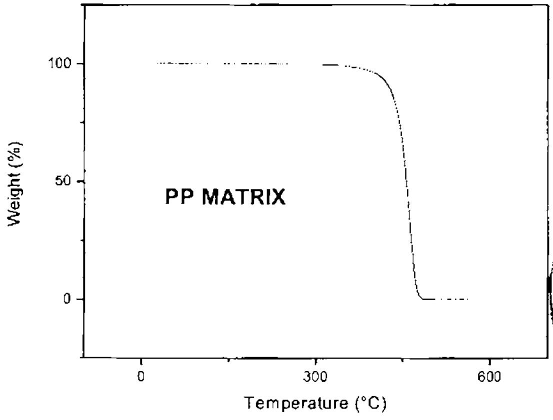


Figure 6.13: TGA curve of PP matrix.

The onset temperature of DCP modified PP is higher than that of unmodified PP, all composites having lower onset temperatures than the matrix. The temperature for 50% decomposition is nearly constant at 455°C for the matrix as well as the composites. The residue left over is around 0.5%.

***Table 6.2:** Comparison of TGA scans of PP matrix composites.*

Material studied	Weight Loss at			50% Decomposition at	Onset Temperature °C	Residue %
	300°C	400°C	450°C			
PP	0.40%	3.83%	35.45%	456.05°C	366.20	0.04%.
NYLON A	0.33%	3.99%	36.05%	455.78°C	365.18	0.34%
NYLON B	0.20%	17.72%	64.27%	441.28°C	329.41	0.66%
NYLON C	0.42%	4.56%	38.34%	453.86°C	353.45	0.36%
PP/DCP	0.39%	4.94%	37.82%	455.28°C	372.7	0.41%
NYLON A	0.31%	4.28%	37.03%	455.32°C	361.27	0.50%
NYLON B	0.38%	4.66%	37.27%	455.55°C	365.08	0.32%
NYLON C	0.71%	13.36%	46.66%	452.80°C	327.85	0.31%
PP/MA	2.22%	6.01%	37.21%	455.92°C	286.36	0.42%
NYLON A	2.01%	5.32%	30.45%	460.37°C	301.23	0.32%
NYLON B	1.38%	4.0%	21.95%	466.26°C	316.84	0.20%
NYLON C	2.06%	4.98%	24.27%	464.62°C	359.13	0.04%

Grafting maleic anhydride onto PP lowers the onset temperature to 286.4°C for the matrix. All composites show comparatively lower values than the composites of PP or DCP modified PP matrix. The temperature for 50% decomposition is highest in the case of composites of ma-g-PP matrix.

Comparison of TGA data of PP – nylon mat composites indicate very low percentage of volatile matter to be present in the composites. The weight loss is below 0.5% at 300°C, 4% at 400°C and around 35 – 40% at 450°C. The weight loss for nylon mat C reinforced composites are 18% at 400°C and 64% at 450 °C. The composites had lower onset temperatures than the matrix and the same trend is followed for the temperature for 50% decomposition. The thermal stability of the composites are lower than that of the composites (Table 6.2).

DCP modified PP matrix and composites lose around 1% weight at 300°C, 5% at 400°C and 37% at 450°C. The weight loss for nylon mat C reinforced composites are 13% at 400°C and 46% at 450°C. All composites have lower onset temperatures than the matrix. The temperature for 50% decomposition is nearly steady at around 455°C and residue left over is below 0.5%. These results do not indicate a higher thermal stability for the composites with DCP modified PP matrix.

The weight loss recorded for maleic anhydride modified PP matrix are 2% at 300°C, 4 – 6% at 400°C and around 20 – 37% at 450°C. The weight loss for nylon mats B & C reinforced composites are 22 & 24% as compared to 30% for nylon mat A composite and 37% for the matrix. This indicates greater thermal stability for the composites over the matrix. The onset temperatures and temperature for 50% decomposition are greater for the composites than the matrix which substantiates their greater thermal stability.

6.3.2.3 80% HDPE/20% PP BLEND AND COMPOSITES

Studies on 80% HDPE/20% PP blend as matrix showed all composites to have higher onset temperature than the matrix. The onset temperature of the matrix is 370.7°C. The temperature for 50% decomposition is also lowest for the matrix. The residue left over is around 0.4% (Fig 6.14).

Modification of the blend using DCP improved the onset temperature of the matrix. The matrix has an onset temperature of 381.3°C where as the composites have higher values. The temperature for 50% decomposition of the matrix shows improvement but the temperatures for composites are nearly same as for composites of unmodified blend, the values being lesser than that for the matrix. The residue left over is around 0.15%.

Grafting maleic anhydride on to the blend improved the onset temperature of the matrix to 478.8°C. The composite with nylon mat C had a slightly higher onset temperature than the matrix, the other composites showing lesser values. The temperature for 50% decomposition is lesser than that of the unmodified blend, the composites showing greater values. The residue left over is around 0.3%.

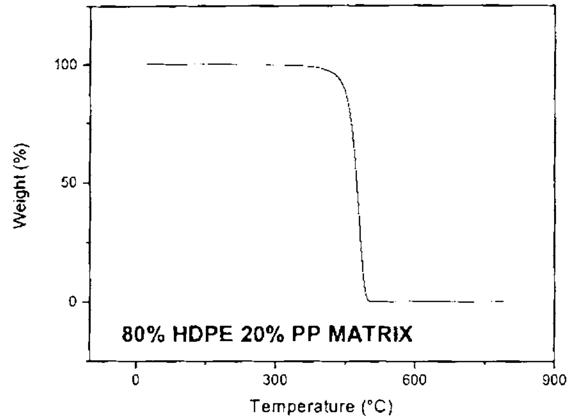


Figure 6.14: TGA curve of 80% HDPE/20% PP blend matrix

The weight loss recorded for the composites are below 0.4% at 300°C, 1 – 2% at 400°C and around 8 – 12% at 450°C. The weight loss for the matrix is higher at 0.55% at 300°C, 13% at 400°C and 49% at 450°C. The onset temperature and temperature for 50% decomposition are higher for the composites than the matrix and the residue left over is around 0.4%. These observations indicate the composite to have greater thermal stability than the blend matrix (Table 6.3).

The DCP modified blend matrix and composites recorded weight loss of below 0.4% at 300°C, below 1.7% at 400°C and 13% at 450°C. The weight loss in the case of nylon mats A reinforced composites are 3.5% at 400°C and 25% at 450°C. All composites had higher onset temperatures as well as temperature for 50% decomposition over the matrix indicating greater thermal stability for the composites.

Table 6.3: *Comparison of TGA scans of 80% HDPE + 20% PP blend matrix composites*

Material studied	Weight Loss at			50% Decomposit -ion at °C	Onset Temper -ature °C	Residue %
	300°C	400°C	450°C			
BLEND(80PE)	0.55	13.31	48.58	451.31	370.7	0.32
NYLON A	0.35	2.14	11.46	479.75	375.24	0.04
NYLON B	0.25	1.28	8.13	480.45	383.35	0.17
NYLON C	0.28	2.01	12.03	474.62	373.26	0.10
BLEND/DCP	0.28	1.28	9.38	479.91	381.30	0.19
NYLON A	0.31	3.43	25.39	474.93	384.13	0.27
NYLON B	0.30	1.39	9.61	479.78	396.83	0.02
NYLON C	0.38	1.69	13.0	474.05	381.32	0.11
BLEND/MA	1.85	3.10	9.86	478.77	426.03	0.07
NYLON A	3.47	8.73	32.23	466.68	386.11	0.04
NYLON B	2.84	9.73	33.26	467.33	389.69	0.01
NYLON C	2.73	3.95	11.09	478.39	395.56	0.15

Comparison of TGA data of composites with maleic anhydride modified blend as matrix show lower thermal stability for the composites. The weight loss at 300°C is 1.8% for the matrix while the composites loose around 2.7 – 3.5%. At 400°C, the weight loss is 3% for the matrix while the composites loose about 10%. The weight loss for nylon mat C reinforced composites is around 4%. The matrix and composites with nylon mat C as reinforcements lose around 10% at 450°C while the other two composites loose around 32%. All composites have lower onset temperatures and temperature for 50% decomposition than the matrix.

6.3.2.4. 20% HDPE/80% PP BLEND AND COMPOSITES

The studies conducted on 20% HDPE/80% PP as matrix for composites show the composite with nylon mat B as reinforcement to have the highest temperature for 50% decomposition. The onset temperature for nylon mat A as reinforcement is lesser than the matrix while that for nylon mat B as reinforcement is higher. The residue left over is around 0.05% (Fig 6.15).

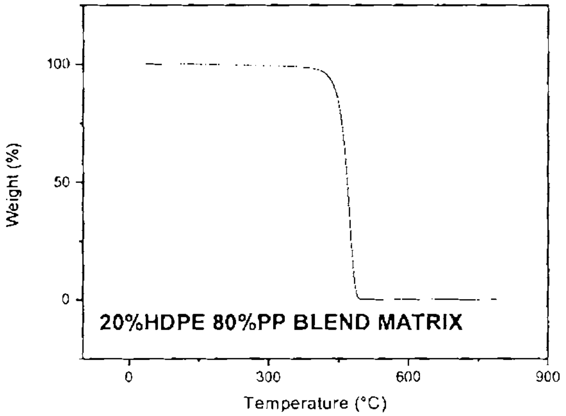


Figure 6.15: TGA curve of 20% HDPE/80% PP blend matrix

Modification of the blend with DCP lowered the onset temperature of the matrix and the composites to have lower onset temperature than the unmodified blend and composites. The temperature for 50% decomposition is also lowered in the same manner. The residue left over is slightly greater than that for the unmodified blend.

Introduction of maleic anhydride into the blend further lowers the onset temperature of the blend. The composites have higher onset temperatures than the matrix. The composites have higher temperature at which 50% decomposition took place. The residue left over is slightly higher for the matrix and composite with nylon mat A as reinforcement (Table 6.4).

Table 6.4: Comparison of TGA scans of 20% HDPE/80% PP blend matrix composites.

Material studied	Weight Loss at			50% Decompn. At °C .	Onset Temp °C	Residue %
	300°C	400°C	450°C			
BLEND(20PE)	0.61	2.05	16.77	468.35	380.32	0.04
NYLON A	0.41	15.35	52.94	447.61	322.81	0.02
NYLON B	0.39	2.0	13.62	472.72	386.38	0.04
NYLON C	0.39	1.36	18.11	466.37	381.32	0.04
BLEND/DCP	0.48	3.95	27.27	461.88	330.88	0.04
NYLON A	0.60	24.98	62.76	438.19	306.66	0.05
NYLON B	0.53	8.58	36.37	458.39	328.26	0.09
NYLON C	0.36	4.18	26.63	462.47	340.97	0.16
BLEND/MA	2.16	11.81	42.19	456.55	320.64	0.14
NYLON A	0.39	5.10	28.34	462.60	352.39	0.35
NYLON B	1.43	3.08	18.01	468.69	371.43	0.03
NYLON C	2.21	3.93	18.05	468.88	380.32	0.03

The study of unmodified blend matrix and its composites indicate weight loss of below 1% at 300°C, around 2% at 400°C and 13 – 18% at 450°C. The composite with nylon mats A as reinforcement has greater weight loss of 15% at 400°C and 53% at 450°C. All composites except that of nylon mat B as reinforcement have lower onset temperature than the matrix. Similar is the observation regarding temperature for 50%

decomposition. The residue left over is below 0.05%. These results indicate composites with nylon mat B as reinforcement to have greater thermal stability.

The weight loss recorded for DCP modified blend matrix and its composites are below 0.1% at 300°C, 4% for the matrix and composite with nylon mat C as reinforcement at 400°C and 27% at 450°C for the same. The composites with nylon mats A & B as reinforcements recorded weight loss of 25 & 8% at 400°C and 63 & 36% at 450°C respectively. The composites with nylon mat A & B as reinforcements have lower onset temperature as well as temperature for 50% decomposition than the matrix. The composite with nylon mat C as reinforcement has greater thermal stability than the matrix.

Comparison of TGA data of maleic anhydride modified blend matrix and composites indicate all composites to have greater thermal stability than the matrix. The weight loss recorded by the composites are below 2.2% at 300°C, around 5% at 400°C and around 20% at 450°C. The matrix recorded weight loss of 12% at 400°C and 42% at 450°C while composite with nylon mat A as reinforcements recorded 5 & 28% weight loss at 400°C & 450°C respectively. Residue left over is around 0.5%.

6.4. CONCLUSIONS

1. The storage modulus of unmodified and modified HDPE – Nylon mat composites decreases with increase in temperature for the matrix as well as composites of unmodified and modified HDPE. The storage modulus of composites of unmodified and modified matrix are greater than their matrix at all temperatures. The loss modulus of of composites of unmodified and modified matrix are

greater than their matrix except for nylon mat C reinforcement of DCP modified HDPE. The tan δ values of all composites of unmodified and DCP modified HDPE are lesser than the matrix. The tan δ values for nylon mat A & B reinforced composites of maleic anhydride modified HDPE are greater than the matrix.

2. The storage modulus of modified PP – Nylon mat nylon mat A reinforced composite is greater than the unmodified matrix. The storage modulus of composites of DCP modified PP are greater than the matrix while the reverse trend is observed in maleic anhydride modification. The loss modulus of nylon mat A reinforced composite is greater than the unmodified matrix. The loss modulus of composites of DCP modified PP are lesser than the matrix. The maleic anhydride modified matrix has greater loss modulus than unmodified PP but composites have lower loss modulus. Composites of unmodified and maleic anhydride modified matrix has higher tan δ values than their matrix.
3. The storage modulus of nylon mat A & B reinforced composites of unmodified 80% HDPE / 20% PP blend blend are lower than their matrix. The storage modulus of nylon mat B & C reinforced composites of DCP modified blend are lower than their matrix. The storage modulus of all composites of maleic anhydride modified blend are higher than their matrix. The loss modulus of nylon mat B & C reinforced composites of unmodified blend are greater than their matrix. The same trend is observed for DCP modified blend. The loss modulus of all composites of maleic anhydride modified matrix are greater than their matrix. The tan δ

values of all composites of unmodified blend are greater than the matrix. when DCP modified, nylon mat B reinforced composite had greater tan δ value than the matrix. The tan δ values of maleic anhydride modified matrix composites are lower than those of the matrix.

4. The storage modulus of all composites of unmodified and maleic anhydride modified 20% HDPE / 80% PP blend are lower than their matrix. The storage modulus of nylon mat B & C reinforced composites of DCP modified blend are higher than their matrix. The loss modulus all composites of unmodified and modified blend are lower than their matrix. The tan δ values of all composites of unmodified blend are greater than the matrix. When DCP modified, reverse trend is observed. The tan δ values of maleic anhydride modified matrix composites are higher than those of the matrix.
5. The onset temperature of decomposition nylon mat A reinforced composites of unmodified HDPE is greater than that of the matrix. Nylon mat B & C reinforced composites have greater temperature for 50% decomposition to be complete. All composites of DCP modified matrix have lower onset temperature of decomposition and temperature for 50% decomposition to be complete. Nylon mat A reinforced composite of maleic anhydride modified HDPE matrix has higher onset temperature of decomposition as well as temperature for 50% decomposition to be complete than the matrix.

6. All composites of unmodified PP and its DCP modification exhibit lower onset temperature of decomposition and temperature for 50% decomposition to be complete. The temperature for 50% decomposition to be complete for DCP modified PP matrix and its composites with nylon mats A & B are nearly the same. The onset temperature of decomposition and temperature for 50% decomposition to be complete for the maleic anhydride modification are found to be higher than the matrix.
7. The onset temperature of decomposition and temperature for 50% decomposition to be complete of all composites of the unmodified 80% HDPE / 20% PP blend are higher than the matrix. On DCP modification, the onset temperature of decomposition has the same trend but the temperature for 50% decomposition to be complete is lowered. The composites of maleic anhydride modified blend had lower onset temperature of decomposition and temperature for 50% decomposition to be complete than their matrix.
8. The onset temperature of decomposition and temperature for 50% decomposition to be complete of nylon mat B reinforced composites of unmodified 20% HDPE/80% PP blend are higher than that of the matrix. The same pattern is observed when nylon mat C is used to reinforce the DCP modified blend matrix. All composites of maleic anhydride modified blend have higher onset temperature of decomposition and temperature for 50% decomposition to be complete than the matrix.

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CHAPTER 7

CONCLUSIONS

The blend system discussed in this thesis is that of the most widely used commodity plastics HDPE and PP. This work explores the preparation of the blend, its modification with dicumyl peroxide – a low molecular weight modifier known to produce chain scission in PP and cross-linking in HDPE. The mechanical properties – tensile properties, flexural properties and impact strength, the thermal properties – thermal stability, storage modulus and tan δ and rheological properties – melt viscosity and die swell ratio were examined for the unmodified and modified HDPE/PP blends.

The study shows that DCP can be used to modify the mechanical, thermal and rheological properties HDPE, PP and their blends. The mechanical properties of the blend vary with the blend composition as well as concentration of the modifier used. All unmodified blends examined show mechanical properties in between those of the pure components. DCP modification shows significant improvement in mechanical properties of the blends.

The mechanical properties of the blend vary with the processing method used. Extruded samples of unmodified and modified HDPE/PP blends exhibit higher mechanical properties than the injection moulded samples. 20% HDPE/80% PP blend shows highest mechanical properties for the unmodified and modified versions.

Measurement of melt viscosity of unmodified and modified blends indicate pseudoplastic nature in the molten state. The shear viscosity of

PP rich blends – 20% HDPE/80% PP and 40% HDPE/60% PP, decrease with increase in DCP concentration. The shear viscosity of HDPE rich blend 60% HDPE/40% PP blend increases with concentration of DCP to a maximum value at 0.3phr DCP and then decreases. The shear viscosity of 80% HDPE/20% PP blend exhibits a steady increase with increase in DCP concentration. This variation in shear viscosity is shown by the blends at all three temperatures. This shows that the blend which exhibits the best mechanical properties has also low melt viscosity and is easy to process. Thus DCP is a potential modifier to optimize the properties of HDPE/PP blends.

The extrudate swell ratios of all the four blends refered to above and their DCP modified versions increase with increase in shear rate. The extrudate swell ratios of PP rich blends decrease with increase in DCP concentration. This further shows that DCP is useful in controlling the elastic behaviour of HDPE?PP blends.

The thermal degradation studies indicate that the modified blends to have higher thermal stability than the unmodified blends. The stability increases with DCP content and the highest stability is observed for 0.3phr DCP modification. All DCP modified versions of the 80% HDPE/20% PP blend show higher storage modulus than the unmodified blend. The tan δ values increase with increase in temperature for both the blends and their modified versions. All DCP modified versions of 80% HDPE/20% PP blend show lower tan δ values than the unmodified blend. The tan δ values of 20% HDPE/80% PP blend increase with increase in DCP concentration, reach a maximum at 0.3phr and then decrease.

Differential scanning calorimetry indicates two melting peaks for the blends corresponding to the two polymers used and a single crystallization peak. This shows that the blends on cooling after melt mixing can develop a favourable morphology to obtain good mechanical and thermal properties. Melting point of HDPE increases to a maximum at 0.3phr DCP and then decreases. Melting point of PP decreases with increase in DCP concentration.

Composites prepared with 80% HDPE/20% PP and 20% HDPE/80% PP blends using nylon mats as reinforcements generate a useful class of recyclable composites. The composites with nylon mats of fibre diameter 0.2mm and 0.4mm have greater tensile strength, tensile modulus, flexural strength, flexural modulus and impact strength than the respective matrix. the DCP modification improves the properties of 80% HDPE/20% PP matrix composites. The highest value is observed in the case of composites employing a maleic anhydride modified matrix. recycled blends and composites show superior properties compared to the unmodified blends indicates that they are short nylon fibre reinforced composites.

The storage moduli and loss moduli of all composites of maleic anhydride modified 80% HDPE/20% PP blend are higher than those of their respective matrix. The storage moduli of all composites of unmodified and maleic anhydride modified 20% HDPE/ 80% PP blend are lower than their respective matrix. The onset temperature of decomposition and temperature for 50% decomposition of all composites of the unmodified 80% HDPE / 20% PP and 20% HDPE / 80% PP blend are higher than those of their respective the matrix.

Abbreviations and symbols

ASTM	American standards and testing methods manual
AFM	Atomic Force microscopy
BET	Brunauer, Emmett and Teller
b	Width of specimen tested
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Derivative thermogravimetry
E'	Storage modulus
E"	Loss modulus
EB	Elongation-at-break
GP	General Purpose
GPa	Giga pascal
HDPE	High density polyethylene
hrs	Hours
Hz	Hertz
IR	Infra Red Spectroscopy
l_c	Critical fibre length
LDPE	Low density poly ethylene
L.R.	Laboratory reagent
m	metre
MA	Maleic anhydride
MA-g-HDPE	Maleic anhydride grafted high density polyethylene
MAPE	Maleic anhydride grafted high density polyethylene
MAPP	Maleic anhydride grafted PP
MA-g-PP	Maleic anhydride grafted PP
min	Minutes
mm	millimetre
mol	Mole
μm	Micrometer

MPa	Mega Pascal
MMC	Metal matrix composite
Nm	Newton meter
PE	Polyethylene
PET	Polyethylene terephthalate
phr	Parts by hundred parts by weight of resin
PMC	Polymer matrix composite
PP	polypropylene
rpm	Revolutions per minute
SEM	Scanning electron microscopy
tan δ	Loss factor
T	Temperature
T_g	Glass transition temperature
TGA	Thermo gravimetric analysis
UTM	Universal Testing Machine

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