Recyclable Short Fibre Reinforced Plastics

PP/Nylon and HDPE/Nylon composites

Thesis submitted to the
Cochin University of Science and Technology

BY
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In partial fulfillment of
The requirements for the award of the degree of

DOCTOR OF PHILOSOPHY
UNDER THE FACULTY OF TECHNOLOGY

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN 682 022, INDIA
AUGUST 2005

Thus Far The Lord Has Helped Us...

(1 Samuel 7:12)

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CERTIFICATE

This is to certify that the thesis entitled "Recyclable Short Fibre Reinforced Plastics-PP/Nylon and HDPE/Nylon composites" is an authentic report of the original work carried out my Mr. Thomas N Abraham under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin–682 022. No part of the work reported in this thesis has been presented for any other degree of any other institution.

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22.08.05

DECLARATION

*I here by declare that the thesis entitled "**Recyclable Short Fibre Reinforced Plastics-** PP/Nylon and HDPE/Nylon composites" is the bonafide report of the original work carried out by me under the guidance of Prof. Dr. K .E. George, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, and no part of this thesis has been presented for any other degree of any other institution.*

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Thomas N Abraham

Acknowledgements

When I think of the last three years of my life as a research student in the department of PS & RT, I cannot but thank and worship my dear Lord, Jesus for giving me this wonderful opportunity, giving me good teachers and friends, keeping me in good health and bringing my research to a meaningful completion.

I would like to express my earnest thanks to my guide Prof. Dr. K.E. George for his support and guidance through out the entire course of my Ph.D. I am also thankful for the motivation and care that he has given me during my research, in my personal life and also in my spiritual life.

Next I would like to express my thanks to the head of the department, Prof. Dr. Rani Joseph for her support and help during my research. I would also like to extend my thanks to Dr. Sunil K Narayanankutty, Dr. Philip Kurian, Dr. Eby Thomas Thachil, Dr. Thomas Kurian, Dr. Honey John, Dr. Soney Varghese, Ms. Jayalatha Goplakrishnan and Ms. Lity Alen Varghese, the faculty members of PS & RT, for their timely help.

I would like to thank all the research scholars (Rinku, Sreelekha, Dhanya, Saritha, Abhilash, Bipin) especially Nishachechy, Anoop & Sinto and all FIP teachers for their help and words of encouragement. I also express my earnest thanks to Ushachechy (Dept. of Chemistry, St:Theresas College) and Jacob Samuel (Yamagata University, Japan), Rajesh (Project Assistant) for their help and support during my initial stages of research. The assistance received from my friend Newsun Jose is beyond words. I am also grateful to the administrative staff of PSRT, Special thanks to Bakker mash for his special interest. At this moment of great happiness, I would also like to remember all of my former teachers.

I am always grateful to Prof.M.Y Yohannan, Retd. Principal, St: Peter's College, Kolenchery (President, Christian Revival Fellowship) for his advice and prayers throughout my research days. Christian Revival Fellowship, Kolenchery has been my constant source of strength all these years. Finally I am obliged to my Appachan and Ammachi for their moral and affectionate support. I would also like to express my thanks to my sisters (Mary, Annamma, Jessy, Alice, Sindhu & Silla) as well as the rest of my family for their whole hearted support.

Thomas N Abraham

Summary

The objective of this study has been to upgrade standard plastics like polypropylene and high density polyethylene as environment friendly engineering plastics. For this end, these plastics have been reinforced with an industrially important fibre, nylon. Since both the matrix and reinforcement are made of polymers these composites are completely recyclable. The salient features of the study are,

- Recyclable polymer composites were prepared in a Thermo Haake batchmixer by mixing polypropylene/high density polyethylene and nylon fibres. The temperature and shear rate of mixing were fixed to keep the matrix polymer in molten form and the reinforcement as fibre.
- In order to improve adhesion between the matrix and the reinforcing fibre the matrix polymer was grafted with maleic anhydride in presence of styrene.
- The tensile and flexural moduli of the composite show that the fibre can reinforce the matrices, more so when modified.
- The optimum processing parameters of the composites can be identified from 'moldflow' software.
- The thermal degradation behaviour of the matrix and nylon are similar and hence the thermal degradation behaviour of the composite remains the same as those of the original matrix/fibre.
- DSC studies show that the crystallization behaviour of the matrices are modified in the presence of the fibre.
- The dynamic mechanical analysis of the composites shows that the composite containing a low amount of reinforcing fibre can carry more dynamic loads compared to the matrix alone.
- The composite can be subjected to two types of recycling, low temperature recycling where the fibre is not melted and high temperature recycling where the fibre is also melted.

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Chapter 1

Introduction

Chapter 1

Introduction

Man's odyssey on earth has actually passed through a succession of ages-stone, copper, bronze, iron, plastics and silicone before culmination in the present age of designed materials or composites. Composite materials combine more than one material, most commonly a matrix material and high strength fibres. Glass fibres have been one of the most common reinforcing materials for composites, but pose health and environmental problems and are energy intensive. Biological fibres and natural or synthetic matrix materials can be used to make ecocomposites that are equally strong and environment friendly [1-3].

1.1 Composite materials

One of the earliest known composite materials is adobe brick in which straw (a fibrous material) is mixed with mud or clay. The straw allows the water in the clay to evaporate and distributes cracks in the clay uniformly, greatly improving the strength of this early building material. Another form of a composite material is the ubiquitous construction material we call plywood. Plywood uses natural materials (thin slabs of wood) held together by a strong adhesive, making the structure stronger than just the wood itself. In nature, bamboo is often cited as an example of a wood composite structure, combining a cellulose fibre and lignin, with the lignin providing the adhesive to hold the fibres together [4-10]. Of course, we probably drive a car across a composite highway every day. Reinforced concrete is a combination of two remarkable materials, concrete (a composite by itself) and steel that takes advantage of the strengths of each material to overcome their individual limitations in each. Steel has very high tensile strength, while concrete has very high compressive strength. In combination, they make a superior material for road and bridge construction. The structure, properties and applications of various composites were reported by a number of researchers all over the world [11-26].

Today, when we speak of composite materials, or just "composites", we are referring to the highly engineered combinations of polymer resins and reinforcing materials such as glass fibres. A fibre glass composite structure is a combination of glass fibres of various lengths and resins such as vinyl ester or polyester. The term FRP is often used, meaning Fibre Reinforced

Plastic. FRP is a very general term for many different combinations of reinforcement materials and bonding resins. Thus, the term "composites" is used extremely broadly to describe many materials with many different properties targeted at an even larger number of applications.

Polymer fibre composites are based on thermosetting or thermoplastic polymers and contain fibres ranging in length from short to continuous. In addition to fibres, polymer composites may contain particulate fillers, pigments, fire retardants and other process aids and property modifiers. Together with the different types of matrices, i.e. thermoset or thermoplastic, and the need to retain fibre length, these fillers impose major constraints on recyclability. However, as an alternative to recovering the original material in a recycling operation, it is possible to recover the energy locked in the material and to use the composite as a source of fuel. Several problems exist in this respect. For instance, one of the most difficult composites to reprocess is automobile tyre. Retreading, pyrolysis and cryogrinding to produce crumb are possibilities. The main problems have been economics of production and the identification of suitable markets for the products. Incineration to recover inherent energy is currently the most promising route. There are similarities between tyres and thermosetting polymer composites. Incineration has been used extensively with plastics for some time. Considerable amounts of domestic refuse containing plastics are incinerated each year. However, the rapid introduction of legislation and public opinion is causing a far reaching analysis of the incineration route. Recycling is a much superior option to incineration.

1.2 Recycling

Today, composites are an integral part of everyone's lifestyle with application varying from common place articles to sophisticated scientific and medical instruments. However, there is downside: composite is one of the least friendly materials. Low-cost plastics such as single use packaging appear more frequently in the waste stream than the polymers used in making durable goods. Some of the plastic products other than packaging enter the waste stream one year or more after fabrication. The rapid growth of electrical and electronic equipment scan be attributed to the speed of new developments in technology, which has resulted in a reduction in product life to less than 2 years in some cases, for both domestic and commercial products. In 1998 the amount of waste electrical and electronic equipments, for example, in Europe reached an estimated 6 million tons, an amount expected to double over the next decade [27]. The global figure of dismantled cars was around 24 million in 1995, generating 2.2 million tons of plastic scrap [28].

Plastic is a non-biodegradable material, so we cannot eliminate plastic wastes either by land filling or burning. Use of landfills to dispose plastic wastes prevents plant roots from growing and negatively affects the agricultural enterprises. Burning of plastic wastes produces great amounts of harmful gases, which harmfully affects all kinds of organisms. Currently there is increasing worldwide interest in biodegradable polymers and composites, which are viewed as a major part of global efforts to overcome serious environmental problems in the 21st century. Biodegradable polymers offer scientists a possible solution to waste disposal problems associated with traditional petroleum derived plastics [29-41]. For scientists, the real challenge lies in finding applications that would consume sufficiently large quantities of these materials to allow cost reductions, thus allowing biodegradable polymers to compete economically in the market.

Attention focused on polymer recycling has increased in the past decade [42] because more efficient reuse of materials will reduce the quantities sent to landfills, as well as reduce raw material extraction [42-52]. Recycling of waste plastics has been an interesting subject in the field of environmental science and technology for a long time and several methods have been proposed for recycling waste plastics. Recycling of plastics mainly includes three options:

- Mechanical recycling
- Chemical recycling by depolymerization
- Energy recovery

Polyolefins and poly esters which have been given significant attention in the research and technology are the most frequently recycled polymers. De Winter presents a review on recycling of PET film and Neumann on a co-injection technology, which allows one to use recycled PET as an intermediate layer in bottles. Both processes are common in industrial practice and are thus able to offer an overview of experience in plastic recycling which is of interest in other areas of recycling as well. Other references to PET recycling are presented by Sereni and La Mantia, Perrone and Bellio [53-74].

Recycling of polyethylene (PE) and other polyolefines are also reported. La Mantia and Curto propose methods of recycling of photooxidized polyethylene in blend with nylon 6. It is shown that the recycled PE behaves like a functionalized PE, having compatibilizing attributes due to which blends exhibit improved mechanical properties [75-76].

Recycling of urban wastes has been discussed by Gattiglia *et al.* and by Laguna *et al.* Generation source, separation possibilities, and cleaning technology are discussed in relation to blend properties, such as rheology, morphology and mechanical properties. Comparison is also made with blends having similar composition but made from virgin polymers [77-78].

The major problems in recycling of mixed plastic waste are due to their inferior processability, which results in materials having poor mechanical properties. La Mantia *et al.* and Vezzoli *et al.* present experimental results, which disclose the possibility of obtaining recycled materials with acceptable properties from mixed plastic waste [79].

Recycling of plastic components from car scrap is a very important challenge for the plastics industry and car manufacturers, since the plastic content in cars is systematically increasing [79-90]. Henstock and Seidl have discussed the recycling of plastic fuel tanks. Oliphant *et al.* have described the methods of application of ground discarded tires as a filler in polymer composite; Vezzoli *et al.* have presented new strategies of design of easily recyclable car interiors; while Heil and Pfaff have shown how battery recycling can utilize all initial components, offering quality assurance for recycled polypropylene [91-104].

1.2.1 Recycling of composites

Composite materials contribute to a significant weight saving per vehicle, translatable into a worthwhile fuel saving. Plastic composites make a valuable contribution but they feature more strongly in volume, high value production than in mass produced vehicles; this situation is likely to continue. The main components made from composites are body panels, structural members, suspension parts and bonnet components [105]. This situation is even more apparent in the aerospace industries where 65% of the structural weight of commercial aircraft is composed of composites and most of that is likely to be plastic based. The composites used in aerospace applications are generally more sophisticated and have higher property profiles than those used in automotive applications. At the same time, design lives are much longer, for example 25 years compared with 10 years. The total consumption of aerospace composites is lower than automotive composites; therefore we are confronted with high value, low volume composites in aerospace that will not become available for recycling for 25-30 years. On the other hand, the automotive industry will generate large quantities of scrap plastics and composites from a much earlier date, although the inherent value per kilogram will be less. Careful economic analysis is necessary to identify appropriate strategies. In the automotive industries, margins are very narrow and environmental pressure is very great. There is an urgent need for a sophisticated recycling industry that must be developed to deal with plastics and composites as the quantities involved become higher. It is unlikely to be acceptable simply to use these materials as landfills or to incinerate them in an unsophisticated manner. Separation procedures must be developed so that metals can be separated from plastics and one type of plastic and composite separated from one another. It is becoming increasingly apparent that considerable thought must be given to component design in order to render the separation process workable at the recovery and recycling stage.

For certain components, recycling presents little problem. If they are composed of a single material and can be easily separated then recycling is straightforward. All that is necessary is a simple means of identification such as bar coding or a similar method. It has been proposed that a 'closed loop' approach is adopted where components are reprocessed into similar components at some future time. However, this entails a very long range approach to material selection, which is not likely to be very practical. Where components are constructed from several polymeric materials, it is sensible to ensure they are compatible. For example, a bumper system composed of a reinforced plastic, energy absorbent core and a flexible cover should be based on compatible polymers, e.g. polypropylene. Then recycling is simplified as the plastic components as a whole can be shredded and compounded to recover a reinforced compound with useful properties.

A significant proportion of composites production is in the form of thermosetting materials such as SMC and BMC. The merits of incineration as a means of recovering the inherent energy values of these materials, the energy values available in these materials and the problems involved in the incineration process are being investigated [106]. After incineration, a considerable quantity of inert reinforcement and filler is left; one objective of these studies is to find worthwhile uses for it. The calorific values of thermosetting plastics used in polymer fibre composites such, as polyesters, vinyl esters and epoxies are approximately 30 $MJkg^{-1}$. These values are generally reduced in direct proportion to their filler and reinforcement contents. Many thermosetting composites contain upto 80 % fillers and reinforcements, so their calorific values are significantly reduced. But endothermic reactions can absorb considerable amounts of energy; when 1 kg of calcium carbonate decomposes at between 800 and 900 °C to yield lime, it absorbs 1.8 MJ. Some fillers and polymers may react to form sulphur dioxide, nitrogen oxides etc. Table 1 shows some typical calorific values for comparison purposes.

Table 1 Comparative calorific values

Material	Approximate calorific value ($MJkg^{-1}$)
Thermosetting plastics, e.g. polyester, vinyl ester and epoxy	30
Thermosetting fibre composite containing 80% fibre/filler	6
Tyres	31
Polyethylene	46
Domestic refuse	10
Polymers in domestic refuse (average)	38

Flue gas emissions are a possible problem but initial studies on polymer composites have not revealed major problems. The indications are that particulate and gaseous emissions should be within legislative limits [106]. Polyester, vinyl ester and epoxy based composites give low char yields and the ash yield depends on the resin content. Phenolics and urea based composites give much higher values. Work is in progress to find uses for the recovered fillers in, for example, the cement industry, where the energy recovered would be of considerable use. Lime produced by the decomposition of calcium carbonate described above is potentially useful in this respect.

Short fibre thermoplastic composites can be granulated and melt processed by injection moulding or extrusion. However, some mechanical reduction of fibre length is inevitable, together in some cases, with degradation of the matrix. In–house recycling at the initial production stage is straightforward. In other cases, the situation is less satisfactory although the presence of fibres is often a help in compatibilizing systems comprising mixtures of polymers and composites. Thermosetting composites can be re-used by shredding them into fine particles using them as a filler in other polymeric materials.

In the case of long fibre polymer composites, it is an advantage to preserve fibre length as far as possible in a recycling processes in order to maximize properties and value. This is difficult to achieve but is worth considering in view of the probable high cost of the fibres and polymer matrix. Studies have been made on recycling a thermoplastic composite based on poly ether ether ketone (PEEK) with 68 % continuous carbon fibres [107]. In pattern cutting, the prepreg material utilization is unlikely to be more than 75 %. Thus re-use of the offcuts is desirable. Studies have been made on the use of controlled size pieces of offcut prepreg followed by reconstitution by hot pressing. Good properties are achievable as can be seen from Table 2. It is conceivable that this approach could be extended to pattern cutting offcuts of thermosetting composites but handling and shelf lives present considerable problems. Injection moulding of the reclaimed material after granulation and dilution with PEEK is also possible and typical results are included for comparison.

Table 2. Comparison of reclaimed composite, reconstituted and an original continuous fibre composite

Property	Reclaim with PEEK (40% carbon fibre) injection moulded	Reconstituted single prepreg piles (25.4 mm) hot pressed	Original continuous fibre composite
Flexural modulus (GPa)	30.4	37.2	40.9
Flexural strength (MPa)	410	440	616
Tensile strength (MPa)	242	290	704

1.3 Short fibre reinforced thermoplastic composites

Polymer composites are playing an increasing role as construction materials in a wide variety of applications. In particular, thermoplastic polymer composites are falling under increasing scrutiny due to their potential to be easily repaired and/or reshaped, making them easier to recycle and reuse compared with thermosetting matrix composites. Short fibre reinforced thermoplastic moulding materials are very widely used in industry. They are attractive because the addition of short fibres to the thermoplastic results in some very cost effective property improvements whilst retaining the processability of the thermoplastic. The main applications are for relatively small intricate, load bearing components. These vary from small mechanical details, such as gearwheels, pawls and levers to castings for electric hand tools and electronic equipments.

There are now two main classes of these moulding compounds, those containing very short fibres and those containing longer fibres. The fibres are most frequently E-glass of 10-20 μm diameter, the short fibres are typically less than 1 mm long in the moulding compound, the long fibres are typically 10 mm long at this stage. In both cases, some fibre breakage occurs during moulding so the lengths will be further reduced. The short fibre material is manufactured by mixing either prechopped E-glass roving or continuous glass roving with the thermoplastic in a twin-screw compounding extruder. The most effective technology is to introduce the continuous roving at a venting port directly into the molten thermoplastic. The high shear in the extruder ensures the fibre and plastic are intimately mixed; in this type of materials the fibres are dispersed as individual filaments instead of bundles or strands, as is usual in bulk or sheet moulding compounds, for example. The compound is then extruded through a 'spaghatti' die then either chilled and chopped into pellets or chopped directly with a hot face cutter. The resultant pellets or chopped directly with a hot face cutter. The resultant pellets are dried and shipped to the injection moulder. They are typically about 4 mm in diameter and length and contain up to 30% by volume of fibre (up to 50 % by weight according to the density of the polymer).

Passing continuous roving through liquid polymer using a fluidized bed of polymer powder or a crosshead die on an extruder makes the long fibre material. The material is passed through a die to force the polymer to infiltrate the roving. Finally it is chopped into pellets, typically 10 mm long and 4 mm in diameter. The fibre runs the full length of these pellets. When moulded, some fibre breakage occurs but the overall fibre length distribution will be much higher than for the short fibre material. This allows greater reinforcement efficiency to be attained, together with greater relative toughness.

The attraction of these materials lies in a combination of enhanced mechanical properties coupled with good processability. In general, stiffness is strongly enhanced in proportion to the stiffness of the fibre used, the fibre fraction, the length distribution and the orientation distribution achieved in the moulding. Strength is also enhanced but not as much as the stiffness; this is due to a reduction in the fracture strain. This low fracture strain, often only 1-2 %, is some times an embarrassment but the impact energy is often enhanced by fibre reinforcement. A better balance of properties is often achieved by a judicious combination of fibre reinforcement and rubber particle toughening. There are two further important effects: the heat distortion temperature is raised and the coefficient of thermal expansion is reduced. This allows the fibre reinforced grade to be utilized at higher service temperatures, reduces in-mould shrinkage and generally improves dimensional stability. Dimensional stability is very important for intricate components, which need to be manufactured to close tolerances. Some typical properties are given in Table 3.

Processability is generally very good. Although the addition of the fibres tends to increase the melt viscosity and hence the mouldability, the pseudoplastic nature of thermoplastics means their apparent viscosity decreases with increased shear rate. The presence of rigid fibres in the melt has the effect of increasing the local shear rate so mouldability remains good up to quite high fibre loadings. The main processing problems arise from flow induced fibre orientation. In regiments of converging flow, the fibres tend to align in the direction of the flow; in regiments of divergent flow, the opposite is the case. Practical mouldings tend to be composed of thin shell-like sections so good heat transfer to the mould can be achieved with consequent reduction in the moulding cycle time. In these sections, the orientation is modified by interactions at the (cold) mould surfaces. This may affect the mechanical properties of the moulding, but the more important implication is that it can lead to distortion due to differential shrinkage between sections with different fibre orientations. This can destroy the advantages of the reduced coefficient of thermal expansion mentioned above. A further effect is the formation of knit or weld lines where melt fronts intersect. This occurs wherever there is bifurcated flow, e.g. around a cored feature, or when multiple gates are used (Figure 1). These can be controlled by multilevel feed technology.

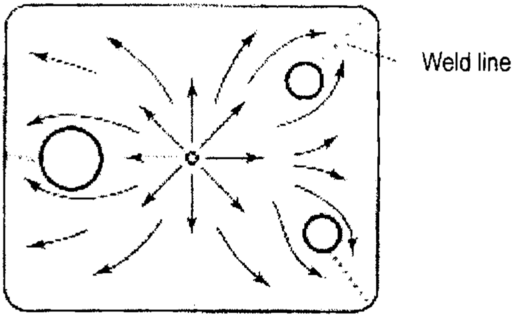

Figure 1 Weld or 'knit' lines are formed wherever melt fronts rejoin after flow around a cored feature. In this case the flow is illustrated for a centre-gated plate with three circular holes

Thermoplastic polymers differ from thermosetting resins. They are not crosslinked and derive their strength and stiffness from the spatial arrangement of the monomer units that form high molecular weight chains. In general, fibre reinforcement is used in discontinuous or short fibre form to extend the mechanical property advantages which in turn depend on the average length of the fibres on moulding. While the property gain from adding fibre reinforcement may seem modest in comparison with continuous fibre systems, the improvements in either Young's modulus or toughness justify their use for many applications.

In amorphous materials, heating leads to polymer chain disentanglement and a gradual change from a rigid to a viscous liquid. In crystalline materials, heating results in the sharp melting of the crystalline phase to give an amorphous liquid. Both amorphous and crystalline polymers may have anisotropic properties resulting from molecular orientation induced during processing and solidification. In composite systems, however, the properties are largely dictated by the character of the fibre reinforcement.

These polymer composite systems are often termed 'engineering compounds' because their mechanical properties extend beyond the commodity levels expected from bulk polymers and they are used in multicomponent compounds for specific applications. Compounds may include colorants, viscosity modifiers, stabilizers, matrix modifiers, interfacial bond enhancers or secondary fillers.

Table 3 Typical properties of selected short fibre reinforced thermoplastics

Polymer	Fibre	V_f	E (GPa)	X_T (MPa)	Charpy impact (KJm^{-2})	HDT (°C)
Polypropylene	None	0	1.9	39	2.7	60
Polypropylene	Glass	0.20	7.5	110	8.0	155
Polyamide 6,6	None	0	3.2	105	>25	100
Polyamide 6,6	Glass	0.20	10	230	40	250
Polyamide 6,6	Carbon	0.20	20	250	10	255
Polycarbonate	Glass	0.20	9.0	135	40	160
Polyoxymethylene	Glass	0.20	9.0	140	9.0	165
Polyphenylenesulphide	Glass	0.20	11	155	20	263
Polyphenylenesulphide	Carbon	0.20	17	185	20	263
Poly ether ether ketone	Carbon	0.20	16	215	-	310

V_f = Volume fraction, E Young's modulus, X_T = Tensile strength, HDT= Heat distortion temperature

These commodity polymers are typically used in conjunction with short fibre reinforcement; mineral fillers are also commonly used in lower performance applications. E-glass fibres are used in the vast majority of reinforced injection moulding compounds on cost grounds, but carbon fibres (usually high strength type) and Kevlar type fibres may be compounded for specialist applications. Conductive fibres such as steel are used to impart dielectric properties.

The importance of commodity polymers may be seen from Figure 2. The left triangle shows the prediction made in 1975 for 1995. It was presumed that commodity polymers would be more or less wiped out and engineering and specialty polymers will rule the market. The right triangle shows the actual situation for 1997 where commodity polymers still hold more than 80 % of the polymer market. This clearly shows the importance and need for upgrading commodity polymers for more critical applications.

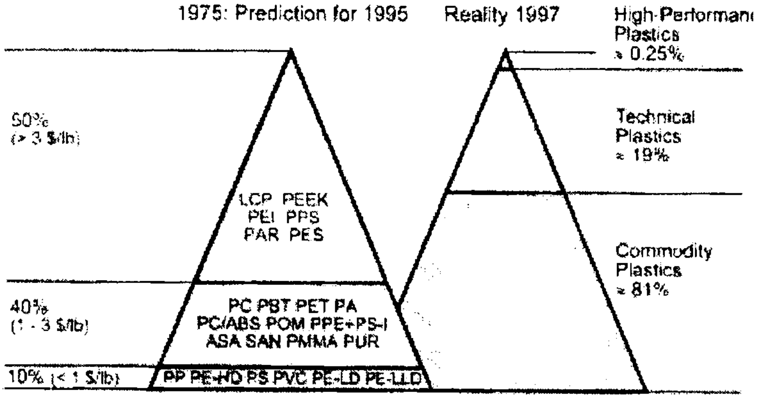

Figure 2 Prediction in 1975 and reality 1997 of the usage of thermoplastic materials

1.3.1 Fibres used in composites

The fibre contributes the high strength and modulus to the composite. It is the element that provides the resistance to breakage and bending under the applied stress or load.

The most common fibre reinforcement is glass, usually E-glass. Glass fibres are usually 5-20 μm in diameter and are round and fairly smooth, though their surfaces are never completely defect free. For some short fibre reinforced composites they are provided pre-chopped in length of a few millimeters. A coating is commonly applied to glass fibres to improve processability and to reduce damage during handling. Surface coatings may also be applied to improve the adhesion between the matrix and the fibre.

Carbon fibres, often called graphite fibres although full graphitization is not achieved in their manufacture, are achieving wide acceptance for aircraft applications because of their advanced properties. Two categories of carbon fibres have predominated, distinguished primarily by their elastic moduli: high-strength carbon fibres with a typical modulus range 207-241 GPa and high-modulus carbon fibres with a typical modulus range of 345-380 GPa. Other higher-modulus carbon fibres, more loosely categorized as very high-modulus carbon fibres and ultrahigh- modulus carbon fibres, with moduli up to 830 GPa are also available.

Metal fibres can be used to provide electrical conductivity. The major applications for metal fibres filled conductive thermoplastic composites is as housings for computers and other electrical goods requiring protection against electromagnetic interference and electrostatic discharge. Stainless steel fibres are used and loadings of the order of 1 % by volume (depending up on the application) are common. Commercial grades are available based on several polymers including acrylonitrile butadiene styrene (ABS), various nylons, polycarbonate and polypropylene.

The aliphatic polyamides or Nylons were the first fully synthetic fibres to achieve commercial success (1939). Nylon is a condensation polymer of a diamine and a dicarboxylic acid. Because a variety of diamenes and dicarboxylic acids can be produced, there are very large numbers of polyamide materials available to prepare nylon fibres. The most common versions are nylon 6,6 and nylon 6. Nylon 6,6 which is widely used as fibre is made from adipic acid and hexamethylene diamine. The commercial production of nylon 6 begins with caprolactum. Fibres are produced commercially in various parts of the world but nylon 6,6 has been preferred in non American markets, nylon 6 is more popular in Europe and elsewhere. The polyamide is melt spun and drawn after cooling to give the desired properties for each intended use. The fibre has outstanding durability and excellent physical properties. The main features are exceptional strength, high elastic recovery, abrasion resistance, lusture, washability, resistance to damage from oil and many chemicals, high resilience, colourability, relatively insensitivity to moisture, smoothness and softness. Like polyester, nylon has high melting point which conveys good high temperature performance. Its toughness makes it a major fibre of choice in carpets. Because of excellent tear strength it is used as a blending fibre in some cases. In certain applications, the performance of nylon fibre is hard to beat. Because of its high cost it is used in specialized applications where its performance can justify the cost. Nylon fibres are used for the manufacture of aplittable pie fibres. Non wovens developed from nylon are used in automobile products, athletic wear and conveyer belts.

In the case of rubbery composites, cellulose fibres have been found to give better reinforcement than glass or carbon fibres. The reason for this is probably that the flexibility of cellulose fibres results in less breakage during processing than happens with the brittle glass or carbon fibres which have less resistance to bending. The fibre length used in the preparation of rubber composites is critical. It should not be too long for the fibres will get entangled, causing problems with dispersion; if it is too short the stress transfer area is too small and the fibres do not provide effective reinforcement.

1.3.2 Matrix materials used in composites

The main roles of the matrix are to transmit and distribute stress on to the individual fibres and to maintain the fibres separated and in the desired orientation. The matrix also provides protection against fibre abrasion as well as fibre exposure to moisture or other environmental condition and causes the fibres to act as a team in resisting failure or deformation under load. The maximum service temperature of the composites is limited by matrix.

The most common thermoplastic matrices for generating short fibre reinforced composites are based on polypropylene and nylon. Higher performance thermoplastic composites use poly (ether sulphone) or poly (ether ether ketone)(PEEK), giving higher stiffness and higher working temperature. Also with thermoplastic behaviour are the thermotropic liquid crystal polymers in which the self reinforcing property is further enhanced by the inclusion of fibres. Polyimides, which can show either thermoset or thermoplastic characteristics, are also available in reinforced form.

Thermoset matrices include epoxies and phenolics. Thermosets are generally less suitable than thermoplastics for mass production but the improved properties achieved by adding fibre reinforcement has provided added incentive to develop a suitable means of fabrication. Both natural and synthetic rubbers are candidates for short fibre reinforcement.

1.3.3 Preparation of short fibre thermoplastic composites

Short fibre reinforced thermoplastics are most commonly supplied in the form of granules suitable for use in injection moulding machines. The granules are roughly cylindrical, measuring 3-5 mm long and about 3 mm diameter and the fibres are dispersed fairly uniformly within them. To make the granules, chopped fibres and unfilled thermoplastic polymer powder or granules are fed into an extruder. Mixing occurs on the passage through the extruder and the melt is passed through a die to make a lace that is chopped into granules of the required length. Fibre breakage is a major problem during this process and the design of the screw is of some importance, deep flights being required. Twin screw extruders are often preferred and the fibres are sometimes fed into the barrel part way along so that they enter directly into melt: this is found to reduce fibre breakage.

In most of the common short fibre thermoplastic moulding materials the original fibre length is around 3 mm but few fibres survive mixing and moulding intact, with most fibres present in mouldings measuring fractions of a millimeter. Another class of compound is available known as long fibre thermoplastic, in which the granules measure about 10 mm and contain parallel continuous fibres than span the full length. These granules are produced by chopping up pultruded rod in which a continuous tow of fibres is wetted by the polymer when forced through a heated die. The long fibre compounds are found to behave surprisingly well in conventional injection moulding machinery and the fibre lengths are preserved more completely than in the case with compounds in which the fibres are shorter to begin with.

1.3.4 Mechanical properties of fibre reinforced thermoplastics

Fibre loading levels can have a significant effect on mechanical properties, with higher concentrations of fibre providing an increase in modulus and strength. In general, loadings are typically in the 20-30 wt% range, with loadings up to 50 % commercially available [108]. As the level of reinforcement is increased, the mechanical properties also rise, but this is not a linear relationship [109]. An excellent investigation of how loading level affects reinforcement was undertaken by Hiscock and Bigg [110] for reinforced polyamide 6 (nylon 6). Loadings of 10 and 25 % were studied, using different types of glass fibre and various effects of silane treatment. 10 wt% glass fibre in PA6 gave a tensile strength of 101 MPa and a modulus of 5.1 GPa while PA6 with 25 wt% glass possessed a strength of 169 Mpa and a modulus of 11.1 GPa. These results show that increasing the loading by two and one-half times does not produce a commensurate increase in any of the mechanical properties. This should be expected, because as the concentration of fibre increases, it allows more fibre-fibre interactions which decrease the average fibre size. Smaller fibre aspect ratios increase the importance of stress concentration at the fibre ends, resulting in earlier failure and lower mechanical properties. Another study relating loading level, mechanical properties, and efficiency of reinforcement was performed by Xavier and Misra [111]. Polypropylene was loaded with 10, 20, 28, and 35 wt% glass and injection molded into ASTM standard tensile bars. As the loading was increased from 10 to 35 wt%, the tensile modulus rose from 1.59 to 3.41 GPa. Meanwhile, the average fibre length decreased from 0.55 mm to 0.35 mm and the efficiency of reinforcement decreased from 0.26 to 0.22. This again confirms the relationship that higher loadings produce both lower fibre lengths and a lower efficiency of reinforcement.

Using smaller diameter fibres can also influence final mechanical properties [112-113]. Watkins *et al.* [114] studied glass fibres with diameters from 13.5 mm to 6.5 mm blended in polyamide 6,6 (nylon 6,6), poly(butylene terephthalate) (PBT), poly(ether ether ketone) (PEEK), polycarbonate (PC), and poly(ether imide) (PEI) at loadings from 20 to 40 wt%. All materials were injection molded into ASTM test specimens, which were tested for tensile strength and unnotched impact strength. For every weight fraction of glass, both the tensile strength and impact strength was higher when smaller diameter fibres were used. A typical example is with PA 6,6 at 30 wt%. This showed an increase in tensile strength from 176.6 MPa to 198.7 MPa and in impact strength from 811.7 J/m to 1233 J/m, establishing a strong relationship between smaller fibre diameter and higher mechanical properties.

However, this relationship may not hold for very small fibre diameters. There may be an optimum fibre size to attain the highest possible mechanical properties. In another study, fibres with diameters of 13, 7, 4, and 0.5 microns were used in a PA 6,6 matrix [115]. This investigation showed optimal properties at 7 mm, with 4 mm giving properties equal to the 13 mm fibres and 0.5 mm fibres yielding the lowest tensile and flexural values.

It was speculated that the existence of an optimum fibre size is due to two competing relationships. Loading polymer melt with fibres having smaller diameters results in a larger number of fibres in the melt at the same weight fraction. For example, the number of 6.5 mm diameter filaments would be four times the number of 13 mm diameter fibres at the same weight fraction of reinforcement. This provides more surface area per unit volume of reinforcement, which is beneficial because of the potential for better stress transfer. However, having more fibres also means having more fibre ends, which serve as stress concentrators and lower mechanical properties. Therefore, there may exist a fibre diameter which maximizes the benefits of high surface area while minimizes the detrimental effects associated with the number of fibre ends.

Fibre length has a substantial effect on mechanical properties, with longer fibres providing more reinforcement to the matrix. The best illustration of this is provided by comparing short fibre reinforcement with long fibre reinforcement [116-117]. Using PA 6,6 with 50 wt% glass loading, the short glass fibre had an average length of 0.33 mm while the long fibre had an average length of 2.9 mm. The higher aspect ratios of the long fibre reinforcement consistently provided mechanical properties superior to those measured from short fibre reinforced composites. The most dramatic improvement was observed in notched Izod testing, where the impact strength was 261 J/m for the long fibre case and 139 J/m for short fibre reinforcement. In order to accurately correlate mechanical properties to fibre alignment, it is necessary to produce composite plaques where the fibre alignment has been well controlled. Often, this is accomplished by compression molding plaques using strands with a high degree of uniaxial alignment. For example, McNally [118] extruded 30 wt% glass-reinforced PBT to obtain highly oriented strands. After confirming that the glass was highly oriented by using scanning electron microscopy, the strands were then uniaxially compression molded into plaques. The plaques were cut at angles of 0°, 22 ½°, 45°, 67 ½°, and 90° with respect to the fibre orientation to determine how tensile properties changed. The tensile strength, tensile modulus, flexural strength, and flexural modulus were all observed to decrease by about one-half as the testing proceeded to 90° alignment. Impact testing was even more sensitive to fibre alignment. The highest notched Izod impact strength was 69.9 J/m while the lowest was 32.5 J/m. The reversed notched Izod tests showed similar results, with an impact strength of 265 J/m when the fibres were at a fibre orientation angle of 0°, while just 99.8 J/m when the fibre orientation angle was 90°.

Blumentritt *et al.* [119-120] also investigated compression molded samples, comparing random alignment with uniaxial alignment using a variety of different resins, types of fibre, and loading levels. These studies showed that with glass fibre, a random-in-plane alignment gave significantly lower tensile properties, but the magnitude of the decrease varied from material to material. For instance, loading high density polyethylene (HDPE) with 20 vol% glass produced composites with a tensile strength of 142.7 MPa in unidirectional alignment but only 42.13 MPa in the random mode.

Meanwhile, polycarbonate using the same vol% glass had tensile strengths of 114.4 MPa and 61.36 MPa under the same two methods of alignment . This indicates fibre alignment is not the only factor which affects mechanical performance; interfacial adhesion and how the fibre influences matrix properties may also have a significant effect. The influence of interfacial adhesion on the mechanical properties of glass fibre filled PA6 was examined by Bader and Collins [121]. The test samples were prepared by injection molding, using both an end-gated as well as a side-gated test bars. For dry endgated samples containing 25 wt% glass fibres (12 mm in diameter), one set possessed fibres coated with a silane coupling agent while the second was not. The coated glass had a tensile modulus of 11.1 GPa, a tensile strength of 169 MPa, a notched Charpy impact energy of 19.7 KJ/m^2, and an interfacial shear strength of 44 MPa. Meanwhile, the glass fibres without the silane coupling agent possessed lower mechanical properties, with a stiffness of 10.7 GPa, a strength of 102 MPa, an impact energy of 16.8 KJ/m^2, and an interfacial shear strength of 35 MPa. These results demonstrate that interfacial adhesion can play an important role in maximizing mechanical properties.

One investigation which examined the influence of flow kinematics on the mechanical properties of filled polymers was undertaken by Darlington *et al.* [122], using an end-gated circular disk. The diameter and thickness of the disk was varied to determine the effect those parameters would have on mechanical behavior. It was found that making the disk thinner caused less mechanical anisotropy and that increasing the diameter both reduced anisotropy and improved the measured properties significantly. They attributed this to a balance between the fibre orientation in the core and the surface, with the core's orientation being transverse to the major flow direction. It was also noted that in order to create this balance, the flow behavior of the fluid had to be considered.

Pipes and coworkers [123] moulded end gated tensile bars for their examinations of fibre orientation. The bars were then cut into different sections to examine how the orientation in each layer is reflected in mechanical properties. The edge section was determined to have an orientation parameter of 0.8 and the core a parameter of -0.5. The edge showed a longitudinal tensile modulus of 18.3 GPa and a transverse modulus of 9.0 GPa while the core had moduli of 9.9 GPa and 15.2 GPa in the same two directions. This again shows that the flow kinematics creates fibre orientation in the bars and the change in orientation through the thickness has a measurable effect on mechanical properties. Notch sensitivity between the two sections was determined by drilling holes of different diameters through the test samples. It was found that the more highly oriented skin section was more sensitive to the holes, indicating that strength reduction between machined notches and molded notches will not be equivalent.

1.4 Short fibre reinforcement-stress transfer in discontinuous fibre composites

A discontinuous fibre composite is one that contains relatively short discrete lengths of the fibre dispersed within the matrix. The fibres may be aligned in one direction but are more usually in a random, or semirandom configuration. When an external load is applied to the composite, the fibres are loaded as a result of stress transfer form the matrix to the fibre across the fibre-matrix interface. The degree of reinforcement that may be attained is a function of the fibre fraction, the fibre orientation distribution (FOD), the fibre length distribution (FLD) and the efficiency of stress transfer at the interface. In general the reinforcement is more in the principal stress direction and the interface is 'strong'.

One of the earliest theories of reinforcement developed by Cox [124] is based on shear-lag mechanism observed in fibrous composites. According to Cox, in shear lag analysis, the main aspects of controlling the properties of a composite are critical length of the fibre and interfacial shear strength between fibre and matrix. The critical length of the fibre (l_c) in composites is a parameter, which determines the amount of stress transfered to the fibre. That is, if the length to diameter ratio is higher than the critical aspect ratio, composites show superior properties. When the aspect ratio is smaller than critical aspect ratio, composites show inferior properties. In Cox's treatment, interfacial shear strength is produced on the surface of the fibre due to the 'shear lag' between the fibre and the matrix during the failure of the composite.

Cox theory deals with the net tensile load across the fibre of length l and radius r which must be balanced by the shear force and the fibre matrix interface. Shear stress τ at the fibre-matrix interface will vary along the fibre, so also will the tensile stress in the fibre. A schematic representation of Cox-shear lag analysis is shown in Figure 3.

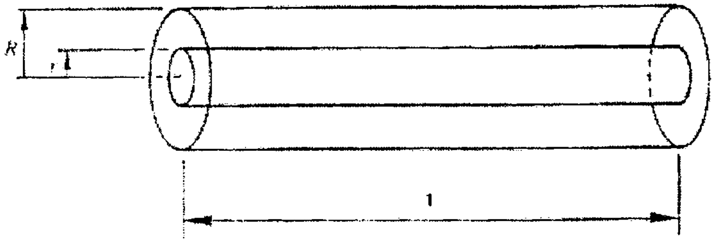

Figure 3 The representative element used in the Cox analysis. The inner cylinder represents the fibre and the outer annulus the matrix

According to this theory, longitudinal Young's modulus M_c is given by the Equation 1.a

$$M_c = M_f V_f \left(1 - \frac{\tanh \beta l/2}{\beta l/2}\right) + M_m V_m \tag{1.a}$$

where M_m and M_f are Young's moduli of matrix and fibre respectively, r is the radius of the fibre, G_m, the shear modulus of matrix R, the centre to centre distance of the fibres, and A_f, the area of the fibre.

$$\beta = \left[\frac{2\pi G_m}{M_f A_f \quad \left(\frac{R}{r}\right)}\right]^{1/2} \tag{1.b}$$

For hexagonally packed fibres,

$$R = \left[\frac{2\pi r^2}{3^{1/2} V_f}\right]^{1/2} \tag{1.c}$$

For square packed fibres,

$$R = r\left[\frac{\pi}{4V_f}\right]^{1/2} \tag{1.d}$$

According to Cox's model, tensile strength (T_c) is given by

$$T_c = T_f V_f \left(1 - \frac{\tanh \beta l/2}{\beta l/2}\right) + T_m V_m \tag{1.f}$$

β is given by the Equation 1.b.

But Cox's shear-lag analysis has two major disadvantages. The first one is that the stress amplification effects at the fibre ends are not taken into account, and the second is that the matrix tensile stress possesses no radial dependence.

The alternative model, due to Kelly and Tyson [125], is based on the concept of frictional stress at the interface. It is considered that a constant shear stress is induced from the fibre ends, this results in a linear stress build up. The frictional stress may be regarded as the interface shear strength (τ_i); this concept is often used for the experimental estimation of interface shear strength by the fragmentation or pull out test. The model is useful in that it allows a precise definition of the transfer aspect ratio R_t. It should be noted that this transfer region increases as the applied strain is increased. If the fibre aspect ratio exceeds $2R_t$, there will be a plateau region along the central portion of the fibre. The reinforcement efficiency is obtained from a similar ratio of areas, as for Cox model and efficiency increases with fibre aspect ratio in a similar manner.

Most discontinuous fibre composites contain fibres with a wide distribution of lengths distributed in a semi random orientation. However, flow processes during fabrication often result in more complex distributions, dependent on component geometry and moulding parameters. To treat the problem of length variations, or more properly aspect ratio distribution. Then, if the interface shear strength is known, the efficiency of each fibre may be determined using the Kelly-Tyson model and the overall efficiency may be computed. Likewise, if the fibre orientation distribution is determined, a further efficiency factor may be computed using standard angle ply theory. This has been attempted by several workers [126] who have obtained quite reasonable predictions for the stiffness of short fibre systems. The simplest procedure is to use the aspect ratio and orientation data to produce two constants which may be applied to the Voigt equation.

$$E_c = \eta_0 \eta_l E_f V_f + E_m V_m \quad \text{-------------} \quad (1.g)$$

where η_l and η_o are the length and orientation constants, respectively. They have a maximum value of unity (long aligned fibres) when the reinforcement efficiency is equal to that of continuous fibres. For short fibre reinforced thermoplastic moulding compounds, value of 0.3-0.5 may be considered typical.

The Bowyer and Bader methodology can be used to predict the stress strain response of short fibre reinforced plastics. According to Bowyer and Bader model, tensile strength of short fibre reinforced thermoplastic composites is the sum of contributions from subcritical and supercritical fibres and that from the matrix [127]. Tensile strength is given by

$$T_c = T_f K_1 K_2 V_f + T_m V_m \quad \text{-------------} \quad (1.h)$$

where K_1 is the fibre orientation factor. Depending on fibre orientations, K_1 also changes [128]. K_2 is the fibre length factor.

For fibres with 1>l_c

$$K_1 = 1 - {}^{l_c}\!/_{2l} \tag{1.i}$$

For fibres with $l<l_c$

$$K_2 = {}^{l}\!/_{2l_c} \tag{1.j}$$

where l is the length of the fibre and l_c is the critical length of the fibre. Young's modulus also can be calculated using the same equation.

$$M_c = M_f K_1 K_2 V_f + M_m V_m \tag{1.k}$$

1.5 Fabrication of short fibre thermoplastic composite-Injection moulding

One of the most common processing methods for thermoplastics is injection moulding [129-131]. The list of artefacts manufactured using this process is almost endless and includes electric drill castings, gearwheels, business machine housings, telephones and brief-cases. The process has been in existence for well over 100 years, although the development of the technique did not really get under way until the 1920s. In essence, the original concepts of the process were based on the pressure die casting of metals.

In principle, the injection moulding process is very straightforward. The polymer, in either granular or powder form is fed from a hopper into a heated barrel, where it softens and becomes a viscous melt. It is then forced under high pressure into a relatively cold mould cavity. When the polymer in the cavity has had sufficient time to solidify (at least partially), the mould is opened and the fabricated part is ejected. The cycles of operations are then repeated. Correctly controlled, this process is very versatile and is capable of fabricating very complex shaped components with considerable speed and precision.

The earlier injection moulding machines were of the plunger variety and there are still many of these machines in use today. The process of melting the polymer relies entirely on heat conduction from the barrel walls. In view of the low thermal conductivity of polymers, this results in a very non-uniform temperature distribution throughout the melt. This implies that any additives, e.g. pigments or antioxidants remain poorly dispersed with consequential problems in the final artefact. However, for certain applications where it is desirable to minimize deleterious effects on the additives, e.g. where processing fibre reinforced thermoplastics, the simple plunger machine does offer some advantages.

Many of the disadvantages associated with the plunger type injection moulding machine are overcome in the screw injection moulder, which now largely dominates the market. Basically, this machine uses an extruder type screw which acts in a dual role; it is initially used for the injection process itself. The arrangement of the screw in the barrel is shown schematically in Figure 3. The mould is initially closed and melt is injected into the cavity using the screw as a plunger. The pressure on the screw is maintained until solidification at the gate(s) has occurred. The screw is then allowed to rotate so it coveys fresh polymer towards its front. But the moulded part is still in place, so the screw moves backwards against a predetermined back pressure and the melt is fully homogenized, ready for the next shot. During this operation, the fabricated part has cooled sufficiently so the mould can be opened and the part ejected. The mould then closes and the whole cycle repeats. The overall cycle time is typically a few minutes, although this depends on the dimensions of the part. The briefest part of the cycle is injection, which often takes only a few seconds; much of the time is spent in waiting for the moulded artefact to solidify.

The size of an injection moulding machine is usually defined by its capacity to mould in a single shot, e.g. a medium sized machine would be rated 200 g. Machines used for the production of very large items, e.g. rubbish bins, are physically very large pieces of engineering equipment and demand considerable care in operation. The pressure required to inject the polymer melt into the mould can be very high (up to 200 MPa) and this demands the use of high tensile steels for both the injection unit and the mould.

The properties of the moulded part are highly dependent on the processing conditions employed. Barrel and mould temperatures, injection speed and pressure, screw back speed and pressure all influence the properties of the moulded artefact. Especially with some of the newer 'engineering' thermoplastics, minor changes in processing conditions can greatly influence part quality; consequently many of the new generation of injection moulding machines are equipped with 'process controllers'. They allow the continuous monitoring of certain key parameters and enable corrective actions to be taken by means of feedback controllers. Process controllers have done much to develop the injection moulding process into a rapid fabrication route for precision parts.

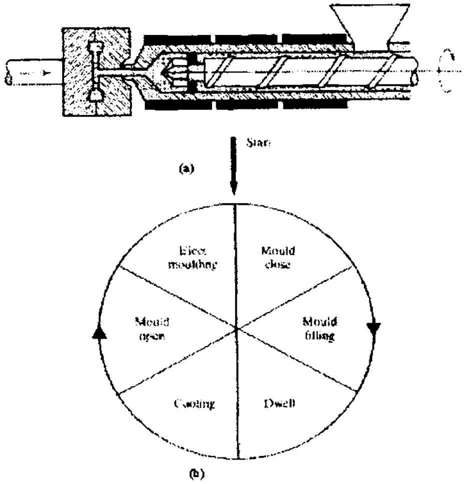

Figure 3 (a) Screw injection moulding machine
(b) Cycle of operations in injection moulding

1.6 Parameters influencing the characteristics of short fibre thermoplastic composites

Fibre aspect ratio, fibre-matrix interaction, short fibre length, fibre orientation and barrel residence time are the major factors which affect the properties of the injection molded thermoplastic composites.

1.6.1 Fibre aspect ratio

Aspect ratio is the l/d ratio of the fibre and is of great significance in deciding the level of reinforcement that can be effected by a fibre.

1.6.2 Fibre-matrix interaction

Once the manufacturing process has successfully achieved a uniform dispersion of matrix material around the reinforcing filaments, the fibre-matrix surface interaction must be considered. Fibre-matrix adhesion is widely considered a necessary condition to ensure good composite mechanical properties [Drzal and Madhukar, 1993]. If there is no adhesion between the two, the composite will respond as if it were the bulk matrix material with voids retaining the shape of the included fibres (at low strains). At higher strains, Poisson's effect may bring about mechanical friction forces between the fibre and matrix phase, thus causing the fibres to bring about a greater influence in material properties.

Adhesion in thermoplastic composite systems is usually enhanced using fibre surface treatments. Itoi and Yamada studied the effect of carbon fibre surface modification by oxidation on adhesion with polyethernitrile [1992]. Nitric acid and hydrogen peroxide were used as oxidation agents. Treated fibres were powder impregnated by the polyethernitrile after which unidirectional laminates were obtained. Improvements in interfacial adhesion were monitored using interlaminar shear strength (ILSS) and transverse flexural strength. Interfacial bonding quality improvements were noted in both cases. Both ILSS and transverse flexural strength increased two-fold with fibre treatment. Microscopic examination of fracture surfaces showed excellent bonding after fibre treatment.

Grafting reaction of maleic anhydride onto polypropylene by reactive processing involves reacting the polymer melt with maleic anhydride, in the presence of organic peroxides. Investigations regarding such reactions have been carried out in equipments like torque rheometers, single screw extruders and in twin screw extruders [132-141]. Y.Li *et al.* reported that the addition of styrene as comonomer to the melt grafting system of maleic anhydride onto polypropylene could greatly improve the graft degree of maleic anhydride [141-145].

1.6.3 Short fibre length

When the fibres are of finite length, stress is assumed to be transferred from the matrix to the fibre by a shear transfer mechanism. For a given fibre, there is a minimum fibre length required to build up the shear stress between fibre and resin to the value of tensile fracture stress of the fibre. Over or equal to this length, the maximum value of the load transfer from the matrix to the fibre can occur. If the fibre length is less than this length, the matrix can not effectively grip the fibre to take the strain and the fibres will slip and be pulled out, instead of being broken under tension. The composite will then exhibit lower mechanical performance. This shortest fibre length (pull-out length) is called the critical fibre length (or the maximum value of load transfer length). This fibre length is an important system property and affects ultimately the strength and elastic modulus of composites.

1.6.4 Fibre orientation

The properties of short fibre-polymer composites are strongly dependent on the fibre orientation and/or orientation distribution. Enormous benefits would be possible, if methods could be developed for exercising tight control over the fibre orientation distribution in moldings made from short fibre polymer composites. In extruded products, the average alignment along the extrusion direction for short fibres is 10-20°, while in injection-molded products the orientation distribution is much more complicated. Several layers of different orientation may develop, depending on the mold geometry and processing conditions, but it is difficult to control. Variables affecting fibre orientation are,

- Flow area reduction/expansion ratio
- Angle of convergence
- Flow Channel diameter (relative to fibre length): wall thickness
- Barrel Temperature, matrix viscosity
- Pressure
- Plunger/ Screw speed
- Flow instabilities, flow rate
- Fibre loading
- Fibre length/ aspect ratio (L/D)
- State of fibre aggregation
- State of compaction
- Residence Time in the mould

1.6.5 Barrel residence time

There is time and temperature dependence for the rate at which thermoplastic materials will degrade. Plastics may degrade when exposed to "high" temperature for a short period of time, or degrade when exposed to "low" temperature for a long period of time. During processing, temperature settings and the amount of time, material is in the injection cylinder are important. The actual residence time may be determined experimentally, or roughly estimated from standard formula.

1.7 Prediction of composite properties by simulation

For the effective design of short-fibre reinforced polymer- based composites, computer simulation can be used. Because of highly nonlinear and complex flow characteristics of polymer and particle-contained suspensions, only numerical solutions including appropriate models are manageable. This economic technique offers a detailed understanding of the process and aids in identifying the cause of the problems.

The mechanical performance of injection moulded short-fibre reinforced thermoplastic components is anisotropic and is highly dependent on the fibre orientation and distribution. Short-fibre reinforced composites are widely used for their high strength to weight ratios and remarkably enhanced physical properties compared to pure polymer products. Compression moulding, extrusion and injection moulding are some of the processes often used. The fibres are suspended in the polymer matrix, and they orient themselves in response to the interactions among kinematics of the flow, other neighbouring fibres and mould cavity. Fibre reinforced composite typically shows anisotropic mechanical, thermal and rheological properties. Prediction of thermo-mechanical properties with given fibre orientation has been well developed to some extent. Therefore, prediction of fibre orientation during the transient mould filling is important for the prediction of such anisotropic properties of final plastic part.

1.7.1 Finite Element Analysis (FEA)

One of the most widely utilized numerical methods for solving engineering problems is finite element analysis. The basic idea behind finite element modelling is dividing a given geometry in a mesh of much smaller elements, hence the name. Each element consists of a number of nodes, which are shared with other adjacent elements. The elements also have defined properties such as modulus of elasticity, Poison's ratio, and any other physical properties that are necessary for the model. Boundary conditions such as loads and torques are added to the mesh to simulate the real world application of the geometry. The FEA program then solves for stress, strain and any other desired output using a stiffness matrix that is generated from the mesh and boundary conditions. Hence, FEA is a very useful design tool that allows initial design analysis to be done with minimal time and expense.

FEA simulation can show how solid materials (including rubber) will deform under stress, including applied forces, pressures and temperatures. Analysis that can be performed include, static stress/displacement analysis, dynamic stress/displacement analysis, transient or steady state heat transfer analysis, transient or steady-state mass diffusion analysis, steady state transport analysis, coupled thermo-mechanical and coupled thermo-electrical analysis, flow inside mould etc.

1.8 Objectives and scope of the work

In the automotive industry, polymers have made a major inroad in the past decades to make parts such as body panels, underbody structures and dashboards, seating components, front ends and bumpers. At present polypropylene (PP) is used for a large number of such kind of applications. It is cheap, can be reprocessed several times without significant loss of properties and can be easily modified to achieve specific requirements. In order to compete with standard engineering plastics such as polyamides, in terms of the high demands on stiffness and strength, PP has to be reinforced and glass fibre is the major reinforcing agent used for this purpose. Although both PP and glass are recyclable, when combined they are not that easy to recycle, neither in mechanical recycling nor in the end-of-life, viz. thermal recycling (incineration). Current trends toward environmentally friendly composite systems focus on the use of natural fibres like flax and hemp as alternatives for glass fibres. Although these fibres do have some ecological advantages over glass fibres since they are renewable and can be incinerated, natural fibres do not have advantages with respect to mechanical recycling. In fact, next to mechanical degradation, the relatively poor thermal stability of these ligno-cellulose fibres may lead to severe additional thermal degradation during subsequent recycling or reprocessing steps. Especially in the case of a polymer like PP, which has the lowest environmental impact of all polymers because of its excellent recyclability, the addition of natural fibres may significantly lower its eco-performance. Hence it is proposed to reinforce standard plastics like PP and HDPE with polymeric fibres to generate a new class of recyclable polymer composite.

The specific objectives of the work are,

- Generate recyclable PP and HDPE composites by reinforcing them with short nylon fibres.
- Investigate methods for enhancing the properties of the composite by improving the fibre-matrix interaction.
- Characterise the composites using mechanical (both static and dynamic), thermal and rheological measurements.
- Suggest methods for obtaining the optimum properties of these composite by simulation technique.
- Evaluate the recyclability of the composites.
- Use process-waste nylon fibres for reinforcement.

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Chapter 2

Materials and Methods

Chapter 2

Materials and Methods

2.1 Polymers

Polypropylene homopolymer (PP) (REPOL H200MA), with a melt flow index of 20g/10min, was supplied by Reliance Industries Limited. High Density Polyethylene (HDPE) (HD50MA 180), with a melt flow index of 18g/10min was supplied by Haldia Petrochemicals. Nylon-6 fibres of diametre 0.3 mm (Style 1680/2 N6 and cord denier of 3771) obtained from Apollo Tyres. Process-waste polyamide (nylon 6) fibres of diameter 0.25 mm (17860 ts/kg, Breaking strength 3.27 kg) and 0.5 mm (4470 mts/kg, Breaking strength 12.25 kg), were both obtained from Covema Industries, CSEZ, Kochi.

2.2 Chemicals

Dicumyl peroxide (DCP - 40% active) was used as the initiator. Styrene and maleic anhydride was supplied by Aldrich. Styrene maleic anhydride (SMA) -grafted PP and styrene maleic anhydride (SMA) -grafted HDPE was prepared as per US patent, 4,753,997.

2.3 Composite Preparation

PP or HDPE granules and nylon fibres were dried by keeping them in an oven at a temperature of 100 °C for four hours. Nylon fibre reinforced PP or HDPE composites were prepared by adding nylon fibres to PP or HDPE melt in a Thermo Haake Rheocord600 mixing chamber with a volumetric capacity of 69 cm^3 fitted with roller type rotors. PP or HDPE together with the nylon fibres was added to the chamber. The temperature was kept at 170 °C which ensured proper melting of PP or HDPE keeping the nylon fibres intact. In the first series, 10, 20 and 30-wt% of nylon reinforced PP or HDPE composites were prepared. In the second series styrene maleic anhydride-grafted PP/HDPE was used. A mixing time of 8 minutes was given at a counter rotating rotor speed of 40 rpm. In all cases the torque stabilized to a constant value in this mixing time. The hot mix from the mixing chamber was immediately passed through a laboratory size two-roll mill and the resulting sheets are cut to small pieces and the test specimens were prepared using a semi-automatic plunger type injection-moulding machine, with a barrel temperature of 190 °C, again ensuring that the polyamide fibres were not melted.

2.4 Mechanical properties

2.4.1 Tensile properties

The tensile properties of the samples were determined using dumb-bell shaped specimens with a Universal Testing Machine (Shimadzu AG1) at a crosshead speed of 50 mm/min according to ASTM-D-638. The length between the jaws at the start of each test was fixed to 40 mm and at least six concordant measurements are taken to represent each data point.

2.4.2 Flexural properties

Flexural property of the composites were measured by three-point loading system using universal testing machine according to ASTM-D-790. The flexural properties were determined using rectangular shaped samples at a crosshead speed of 5 mm/min. Flexural strength is given by

$$S = {}^{3PL}\!/_{2bd^2}$$

Where S= flexural strength, P= maximum load at the moment of break, b= width of the specimen, L= length of the span and d= the thickness of the specimen.

The maximum strain (r) in the outer fibres is given by

$$r = {}^{6Dd}\!/_{L^2}$$

Where, D is the deflection. The flexural modulus is calculated from the slope of initial portion of the flexural stress-strain curve.

2.5 Thermal behaviour

2.5.1 Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) is used to investigate thermal stability. TGA Q 50 (TA Instruments) was used at a heating rate of 10 °C/min from room temperature to 600 °C with 10-12 g of sample, in a nitrogen atmosphere.

2.5.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry DSC Q 100 (TA Instruments) was employed to study the crystallization characteristics of the composites. Indium was used for temperature calibration (T_m= 156.6 °C, ΔH_m = 28.4 J/g). All the samples were dried prior to the measurements and analyses were done in a nitrogen atmosphere using standard aluminum pans. Calorimetric measurements were done while the samples (4-5 mg) were exposed to the following temperature scans: heating at a rate of 20 °C/min to 250 °C, holding for 5 min to erase thermal history effects and then cooling to 50 °C at different cooling rates during which the peak of crystallization exotherm was taken as the crystallization temperature, T_c.

2.5.3 Dynamic Mechanical Analysis (DMA)

The storage modulus and mechanical damping (tan δ) were measured using fixed dynamic analysis techniques. A dynamic mechanical analyser (Q 800, TA Instruments) was made use of for this purpose. Rectangular specimens of 35 mm length, 4 mm breadth and 2 mm thickness were used. DMA tests were conducted at a constant frequency of 1 Hz. A temperature ramp was run from 30 °C to 150 °C at 3 °C/ min to get an overview of the thermo mechanical behaviour of the incorporation of fibres in to the matrix.

2.6 Melt rheology

2.6.1 Melt flow measurements

The melt rheological measurements were carried out using Shimadzu (model AG1) capillary rheometer (50kN) at different plunger speeds from 1-500 mm/min. The capillary used was made of tungsten carbide with a length to diameter (L/D) ratio of 40 at an angle of entry 90°. The sample for testing was loaded inside the barrel of the extrusion assembly and forced down the capillary using a plunger. After giving a residence time of 5 min the melt was extruded through the capillary at 6 predetermined plunger speeds. The initial position of the plunger was kept constant in all experiments and shear viscosities at different shear rates were obtained from a single charge of the material. The measurements were carried out at two different temperatures viz. 180 and 220 °C.

Shear stress was calculated as

$$\tau_w = {}^{PR}\!/_{2l}$$

Where τ_w is the shear stress of the wall, P is the pressure drop, L is the length of the capillary and R is the radius of the capillary.

Shear rate at the wall was calculated using the equation

$$\dot{\gamma}_w = {}^{32Q}\!/_{\pi d^3}$$

where $\dot{\gamma}_w$ is the shear rate , Q is the volumetric flow rate ($mm^3\ s^{-1}$), d_c is the diameter of the capillary (mm).

Viscosity was calculated using the equation

$$\eta = \frac{\tau_w}{\dot{\gamma}_w}$$

2.6.2 Rheological measurements using Haake rheocord

The rheological measurements were also made on Haake torque rheometer since it represents a real processing equipment. The rheological interpretation of the measurements was based on the analysis of Blyler and Daane. Goodrich and Porter considered the torque rheometer measuring head as two adjacent rotational viscometers with irregular concentric cylinders. They succeeded in converting torque rheometer data into fundamental rheological units for materials that exhibit Newtonian viscosity. Blyler and Daane extended this work to materials with non-Newtonian and derived the equation,

$$M = C_{(n)} K S^{n}$$

where M is the torque, K and n are parameters of the famous power law equation,

$$\tau = K \gamma^{n}$$

(The parameter K depends on temperature and often has an Arrhenius type dependence ascribed to it such that,

$$K = K_{0} e^{\Delta E / RT}$$

ΔE is the flow activation energy. R is the gas constant & K_0 is a coefficient), S is the rpm and C(n) a characteristic constant which is determinable but depends implicitly upon other constants.

Lee and Purdon in their work on rheological measurements derived an equation identical in form to that derived by Blyler and Daane. However, the constant C (n) was related to the two instrumental constants, which are experimentally determinable. Hence the rheocord torque and rotor speed can be separately related to some average shear stress and rate of shear, respectively of the polymer melt in the rheocord measuring head. That is rheocord data can now be represented by this universal viscosity unit, the poise, as with other viscometers for both Newtonian and non- Newtonian materials.

The results of Blyler and Daane has the following implications:

- The slope of the log M Vs log S plot at constant temperature obtained for a polymer melt with the Haake should be identical to the slope of the log τ - log γ curve at constant temperature obtained from capillary rheometer. Consequently the power law index may be obtained from Haake data.
- Since C(n) in the above equation is independent of temperature the flow activation energy obtained from Haake and capillary data should be identical.
- The Haake can be calibrated by using melts of known K and n to determine C(n)
- Once the value of C(n) is known, this can be used to characterise a polymer.

2.7 Die swell measurements

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24h of extrusion using a traveling microscope. The die swell ratio was calculated using the relation,

$$\text{Die swell ratio} = \frac{\text{Diameter of the extrudate } (d_e)}{\text{Diameter of the capillary } (d_c)}$$

2.8 Energy required for processing

The energy required to plasticise a polymer for a period of time at a given temperature can be calculated from the area under the torque-time curve at a preset temperature for the specified period of time. The energy W was calculated using the formula at a given temperature and shear rate.

$$w = 2\pi n \int_{t_1}^{t_2} M \, . dt$$

where, n is the number of revolutions of the rotor per min, t_1 is the initial time, t_2 is the final time and M the torque in Nm.

2.9 Morphological studies- Scanning Electron Microscopy

Scanning electron microscope (Cambridge Instruments, S 360 Stereoscanner-version V02-01, England) was used to investigate the morphology of the fractured surfaces. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film. The SEM observations reported in the present study were made on the fracture surfaces of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an E-101 ion- sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was used for SEM analyses.

2.10 Characterization of grafted PP and HDPE-IR Spectroscopy

Fourier transform infrared spectra (FTIR) are generated by the absorption of electromagnetic radiation in the frequency range of 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at charecteristic frequencies. The frequency and intensity of absorption are the indication of the bond strengths and structural geometry in the molecule. FTIR analyses were used to analyse the changes in the structure of the PP and HDPE and taken in Bruker IR spectroscope (Tensor- 27).

2.11 Simulation of recyclable short nylon fibre reinforced PP composites

Moldflow is a finite element analysis based software technique for simulation of flow and many other properties of plastics and composites. Eminently suited for the injection molding processes, the Moldflow helps to predict a number of process parameters that help to minimize the trial and error prevalent in the conventional cut-and-try approach. Making use of the common flow properties of the material and the part geometry from a part modeling and data translation Software, this program simulates the flow of the melt in the mold, during its injection, fill, pack and hold phase.

Chapter 3

Mechanical Properties of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. Mechanical properties of recyclable short nylon fibre reinforced polypropylene composites

Part B. Mechanical properties of recyclable short nylon fibre reinforced high density polyethylene composites

Chapter 3

Mechanical Properties of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. Mechanical properties of recyclable short nylon fibre reinforced polypropylene composites

3a.1 Introduction

Throughout the history of human civilization, man has sought better and better materials to meet his diverse needs. Combining two or more materials to form composites has been one of the methods investigated for this end from very early time. Reinforcing mud with straw recorded in the Bible is perhaps the earliest reference to composites. Hence, the desire to combine materials to effectively upgrade their performance is not a new idea. Today, with strong competition among the various engineering materials cost-effective materials are being continuously developed and expanded. As the technology becomes more and more sophisticated the materials used also have to be much more efficient and reliable. Materials should be light in weight and should possess good strength and modulus. The use of composites has been growing steadily since their introduction in the 1980s due to their attractive properties like durability, easy mouldability, light weight, noncorrosiveness, adequate strength, stiffness and load bearing qualities. Thermoplastic-based composites have received more attention these days due to their easier processing compared to their thermoset counterparts.

Polypropylene is a very versatile polymer. It has many properties that make it the polymer of choice for various applications. There are many ways in which the mechanical properties of polypropylene can be modified to suit a wide variety of end-use applications [1-4]. Various fillers and reinforcements, such as glass fibre, mica, talc and calcium carbonate are typical ingredients that are added to polypropylene resin to attain cost-effective composite mechanical properties. Fibrous materials tend to increase both mechanical and thermal properties, such as tensile strength, flexural strength, flexural modulus, thermal stability etc. Fillers such as talc and calcium carbonate are often used as extenders to produce a less-costly material [5-12].

Nylon is one of the most important industrial fibres due to its high performance, low cost, and recyclability. As outlined earlier, recyclable composites were prepared by reinforcing PP with nylon fibre. The salient features of the study are given below.

3a.2 Experimental

Short nylon fibre reinforced polypropylene composites were prepared in a Torque Rheometer (Thermo Haake Rheocord600). The variation of torque with time of mixing was monitored. The matrix was modified with styrene and maleic anhydride according to US patent, 4,753,997. Dumbbell and rectangular shaped sample were prepared by injection moulding in a semiautomatic laboratory injection moulding machine. The tensile properties of the samples were determined using dumb-bell shaped samples on a universal testing machine (Shimadzu) at a crosshead speed of 50 mm/min according to ASTM-D-638. Flexural properties of the composite were measured by three-point loading system using the universal testing machine according to ASTM-D-790. The morphology of the tensile fractured surface were investigated using scanning electron microscope (SEM).

3a.3 Results and Discussion

3a.3.1 Torque studies

The variation of mixing torque with time of mixing at different fibre loading is shown in Figure 3a.1. A mixing time of 8 minutes was fixed since the torque stabilised to a constant value during this time in all cases. The temperature of the mixing chamber was fixed as 170 °C. The stabilization of the torque may be related to the attainment of a stable structure after a good level of mixing. The initial and final torque values increase with increase in fibre loading. This shows that nylon fibre remains in fibre form and behaves as a fibrous filler under the given conditions.

Initially torque increases with the charging of PP, but decreases with melting. After homogenisation of PP, nylon fibres were added. Then the torque rises again and levels off in about 5 min. Also, it is clear from the figure that there is no change in torque on continued mixing up to 8 min. This may indicate that there is no degradation taking place during the mixing stage.

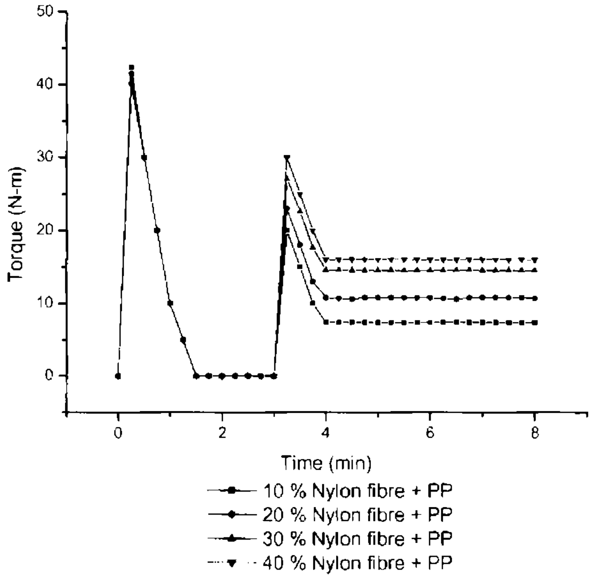


Figure 3a.1 Torque-Time curves of PP composites

a) Effect of fibre length

To study the effect of fibre length on the tensile strength of the present system 10 % nylon fibre filled polypropylene composite were prepared with different average fibre length of 5,10,15, 20 and 25 mm. When the fibres are of finite length, stress is assumed to be transferred from the matrix to the fibre by a shear transfer mechanism. For a given fibre, there is a minimum fibre length required to build up the shear stress between fibre and resin to the value of tensile fracture stress of the fibre. Over or equal to this length, the maximum value of the load transfer from the matrix to the fibre can occur. If the fibre length is less than this length, the matrix cannot effectively grip the fibre to take the strain and the fibres will slip and be pulled out, instead of being broken under tension. The composite will then exhibit lower mechanical performance. This shortest fibre length (pull-out length) is called the critical fibre length (or the maximum value of load transfer length). This fibre length is an important system property and affects ultimately the strength and elastic modulus of composites.

The tensile strength of the composites (Figure 3a.2) is maximum at 10 mm length. Hence 10 mm length was taken as optimum fibre length for further studies.

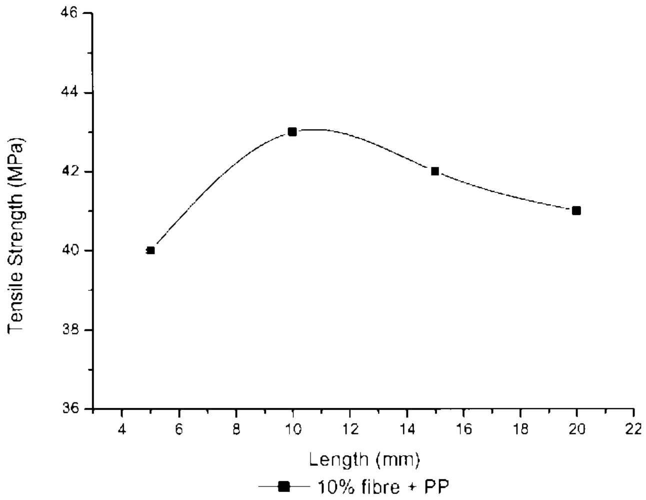


Figure 3a.2 Variation of Tensile strength with fibre length

b) Effect of fibre diameter

Nylon fibres of three different diameters 0.03 mm (A fibre), 0.25 mm (B fibre) and 0.52 mm (C fibre) were used so as to study the effect of the fibre diameter on the tensile properties of the composite.

Figures 3a.3 & 3a.4 show the variation in tensile strength and tensile modulus of the nylon fibre/PP composites with fibre content, for A, B and C fibres. The A fibre composites show highest tensile strength and modulus. This may be probably due to the more efficient load transfer from the matrix to the fibres due to the larger surface area and the higher strength of the thin fibre. Hence nylon A fibre having least diameter was used for further studies on nylon fibre/PP composites.

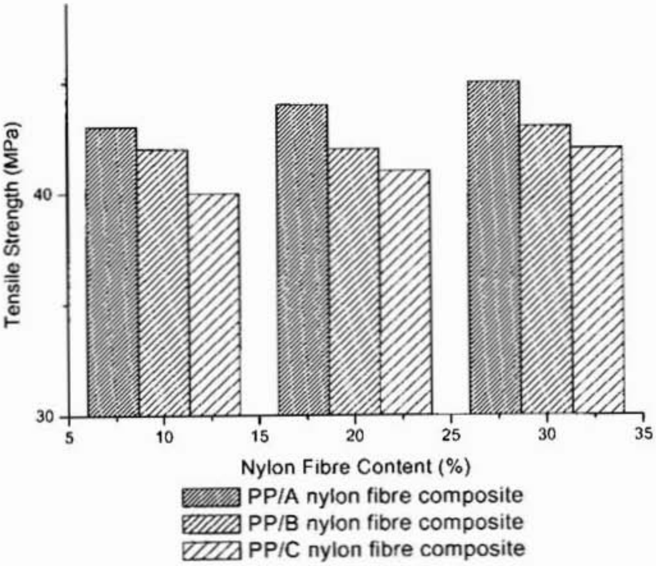


Figure 3a.3 Variation of Tensile strength with fibre diameter

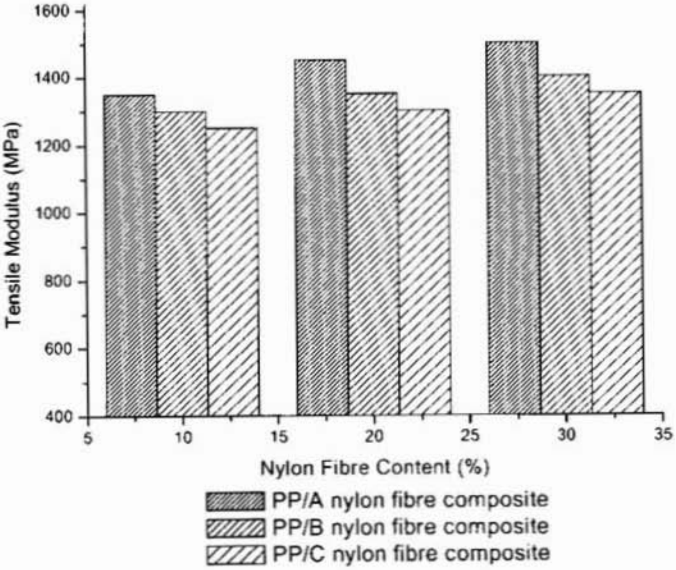


Figure 3a.4 Variation of Tensile modulus with fibre diameter

Scanning electron micrographs of the tensile fractured surfaces of Nylon fibre (A,B & C) /PP shown in Figures 3a.5, 3a.6 & 3a.7 respectively.

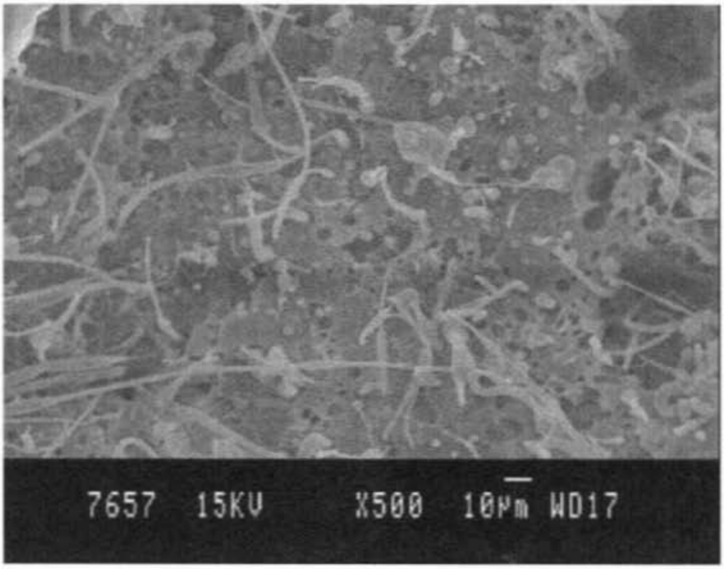


Figure 3a.5 Scanning electron micrograph of tensile fractured surface of Nylon A fibre/PP composite

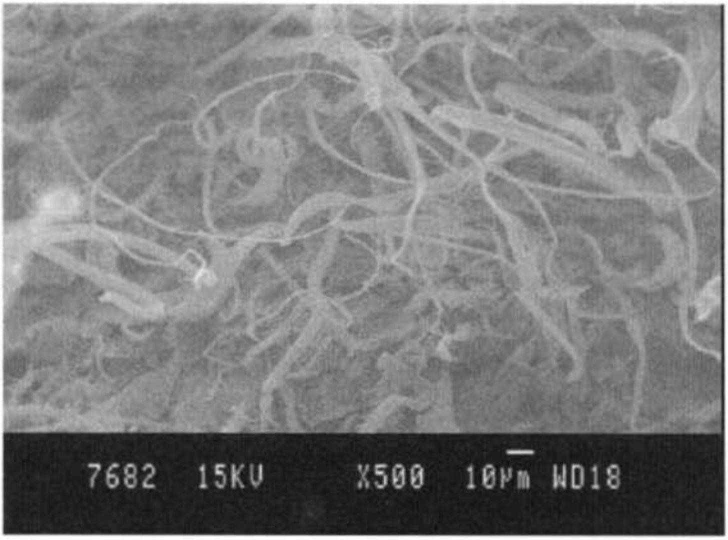


Figure 3a.6 Scanning electron micrograph of tensile fractured surface of Nylon B fibre/PP composite

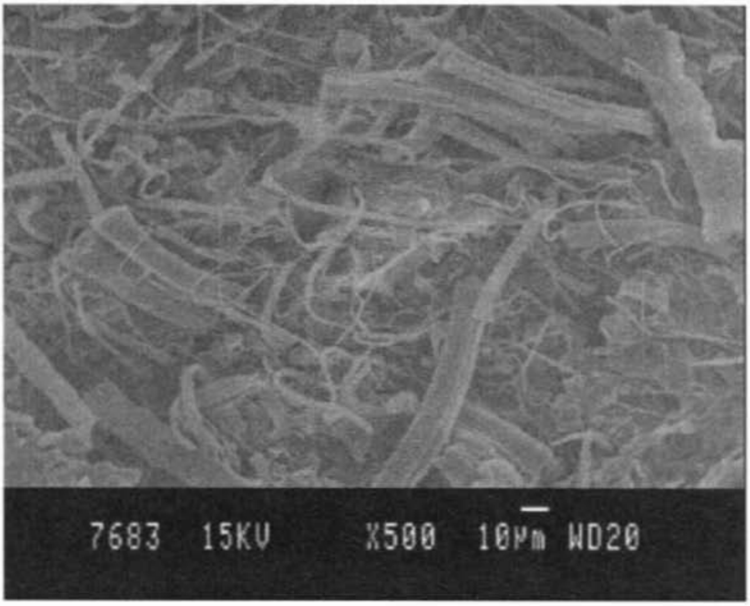


Figure 3a.7 Scanning electron micrograph of tensile fractured surface of Nylon C fibre /PP composite

c) Effect of fibre loading and orientation

Figures 3a.8 & 3a.9 show the variation of tensile strength and tensile modulus respectively of the A nylon Fibre/PP composites with fibre loading. The tensile strength increases with fibre loading up to 30 % but decreases thereafter. The decrease in strength at higher loading is probably due to crowding of fibres, which prevents efficient matrix-fibre stress transfer.

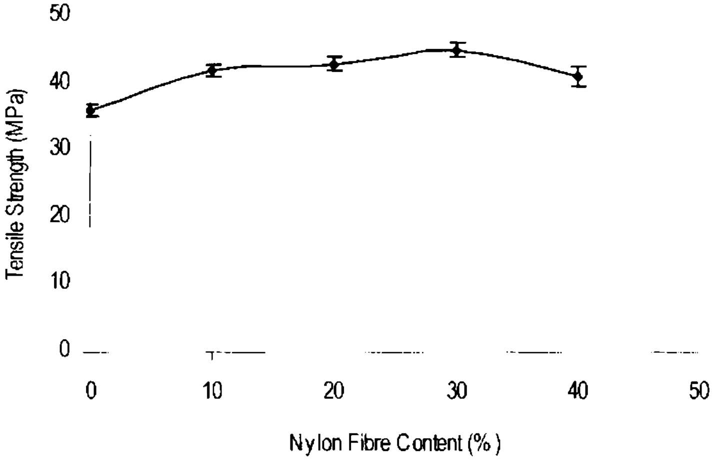


Figure 3a.8 Variation of Tensile strength with fibre loading

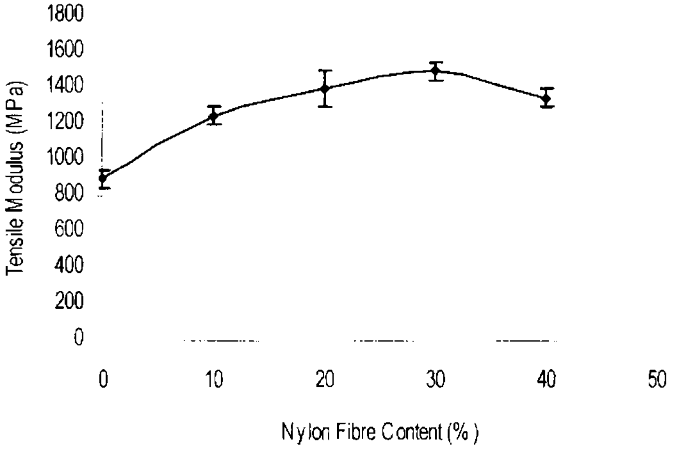


Figure 3a.9 Variation of Tensile modulus with fibre loading

3a.3.3 Flexural properties of short nylon fibre reinforced polypropylene composites

a) Effect of fibre length

The effect of fibre length on the flexural strength is given in Figure 3a.10. Flexural strength increases with increase in fibre length up to 10mm and thereafter decreases as in the case of the tensile strength. This points to a critical fibre length of about 10 mm both in the case of tensile and flexural loads.

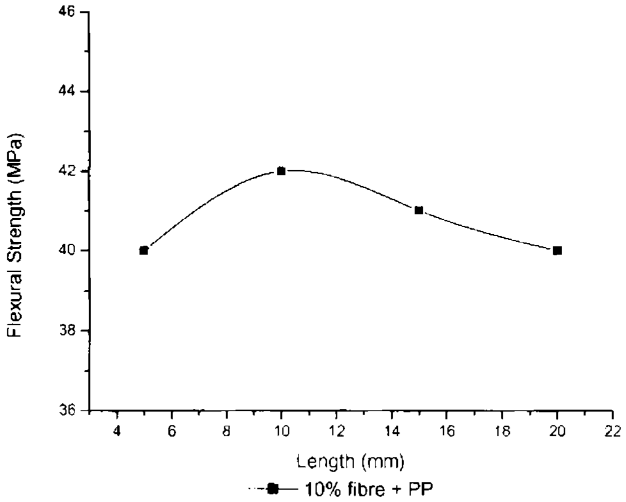


Figure 3a.10 Variation of flexural strength with fibre length

b) Effect of fibre diameter

Nylon fibres of three different diameters 0.03 mm (A fibre), 0.25 mm (B fibre) and 0.52 mm (C fibre) were used so as to study the effect of fibre diameter on the flexural properties of the composite. The variation in the flexural strength and flexural modulus of the composites with fibre diameter is shown in Figures 3a.11 & 3a.12 respectively. In this case also the nylon A fibre composites are superior to nylon B and C fibre composites. Hence further studies in nylon fibre/PP composites were done using nylon A fibre.

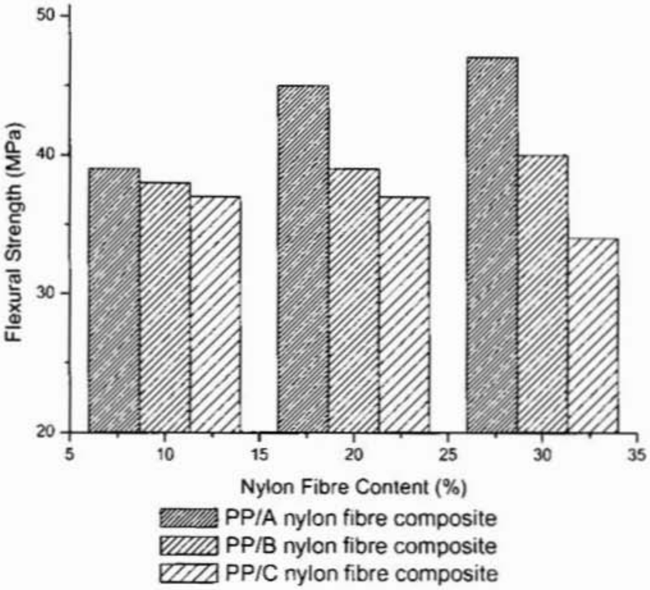


Figure 3a.11 Variation of flexural strength with fibre diameter

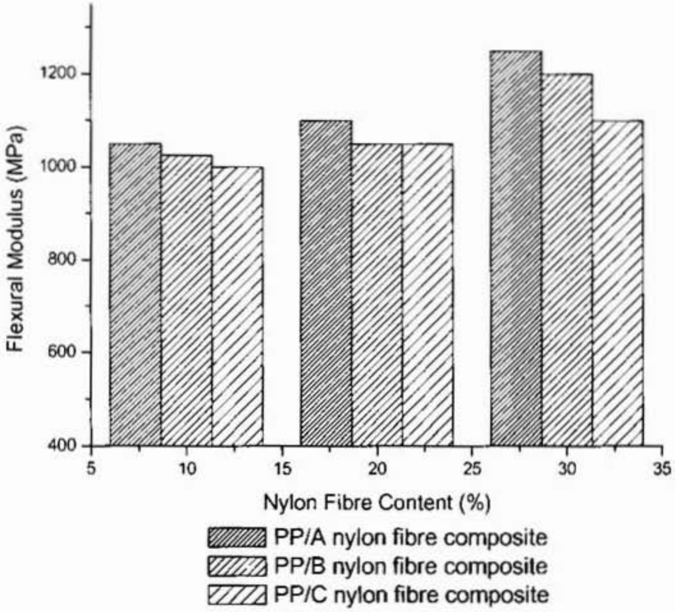


Figure 3a.12 Variation of flexural modulus with fibre diameter

c) Effect of fibre loading and orientation

Figures 3a.13 & 3a.14 show the effect of fibre loading on the flexural strength and flexural modulus of nylon fibre/PP composite. From the figures it is clear that both flexural strength and modulus increase with fibre content. The maximum modulus is observed at 30 % fibre loading.

The loading in flexure in an ideal case causes normal stresses in the direction of fibres and shear stresses in the plane perpendicular to the loading nose. The mode of failure of unidirectional composites in flexure is very complex. Unidirectional composites, when stressed in flexure can fail in tension either longitudinally or transversely, or in shear at the matrix, matrix/fibre interface or fibre. The most common modes of failure are transverse splitting, brittle tensile failure with fibre pullout, interfacial shear failure, compressive failure due to micro buckling or localized kinking of fibres and intra-laminar shear failure. When the span/ thickness l/d ratio is less than 25, the failure occurrs by fibre buckling localized in very narrow bands (kink bands). When loaded, either in flexure or in compression, some relief of local stresses accompanies the micro processes as the crack propagates from compressive side to the neutral plane. Further deflection of the beam causes a tensile failure of fibres on the tensile side of the beam, which leads to catastrophic failure of the specimen. In some cases, some amounts of inter laminar shear failure, initiated from the kink bands, are observed on the compressive side. Constraints imposed on the beam by contact with load pin may also inhibit the initiation of bukling in flexural testing.

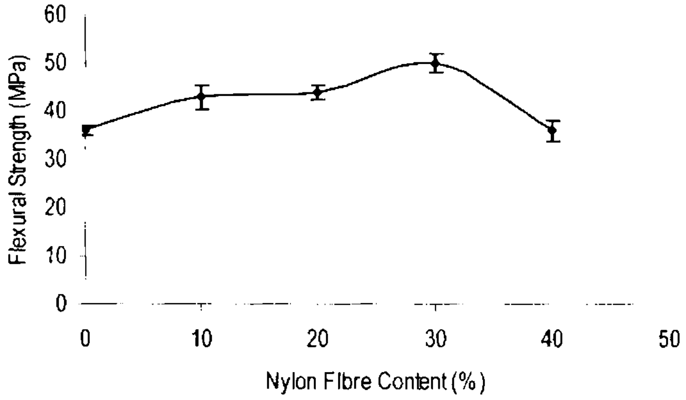


Figure 3a.13 Variation of flexural strength with fibre loading

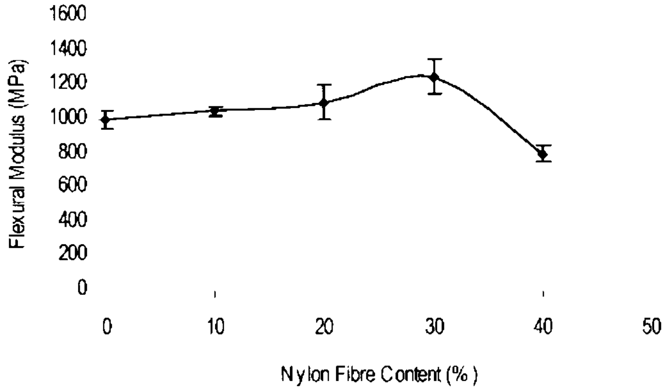


Figure 3a.14 Variation of flexural modulus with fibre loading

3a.4 Effect of matrix modification on the mechanical properties of nylon fibre reinforced polypropylene

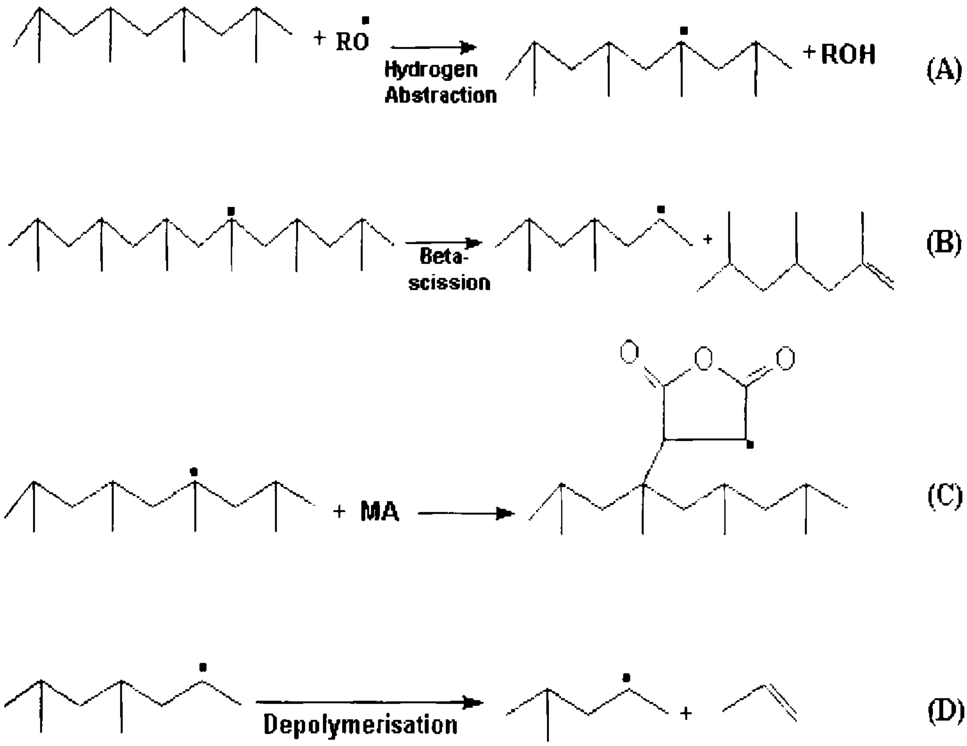
Most fillers and reinforcements used are polar in nature. Polypropylene on the other hand is nonpolar. Poor adhesion between the filler surface and the polymer matrix prevents necessary wetout by molten polymer to break up clumps or aggregates of filler particles. This shortcoming leads to poor dispersion and insufficient reinforcement with accompanying poor mechanical properties. There are a number of things that can be done to overcome these problems. If the matrix is polar and the filler nonpolar, the filler may be modified for better interaction with the matrix or vice versa.

An uncompatibilised blend of nylon and PP has similar mechanical properties to those of PP alone due to poor fibre matrix adhesion. On the other hand, a compatibilised blend of the same constituents (using either maleic anhydride or styrene maleic anhydride copolymer grafted PP) leads to a strong matrix interface adhesion resulting in average mechanical behaviour. A similar approach may be employed for improving the fibre/matrix interface in nylon fibre/PP composite. The fibre matrix interface is the critical factor that determines to what extent the potential properties of the composite will be achieved and maintained during use. Localized stresses are usually highest at or near the interface, which may be the point of premature failure of the composite. The interface must have appropriate chemical and physical features to provide the necessary load transfer from the matrix to the reinforcement.

3a.4.1 Maleic anhydride (MAH) grafted polypropylene

For polypropylene, it is accepted that the free radical produced by peroxide decomposition attacks the tertiary hydrogen atom (pathway A). The resulting polymer radical causes beta scission and polymer molecular weight reduction, as shown in pathway B. If there is an unsaturated monomer present to react with the polymer radical, grafting may occur before chain scission, as shown in pathway C. This will result in a functional group attached pendant to the polymer backbone.

If grafting does not occur depolymerisation may occur (pathway D) which results in



Scheme 3a.1 Mechanism of reaction between Maleated PP and Nylon in presence of dicumyl peroxide

In the FTIR spectrum of PP-g-MAH, new absorption bands at 1781 and 1857 cm^{-1} were observed, which can be assigned to the absorption of the carbonyl groups of cyclic anhydride [17-18]. (Figure 3a.15, 3a.16 & 3a.17)

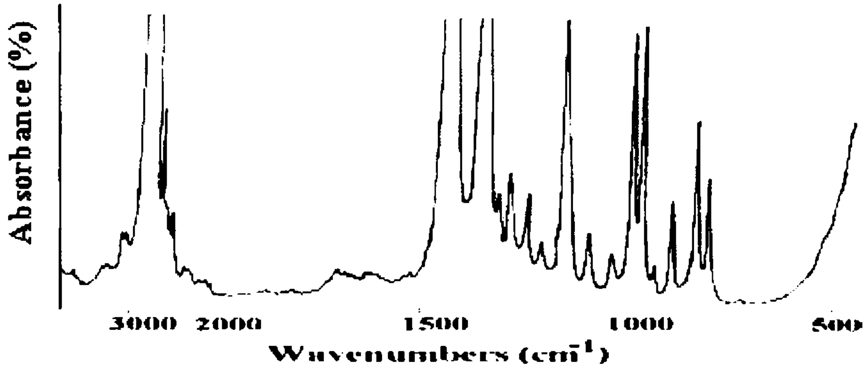


Figure 3a.15 FTIR spectrum of PP

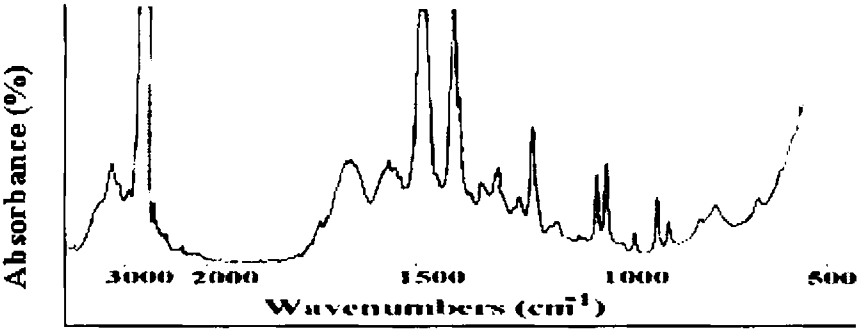


Figure 3a.16 FTIR spectrum of Nylon/PP composite

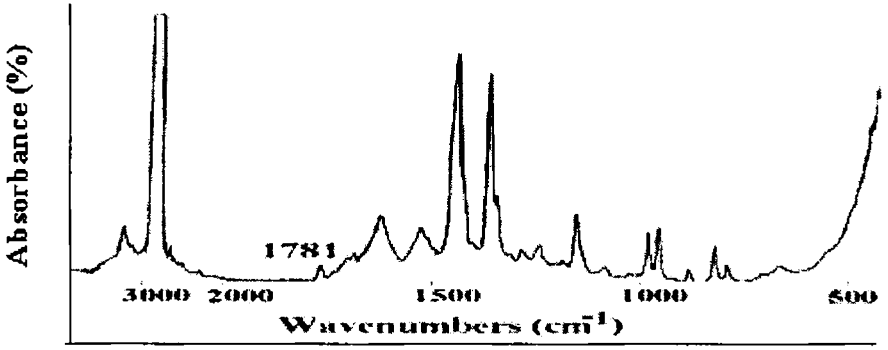
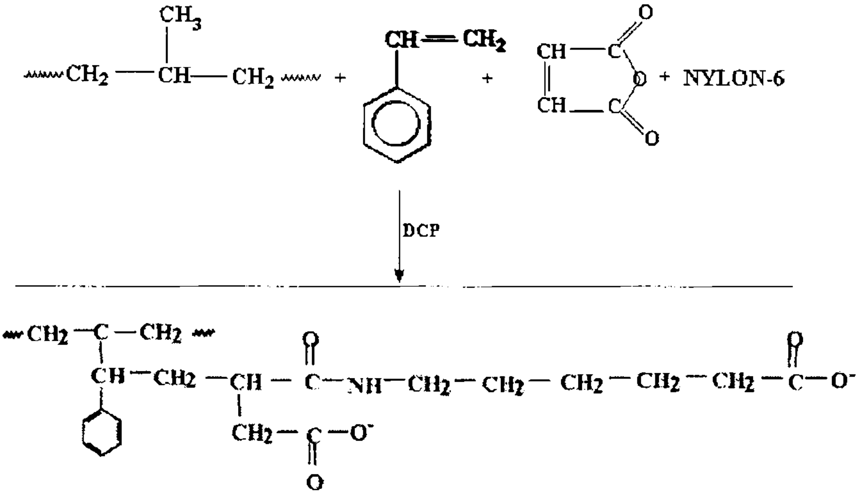


Figure 3a.17 FTIR spectrum of Nylon/MAH-g-PP composite

3a.4.2 Styrene maleic anhydride grafted polypropylene

The melt free-radical grafting process starts with the formation of macroradicals along the PP chain by a hydrogen abstraction. These PP chain macroradicals and PP chain end macroradiacls produced by β-scission can both take part in grafting reaction [19-22].



Scheme 3a.2 Mechanism of reaction between Styro maleated PP and Nylon in presence of dicumyl peroxide

For the melt free-radical grafting of MAH with PP in the absence of styrene, the degree of MAH grafting is very low because of the low reactivity of MAH towards radical reactions. Much of the MAH monomers added are grafted onto PP chain ends after PP undergoes chain scission. When styrene is added, the two monomers can copolymerize with each other under initiation of peroxide to form a chain of maleic anhydride styrene copolymer (SMA), which may then react with PP macroradicals producing branches by termination between radicals. Therefore, the degree of MAH grafting can be significantly improved in the presence of styrene.

In the FTIR spectrum of nylon fibre /SMA-g-PP, new absorption bands at 1781 and 1857 cm^{-1} were observed, which can be assigned to the absorption of the carbonyl groups of cyclic anhydride. (Figure 3a.18)

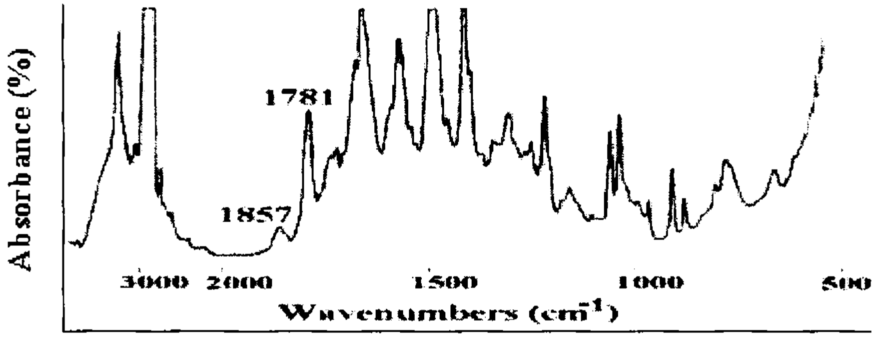


Figure 3a.18 FTIR spectrum of Nylon/SMA-g-PP composite

3.5 Results and discussion

3a.5.1 Torque Studies

The variation of mixing torque with time of mixing at different fibre loading is shown in Figure 3a.19. The mixing time of 8 minutes was fixed since the torque stabilised to a constant value during this time in all cases. The temperature of the mixing chamber was fixed as 170 °C. After grafting also the torque value is found to be steady.

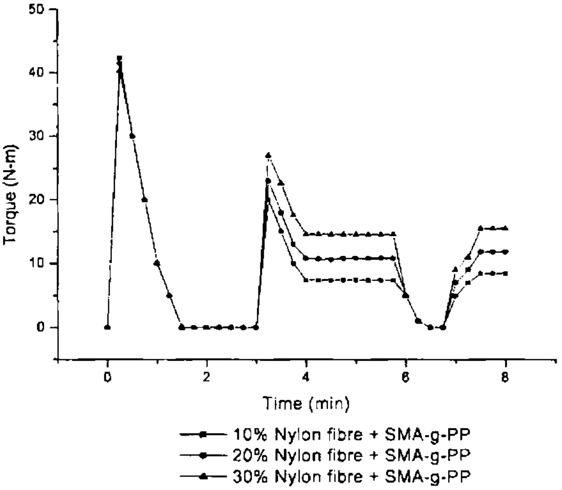


Figure 3a.19 Variation of mixing torque with time

3a.5.2 Effect of matrix modifications on tensile properties

Figure 3a.20 & 3a.21 show the effect of chemical treatment on the tensile properties of nylon fibre/PP composite [23]. From the figures, it is clear that the matrix modification improves the tensile strength of the composites due to the strong interaction between the polar group in nylon fibre and the grafted functional group in the polymer backbone. While the improvement in the case of matrix modification by maleic anhydride is only marginal, there is a significant improvement in the case of modification by maleic anhydride in the presence of styrene. This clearly shows that the degree of maleic anhydride grafting is increased in the presence of styrene. The improvement in the tensile modulus even at 10 % fibre content is particularly significant which shows that the matrix has become stronger by the modification even though this is not very pronounced at higher fibre loading due to fibre crowding.

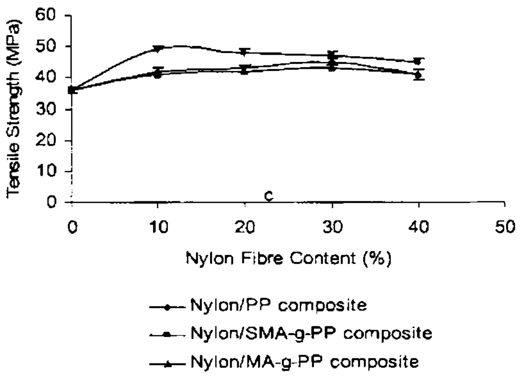


Figure 3a.20 Variation of Tensile strength with fibre

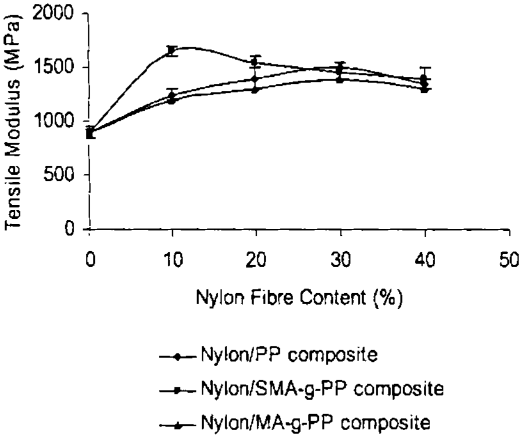


Figure 3a.21 Variation of Tensile modulus with fibre loading

The improvement in adhesion between the fibre and treated matrix can also be seen form the scanning electron micrographs of the fractured surface of nylon fibre/PP composites and that of nylon fibre/SMA-g-PP composites (Figures 3a.22 & 3a.23). The fractured surface of unmodified matrix shows holes and fibre ends indicating poor adhesion between the fibre and matrix while in the case of modified matrix, the fractured surface shows evidence for fibre breakage rather than pullout, indicating better interfacial adhesion.

4a.5.3 Effect of fibre modifications on flexural properties

The flexural properties of the nylon fibre/PP composites are compared with nylon fibre/SMA-g-PP composite in Figures 3a.24 & 3a.25. There is a significant improvement in the flexural strength and modulus with modification at all the fibre composition investigated. The maximum improvement occurs at lower fibre content. This is probably due to decrease in fibre/matrix interaction at higher fibre loadings due to crowding of fibres as discussed earlier.

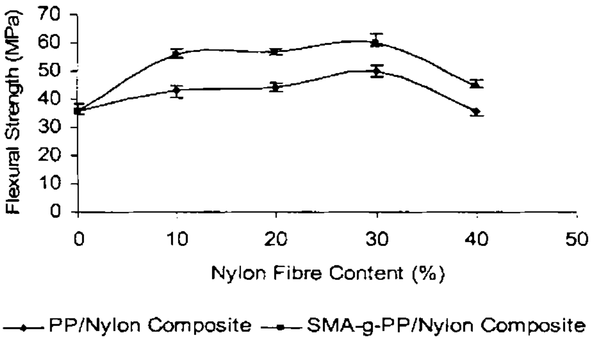


Figure 3a.24 Variation of Flexural strength with fibre loading

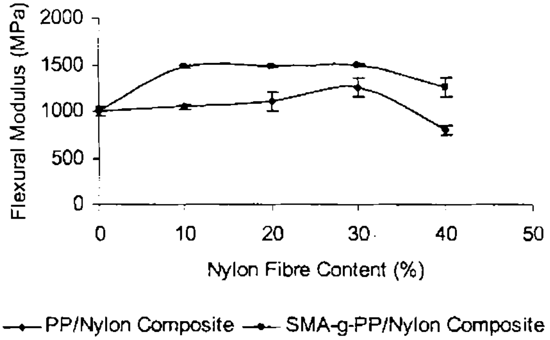


Figure 3a.25 Variation of Flexural modulus with fibre loading

Chapter 3

Mechanical Properties of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part B. Mechanical properties of recyclable short nylon fibre reinforced high density polyethylene composites

3b.1 Introduction

It is a common practice in the plastics industry to compound homopolymers with fillers and fibres to reduce cost and attain desired properties. Such polymer composites obtained can be tailored to achieve desirable property combinations. Short fibres reinforced thermoplastics have attracted a special attention in these days because of the ease in processability of the composites. Of the various thermoplastic matrices used as base material for making composites high density polyethylene (HDPE) is one of the most widely used. There are many ways in which the mechanical properties of HDPE can be modified to suit a wide variety of end use applications. Various fillers and reinforcements, such as glass fibre, mica, talc and calcium carbonate are typical ingredients that are added to HDPE to attain cost-effective composites with useful mechanical properties. Fibrous materials tend to improve both mechanical and thermal properties, such as tensile strength, flexural strength, flexural modulus, heat deflection temperature, creep resistance and impact strength. Fillers, such as talc and calcium carbonate are often used as extenders to produce less costly material. A novel class of polymer composites which are recyclable are proposed to be developed in this study by reinforcing HDPE with nylon fibre. The salient features of the study are given below.

3b.2 Experimental

The short nylon fibre reinforced high density polyethylene composites were prepared in a Torque Rheometer (Thermo Haake Rheocord 600). The torque values of the mixing were monitored. The matrix was modified with styrene and maleic anhydride according to US patent, 4,753,997. The tensile properties of the samples were determined using dumb-bell shaped samples on a universal testing machine (Shimadzu) at a crosshead speed of 50mm/min according to ASTM-D-638. Flexural properties of the composites were measured by three-point loading system using the universal testing machine according to ASTM-D-790.

3b.3 Results and discussion

3b.3.1 Torque studies

The variation of mixing torque with time of mixing at different fibre loading is shown in Figure 3b.1. A mixing time of 8 minutes was fixed since the torque stabilised to a constant value during this time in all cases. The temperature of the mixing chamber was fixed as 170 °C since the matrix properly melted and homogenised at this temperature under the shear employed. The torque-time behaviour of nylon fibre/HDPE composite is similar to that of Nylon fibre /PP composite as expected. As in the case of nylon fibre/PP composites there is no reduction in torque on continued mixing up to 8 min. This suggests that there is no appreciable degradation taking place during this time.

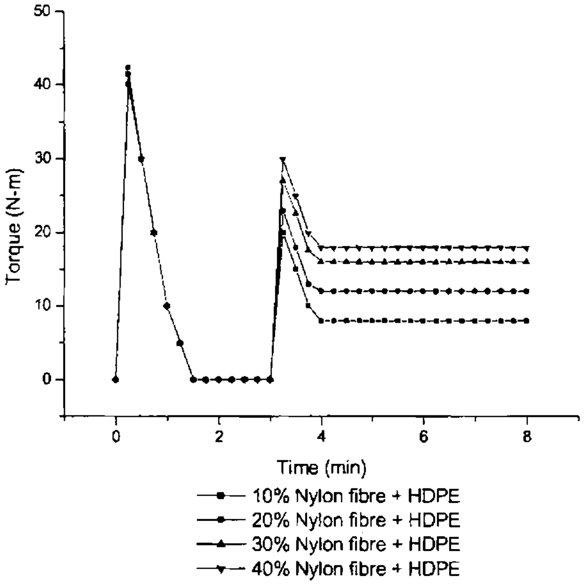


Fig 3b.1 Variation of mixing torque with time

3b.3.2 Tensile properties of nylon reinforced high density polyethylene composites

a) Effect of fibre length

To study the effect of fibre length on the tensile strength of the present system 10 % fibre filled composites were prepared with different average fibre length of 5, 10, 15, 20 and 25 mm and the tensile strengths of the composites were compared.

The variation of tensile strength of the composites with fibre length is shown in Figure 3b.2. The maximum strength is observed for the composites prepared with a fibre length of 10 mm as in the case of nylon fibre/PP composite. Hence 10 mm length was taken as optimum fibre length for further studies.

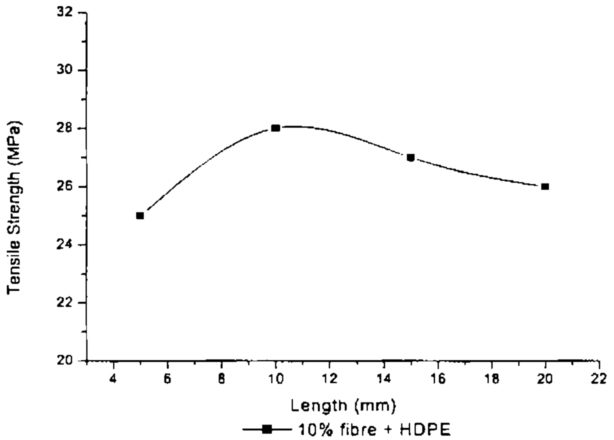


Figure 3b.2 Variation of Tensile strength with fibre length

b) Effect of fibre diameter

To study the effect of fibre diameter on composite properties, nylon fibres of three different diameters 0.03 mm (A fibre), 0.25 mm (B fibre) and 0.52 mm (C fibre) were tried as reinforcement and the tensile properties were compared.

Figures 3b.3 & 3b.4 show the variation in tensile strength and tensile modulus of the nylon fibre/HDPE composites with fibre content, for nylon A, B and C fibres. The nylon A fibre composites show higher tensile strength and modulus as in the case of nylon fibre/PP composite. Hence nylon A fibre was used for further studies on nylon fibre/HDPE composites.

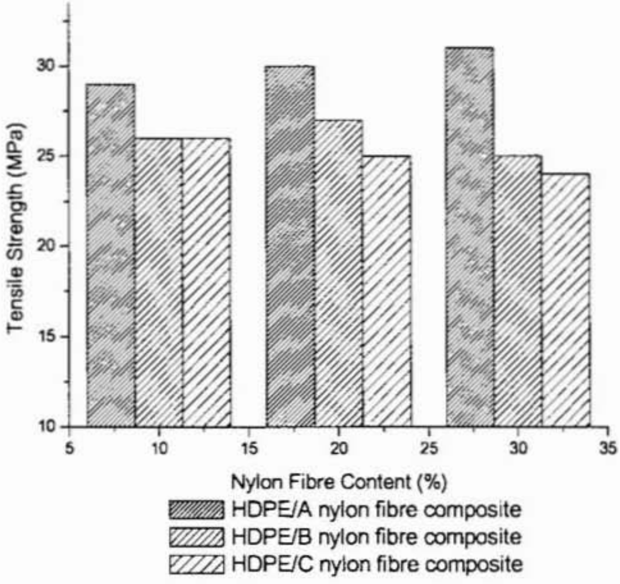


Figure 3b.3 Variation of Tensile strength with fibre diameter

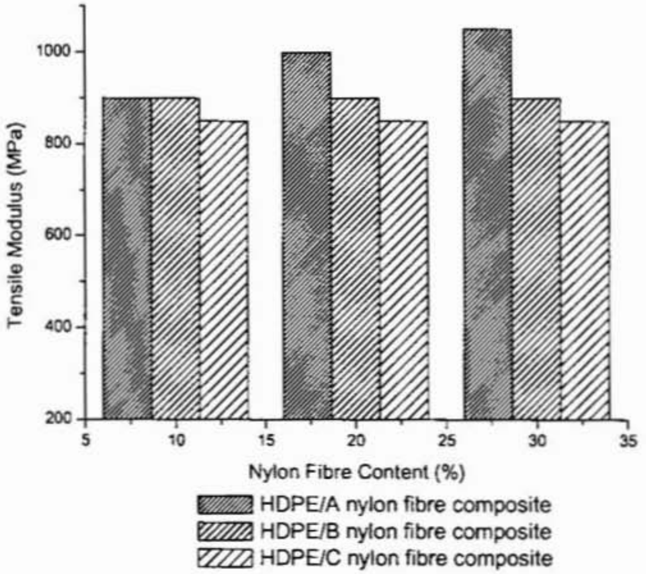


Figure 3b.4 Variation of Tensile modulus with fibre diameter

c) Effect of fibre loading and orientation

Figures 3b.5 & 3b.6 show the variation of tensile strength and tensile modulus respectively of the nylon fibre / HDPE composites with fibre loading. The tensile strength increases with fibre loading up to 30 % and decreases thereafter as in the case of A nylon fibre/ PP composite

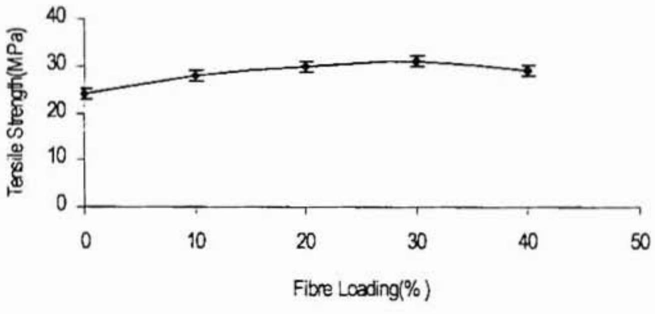


Figure 3b.5 Variation of Tensile strength with fibre loading

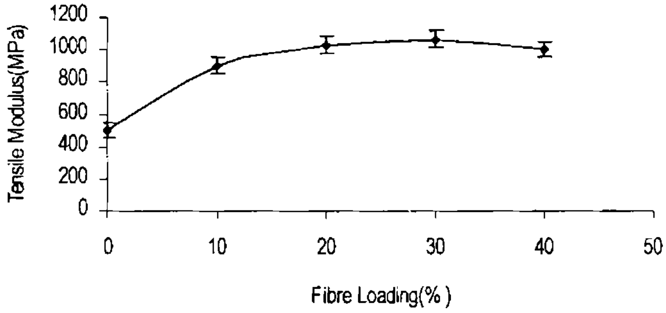


Figure 3b.6 Variation of tensile modulus with fibre loading

3b.3.3 Flexural Properties of short nylon fibre reinforced high density polyethylene composites

a) Effect of fibre length

The effect of fibre length on the flexural strength is given in Figure 3b.7. Flexural strength increases with increase in fibre length up to 10 mm and thereafter decreases. This behaviour is also in uniformity with the result obtained with nylon fibre/PP composites.

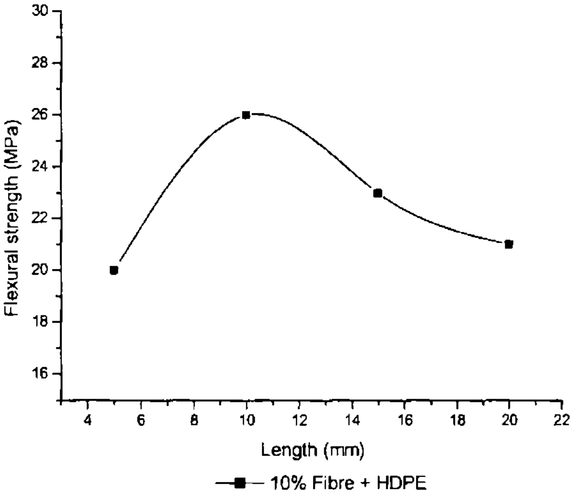


Figure 3b.6 Variation of tensile modulus with fibre loading

b) Effect of fibre diameter

The variation in the flexural strength and flexural modulus of the composites with fibre content for nylon A, B and C fibres are shown in Figures 3b.8 & 3b.9. In this case also the nylon A fibre composites are superior to nylon B and C fibre composites. Hence nylon A fibre was used for further studies.

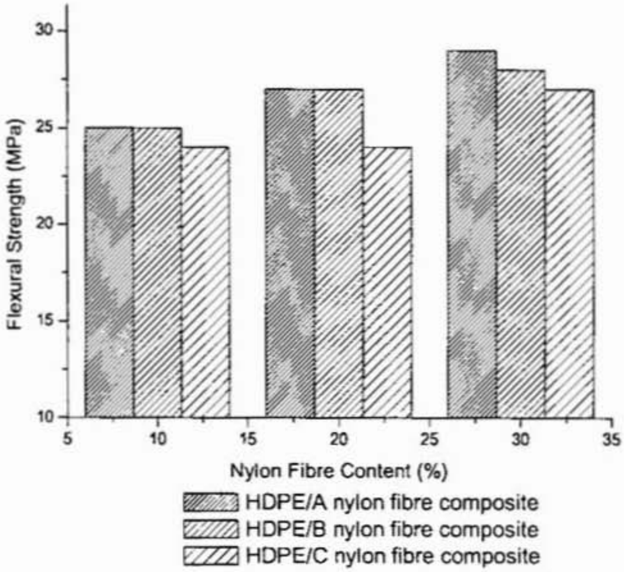


Figure 3b.8 Variation of flexural strength with fibre diameter

c) Effect of fibre loading and orientation

Figures 3b.10 & 3b.11 show the effect of fibre loading on the flexural strength and flexural modulus of nylon fibre/HDPE composite. From the figures it is clear that the flexural strength and modulus increase with fibre content. The maximum modulus was observed at 30 % fibre loading as in the case of the nylon fibre/PP composite.

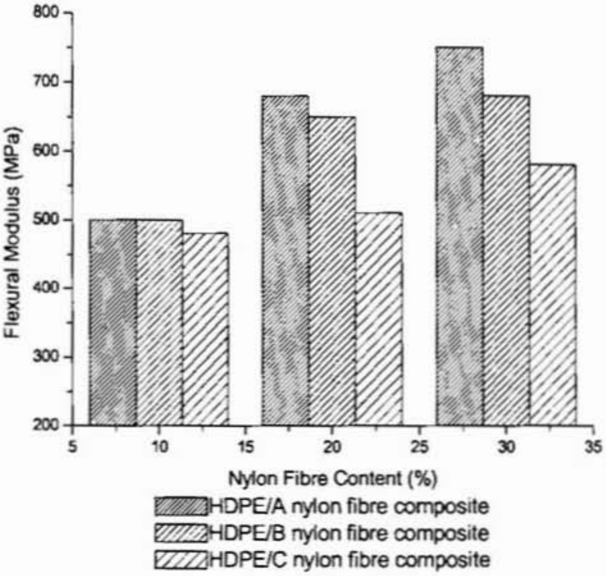


Figure 3b.9 Variation of flexural modulus with fibre diameter

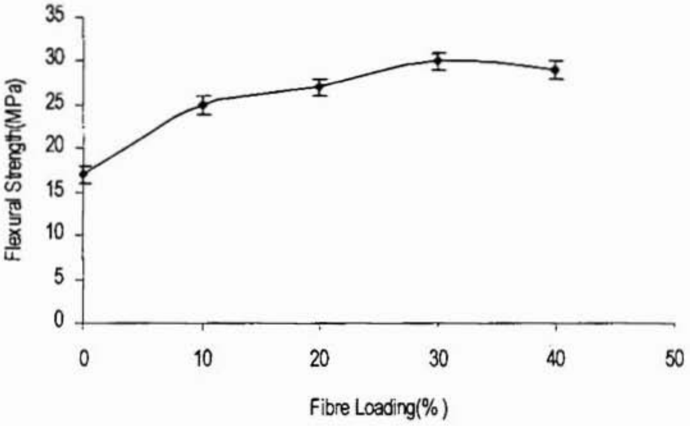


Figure 3b.10 Variation of flexural strength with fibre loading

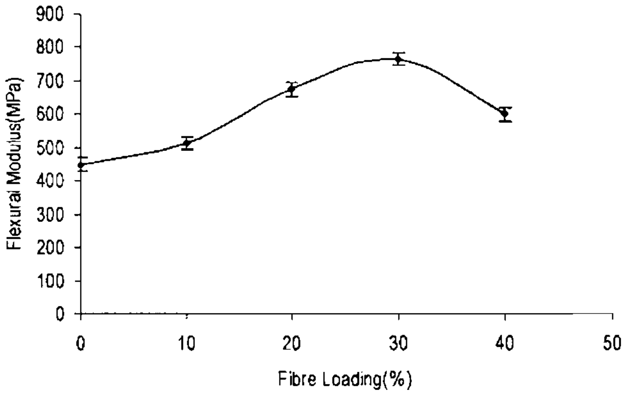


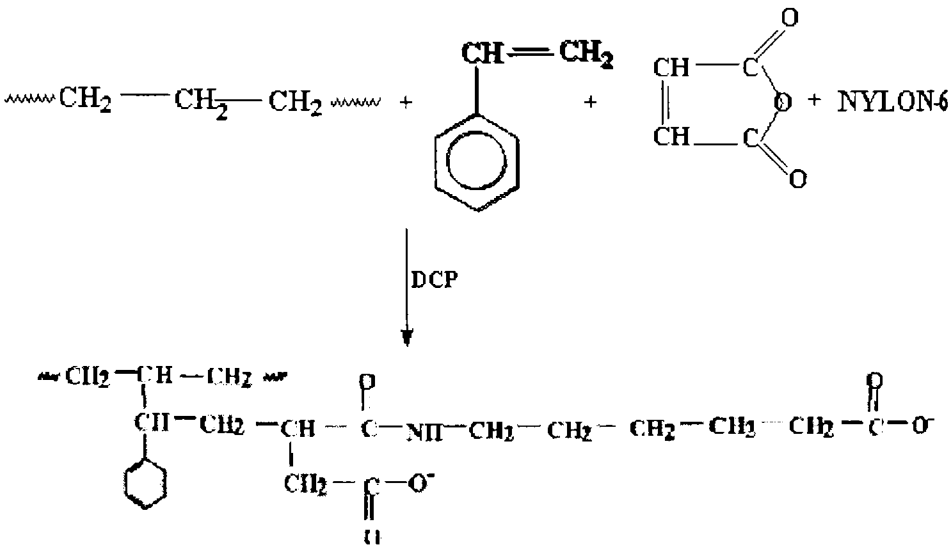
Figure 3b.11 Variation of flexural modulus with fibre loading

3b.4 Effect of matrix modification on the mechanical properties of nylon fibre reinforced high density polyethylene.

The nonpolar HDPE matrix was grafted with polar monomers,namely maleic anhydride and styrene maleic anhydride.

3b.4.1 Styrene maleicanhydride grafted high density polyethylene

The melt free-radical grafting process starts with the formation of macroradicals along the HDPE chain by a hydrogen abstraction. These HDPE chain macroradicals and HDPE chain end macroradicals produced by β-scisssion can both take part in grafting reaction. (Scheme 3b.1)



Scheme 3b.1 Mechanism of reaction of styro maleated HDPE with nylon fibre in presence of dicumyl peroxide

As in the case of nylon fibre/SMA-g-PP, styrene maleic anhydride (SMA) adduct acts as a link between nylon fibre and HDPE matrix.

In the case of nylon/SMA-g-HDPE, new absorption bands at 1781 and 1857 cm^{-1} were observed, which can be assigned to the absorption of the carbonyl groups of cyclic anhydride (Figure 3b.12).

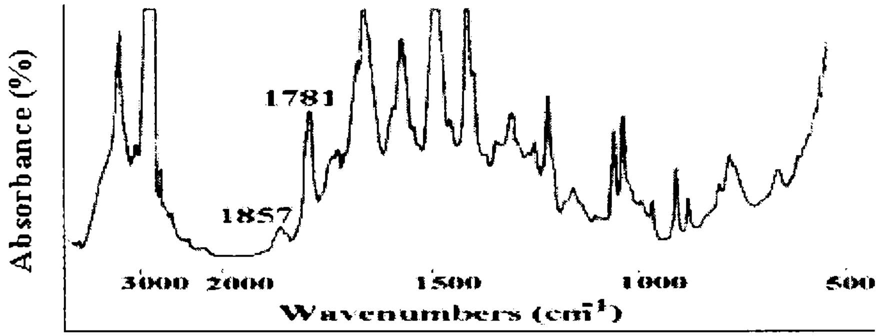


Figure 3b.12 FTIR spectrum of nylon fibre/SMA-g-HDPE composite

3b.5 Results and discussion

3b.5.1 Torque Studies

The variation of mixing torque with time of mixing at different fibre loading with styrene/maleic anhydride modification of the matrix is shown in Figure 3b.13. The mixing time of 8 minutes was fixed since the torque stabilised to a constant value during this time in all cases. The temperature of the mixing chamber was fixed as 170 °C.

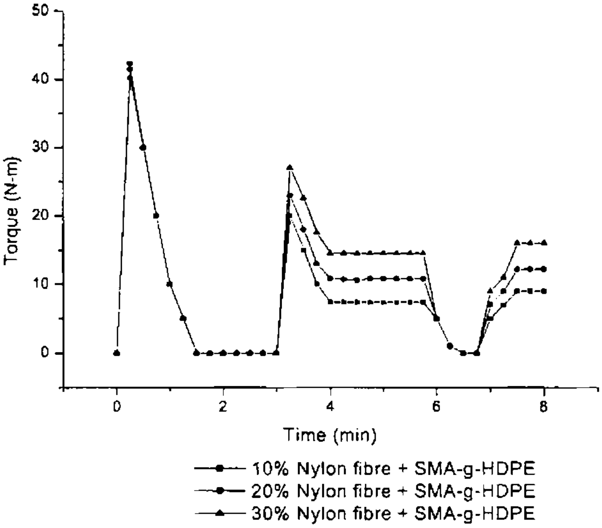


Figure 3b.13 Variation of mixing torque with time

3b.5.2 Effect of matrix modifications on tensile properties

Figure 3b.14 & 3b.15 show the effect of chemical treatment on the tensile properties of nylon fibre/HDPE composites [24]. It is observed that there is a significant improvement in tensile strength and modulus for SMA grafted HDPE compared to the composites prepared form unmodified HDPE as in the case of nylon fibre/PP composite.

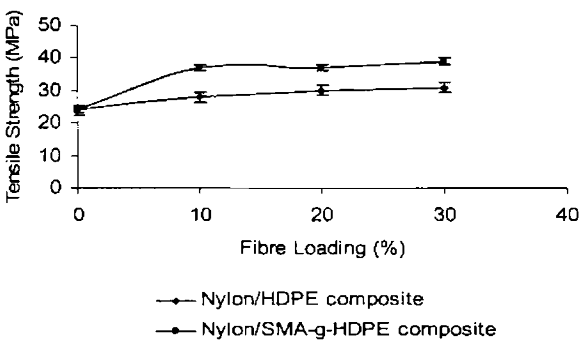


Figure 3b.14 Variation of tensile strength with fibre loading

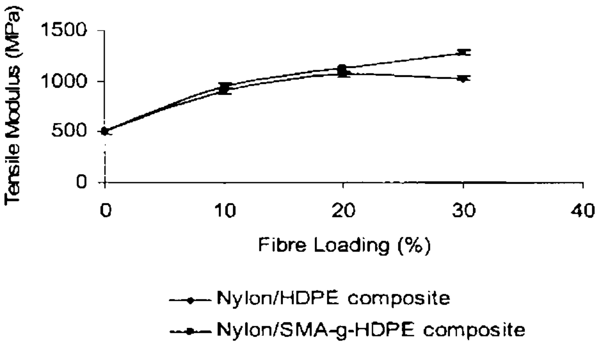


Figure 3b.15 Variation of tensile modulus with fibre loading

The scanning electron micrographs of the fractured surfaces of nylon fibre/HDPE composites and that of nylon fibre/SMA-g-HDPE composite are shown in Figures 3b.16 & 3b.17 respectively. The SEM fracture photographs of the unmodified and modified composites also show a similar variation as observed in the case of the nylon fibre/PP composites.

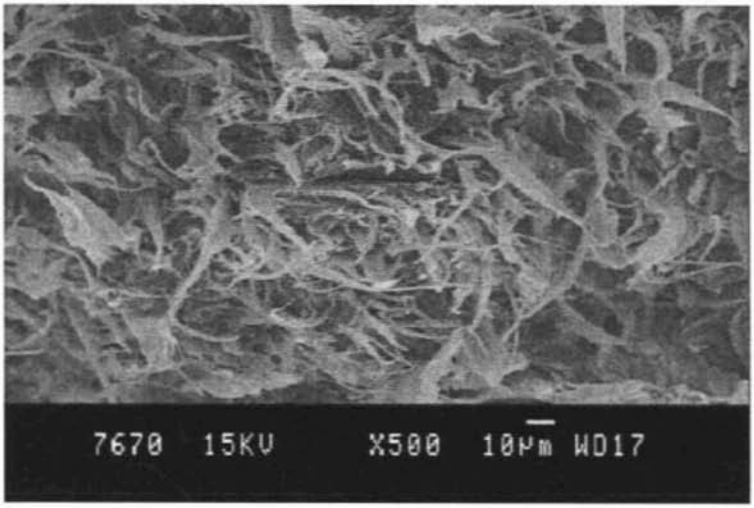


Figure 3b.16 Scanning electron micrograph of the tensile fractured surface of Nylon/HDPE composite

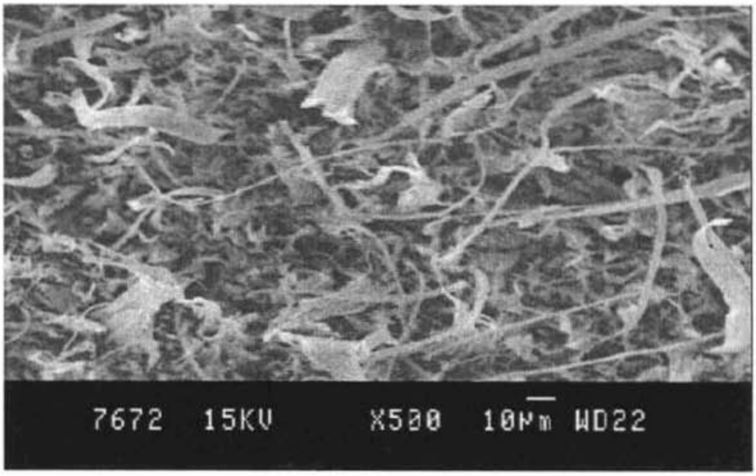


Figure 3b.17 Scanning electron micrograph of the tensile fractured surface of Nylon/SMA-g-HDPE composite

3b.5.3 Effect of fibre modifications on flexural properties

The flexural properties of the nylon fibre/SMA-g-HDPE composites are compared with those of the unmodified nylon fibre/HDPE composite in Figures 3b.18 & 3b.19. There is a significant improvement in flexural strength by the addition of 10 % fibres even though further improvement is moderate as in the case of Nylon fibre/PP composites. In the case of flexural modulus, there is a steady increase up to 30 % fibre content.

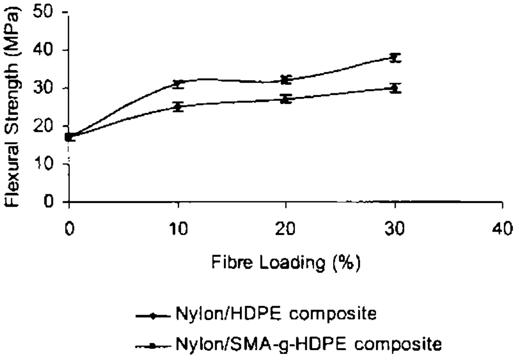


Figure 3b.18 Variation of flexural strength with fibre loading

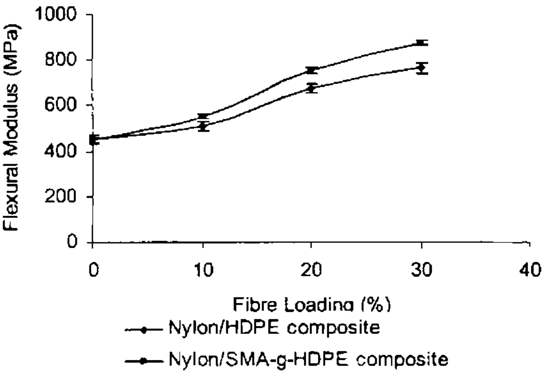


Figure 3b.19 Variation of flexural modulus with fibre loading

Conclusions

The study shows that PP and HDPE can be reinforced with nylon short fibres and the following conclusions can be observed.

- The reinforcement is observed in the range of 0 to 30 % fibre content.
- The critical fibre length for reinforcement is about 10 mm.
- The reinforcement improves with decrease in fibre diameter.
- There is a significant improvement in reinforcement with chemical modification of the matrix. In the case of nylon fibre/PP composite having 10 % fibre content, the tensile modulus increases by 70 % and the flexural modulus by 50 %. In the case of nylon fibre/HDPE composite containing 30 % fibre, the tensile modulus increases by 140 % and the flexural modulus by 70 %.

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Chapter 4

Rheology and Processing Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Chapter 4

Rheology and Processing Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. Rheology and processing behaviour of recyclable short nylon fibre reinforced polypropylene composites

4a.1 Introduction

The incorporation of short fibres to thermoplastics and elastomers to achieve cost reduction [1] and improvement in mechanical properties has become increasingly important in recent years. The rheological behaviour of such composites is important for selecting the processing parameters to fabricate products. A number of investigations on the rheological behaviour of short fibre reinforced thermoplastics and elastomers have been reported [2-5]. Usually, the incorporation of short fibres in thermoplastics and elastomers increases the melt viscosity and may make processing more difficult. The melt viscosity of glass fibre filled polyethylene (PE) and PP was studied by Becraft and Metzner [6-7] and it was found that there is a significant increase in viscosity with fibre loading at low shear rates and little change in viscosity at higher shear rates. A decrease in melt viscosity as a result of the incorporation of short fibres is also reported [8-11].

4a.2 Experimental

The melt rehological measurements were carried out using a Shimadzu capillary rheometer (50kN) at different plunger speeds from 1-500 mm/min. The capillary used had a length of 40mm and diameter 1mm at an entry angle of 90°. The measurements were carried out at two different temperatures viz. 180 and 220 °C.

4a.3 Results and discussion

4a.3.1 Effect of fibre loading and shear rate on viscosity

Figures 4a.1 & 4a.2 show the variation of viscosity of PP composites [12] with shear rate and fibre loading at 180 and 220 °C. These curves are typical of pseudoplastic materials, which show a decrease in viscosity with increasing shear rate. All the systems investigated have been found to obey the power law relationship viz.

$$\eta = k(\gamma)^{n-1}$$

where, n is the power law index and k the consistency index.

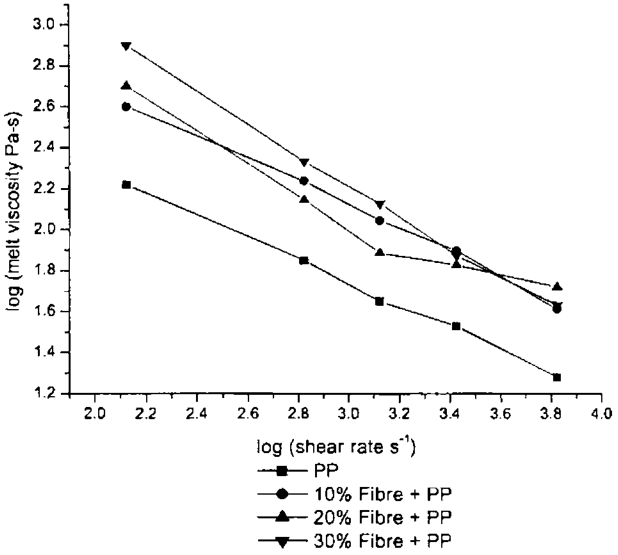


Figure 4a.1 Variation of melt viscosity with shear rate at 180 °C

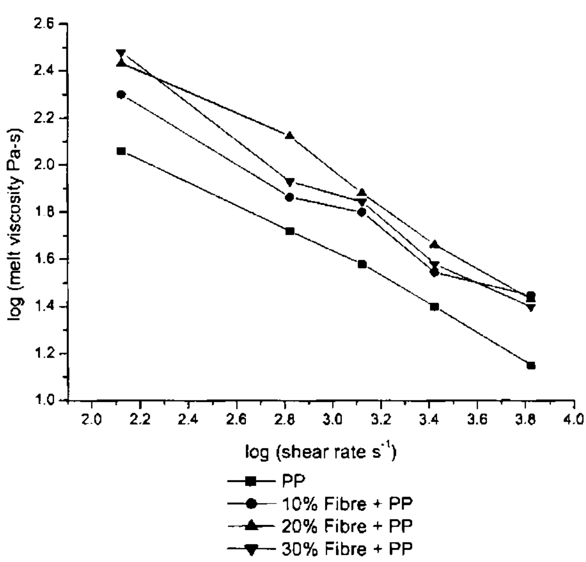


Figure 4a.2 Variation of melt viscosity with shear rate at 220 °C

In the case of nylon fibre/PP composites viscosity increases with fibre loading. The two possible factors affecting the viscosity are 1) increased fibre matrix- interaction that increases the viscosity and 2) increased wall slip due to the presence of longitudinally oriented fibres along the wall/melt interface that decreases the viscosity. In the case of unmodified polypropylene, fibre may stick to the walls due to low fibre matrix adhesion and this may increase the viscosity.

4a.3.2 Effect of matrix modification on melt viscosity

Figures 4a.3 & 4a.4 show the effect of interface modification on the viscosity of nylon fibre reinforced polypropylene composites at 180 and 220 °C. From the figure it is clear that the viscosity of the composite decreases. This is interesting since there is a marginal increase in molecular weight upon modification. In the case of modified polypropylene the fibre matrix interaction is high and hence more fibres may adhere to surface of the matrix resulting in more wall slip and hence viscosity reduction.

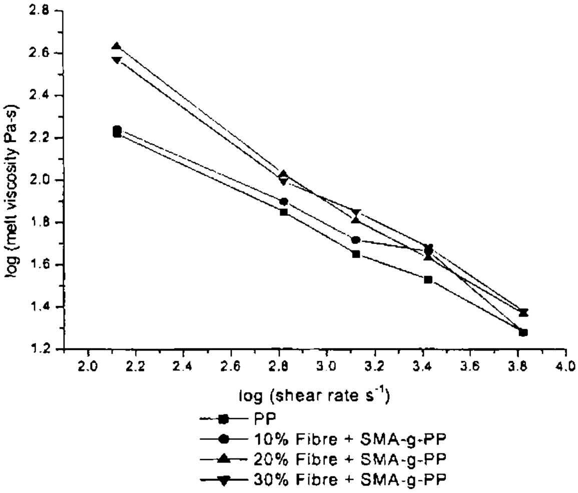


Figure 4a.3 Variation of melt viscosity with shear rate at 180 °C

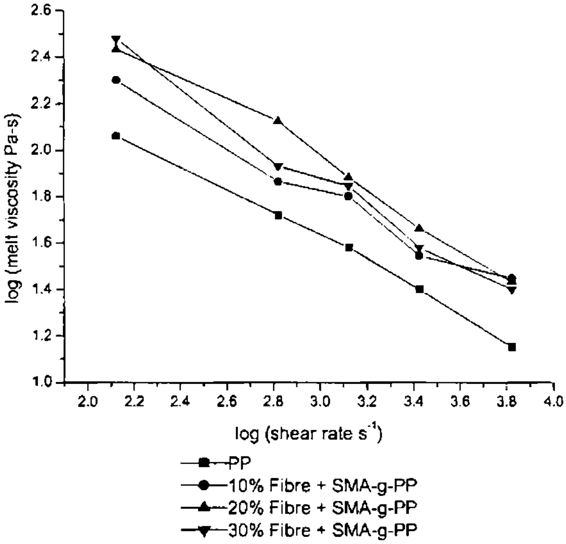


Figure 4a.4 Variation of melt viscosity with shear rate at 220 °C

4a.3.3 Effect of temperature on melt viscosity

The effect of temperature on the viscosity of polymers is important as the polymers are subjected to significant temperature gradient during processing. Figure 4a.5 & 4a.6 show the variation of melt viscosity of the composite at 180 °C and 220 °C at different shear rates. The viscosity of the composite decreases with increase in temperature.

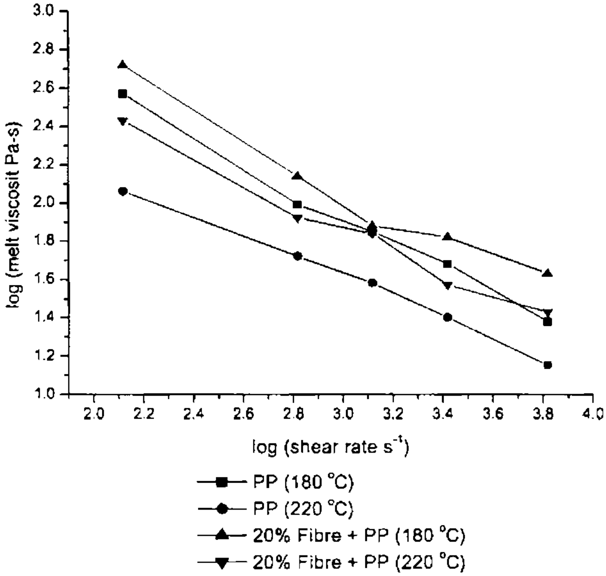


Figure 4a.5 Variation of the melt viscosity of Nylon fibre/PP composites with shear rate at 180 °C and 220 °C

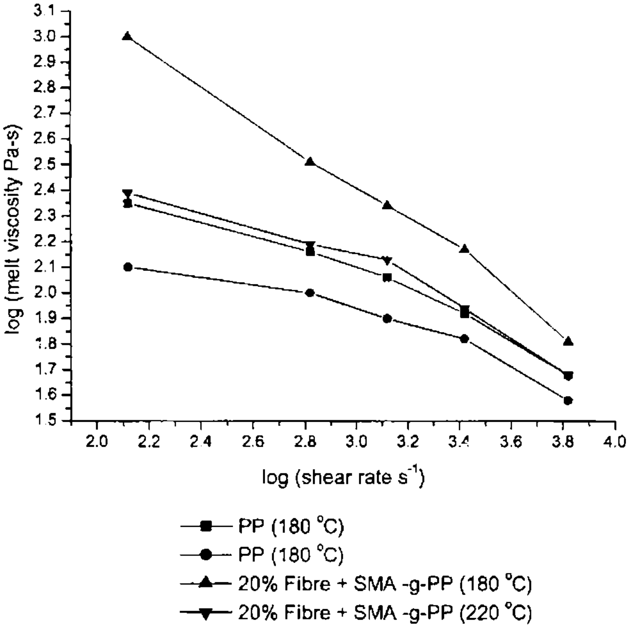


Figure 4a.6 Variation of the melt viscosity of Nylon fibre/ SMA-g-PP composites with shear rate at 180 °C and 220 °C

4a.3.4 Flow behaviour index (n')

The dependence of flow behaviour index on fibre content and interface modifications at two different temperatures viz. 180 and 220 °C are shown in Table 4a.1.

Table 4a.1 Flow behaviour index value for Nylon fibre/PP composite

Material	**Flow behaviour index (n')**	
	at 180°C	**at 220°C**
0% Fibre + PP	0.549	0.530
10% Fibre + PP	0.574	0.511
20% Fibre + PP	0.689	0.603
30% Fibre + PP	0.752	0.636
10% Fibre + SMA-g-PP	0.538	0.220
20% Fibre + SMA-g-PP	0.684	0.424
30% Fibre + SMA-g-PP	0.743	0.561

Non-Newtonian pseudoplastic materials have n' values less than unity. In the case of Nylon fibre /PP composite the n' values were found to be less than unity indicating pseudoplastic nature of the system. It is found that for all the mixes flow behaviour index decreases as temperature increases indicating that the melt becomes more non-Newtonian in nature as the temperature is increased.

4a.3.5 Die swell behaviour of nylon fibre reinforced polypropylene composite

The increase in the diameter of the extrudate as it comes out of the capillary is known as die swell. This phenomenon occurs as a result of the orientation of polymer molecules as they are sheared while passing through the die of extruder. As the melt comes out of the die, reorientation and recovery of the molecules occur and these lead to die swell.

a) Effect of shear rate

Figure 4a.7 shows the die swell behaviour of PP, nylon fibre/PP composite and nylon fibre/SMA-g-PP composite at different shear rates at a constant temperature of 180 °C. There is a decrease in the die swell ratio upon the addition of fibre. At the same fibre loading the die swell ratio increases with shear rate. These observations are in agreement with results reported in literature. In the case of short fibre composites, during flow through the capillary, orientation of polymer molecules and fibres takes place. As the composites come out of the capillary, polymer molecules retract by recoiling effect. Further, the behaviour shows that the fibres remain as fillers at ordinary processing temperatures.

The unequal retractive forces experienced by the two components of the composite can lead to redistribution of fibres. Since the molecules at the periphery undergo maximum deformation, the retractive forces on these molecules will also be higher. Thus retractive force, is mainly responsible for the die swell of short fibre filled composite.

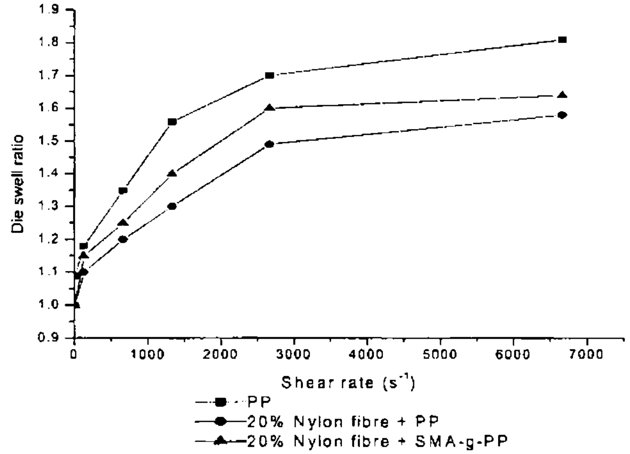


Figure 4a.7 Variation of die swell ratio of nylon fibre /PP composites at different shear rates at 180 °C

b) Effect of temperature

Figure 4a.8 gives the variation of die swell ratio of PP, nylon fibre/PP composite and nylon fibre/SMA-g-PP composite at different shear rates at a constant temperature of 220 °C. There is an increase in the die swell ratio upon the addition of 20 per cent fibre loading. At the same fibre loading the die swell ratio increases with shear rate. At this higher temperature the nylon fibre also gets melted. As the blends come out of the capillary polymer molecules retract by recoiling effect. Therefore the die swell ratio increases.

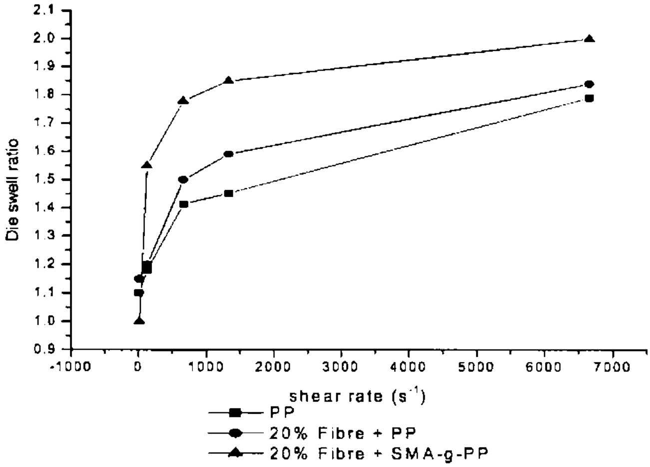


Figure 4a.8 Variation of die swell ratio of nylon fibre /PP composites at different shear rates at 220 °C.

4a.3.6 Activation energy

The variations of melt viscosity with reciprocal of absolute temperature of nylon fibre/PP composites at two different shear rates 1333 and 6666 s^{-1} are reported (Table 4a.2). Activation energies were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates. From the table it can be observed that the activation energy of flow of the composites increases with modification at the lower shear rate, while there is not much increase at the higher shear rate. This is in confirmation with our observations that activation energy of flow increases with modification due to the resulting molecular weight increases, but at higher shear rates the increase is not pronounced due to alignment of molecules in the shear field.

Table 4a.2 Activation energies (kJ/mol) of flow of nylon fibre/PP composites at two shear rates

Sample	**Activation energy (kJ/mol)**	
	at 1333 (s^{-1})	**at 6666 (s^{-1})**
0% Fibre + PP	9.4	8.72
10% Fibre + PP	10	10
20% Fibre + PP	11	11
30% Fibre + PP	11.5	12
10% Fibre + SMA-g-PP	14.8	10
20% Fibre + SMA-g-PP	15.7	12
30% Fibre + SMA-g-PP	15	13

Chapter 4

Rheology and Processing Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part B. *Rheology and processing behaviour of recyclable short nylon fibre reinforced high density polyethylene composites*

4b.1 Introduction

This section describes the rheological behaviour of nylon fibre/HDPE and nylon fibre/SMA-g-HDPE composite.

4b.2 Experimental

The melt rheological measurements were carried out using a Shimadzu capillary rheometer (50kN) at different plunger speeds from 1-500 mm/min. The capillary used had a length of 40 mm and diameter 1mm at an angle of entry 90°. The measurements were carried out at two different temperatures viz. 180 and 220 °C. The rheological measurements were also made on Haake torque rheometer since it represents real processing equipment.

4b.3 Results and discussion

4b.3.1 Effect of fibre loading and shear rate on viscosity

Figures 4b.1 & 4b.2 show the variation of viscosity of HDPE composites with shear rate and fibre loading at 180 °C and 220 °C. The viscosity of the nylon fibre/HDPE composites increases with fibre loading as in the case of nylon fibre/PP.

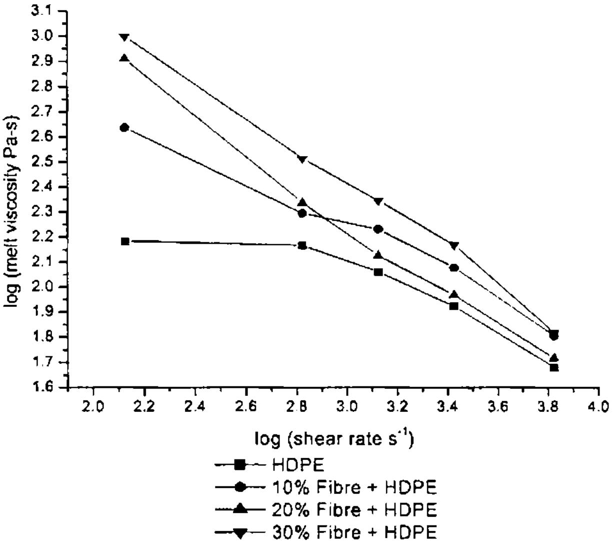


Figure 4b.1 Variation of melt viscosity with shear rate at 180 °C

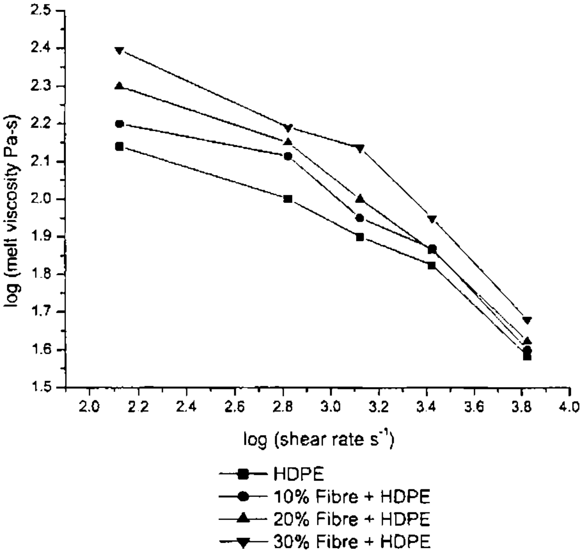


Figure 4b.2 Variation of melt viscosity with shear rate at 220 °C

4b.3.2 Effect of matrix modification on melt viscosity

Figures 4b.3 & 4b.4 show the effect of modification on the viscosity of nylon fibre/ HDPE composites at 180 and 220 °C. From the figure it is evident that the viscosity of the composite decreases with modification as observed in the case of nylon fibre/HDPE composite.

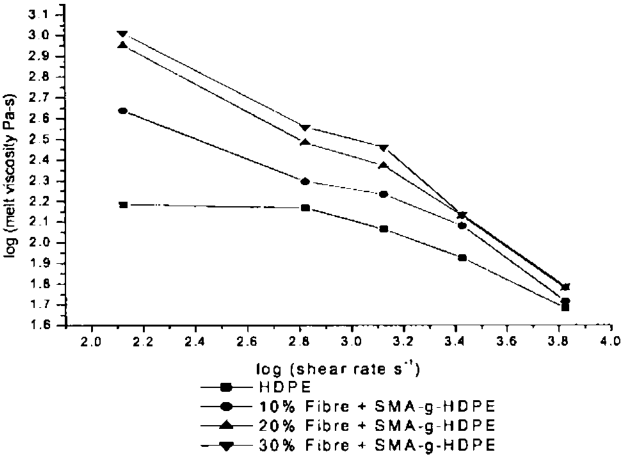


Figure 4b.3 Variation of melt viscosity with shear rate at 180 °C

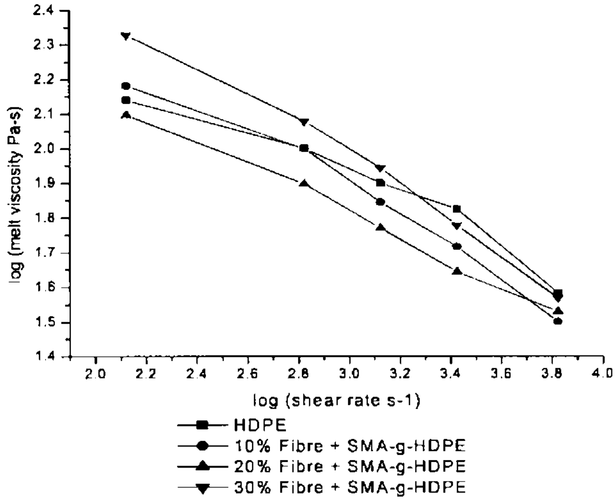


Figure 4b.4 Variation of melt viscosity with shear rate at 220 °C

4b.3.3 Effect of temperature on melt viscosity

Figures 4b.5 & 4b.6 show the variation of melt viscosity of the composite at 180 and 220 °C at different shear rates. The viscosity of the composite decreases with temperature as expected.

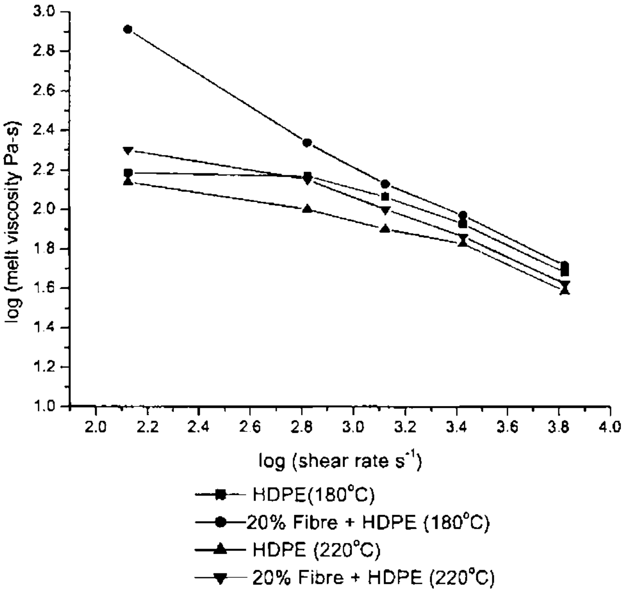


Figure 4b.5 Variation of the melt viscosity of nylon fibre/ HDPE composites with shear rate at 180 °C and 220 °C

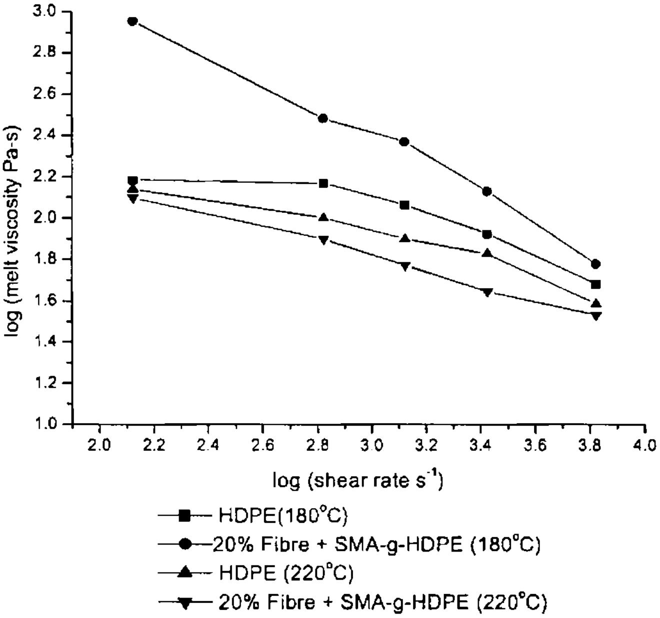


Figure 4b.6 Variation of the melt viscosity of nylon fibre/ SMA-g-HDPE composites with shear rate at 180 °C and 220 °C

4b.3.4 Flow behaviour index (n')

The dependence of flow behaviour index on fibre content and interface modifications at two different temperatures viz. 180 °C and 220 °C is shown in Table 4b.1. In the case of nylon fibre/ HDPE composite the n' values were found to be less than unity indicating pseudoplastic nature of the system same as in the case of nylon fibre/PP composite.

Table 4b.1 Flow behaviour index value for Nylon fibre/HDPE composite

Material	Flow behaviour index (n')	
	at 180 °C	at 220 °C
0% Fibre + HDPE	0.290	0.250
10% Fibre + HDPE	0.468	0.45
20% Fibre + HDPE	0.699	0.679
30% Fibre + HDPE	0.676	0.656
10% Fibre + SMA-g- HDPE	0.510	0.401
20% Fibre + SMA-g- HDPE	0.673	0.342
30% Fibre + SMA-g- HDPE	0.708	0.447

4b.3.5 Die swell behaviour of nylon fibre reinforced HDPE composite

a) Effect of shear rate

Figure 4b.7 shows the die swell behaviour of HDPE, Nylon/ HDPE composite and Nylon/SMA-g- HDPE composite at different shear rates at a constant temperature of 180 °C. There is a decrease in the die swell ratio upon the addition of fibre. At the same fibre loading the die swell ratio increases with shear rate. These observations are same as in the case of nylon fibre/PP composite.

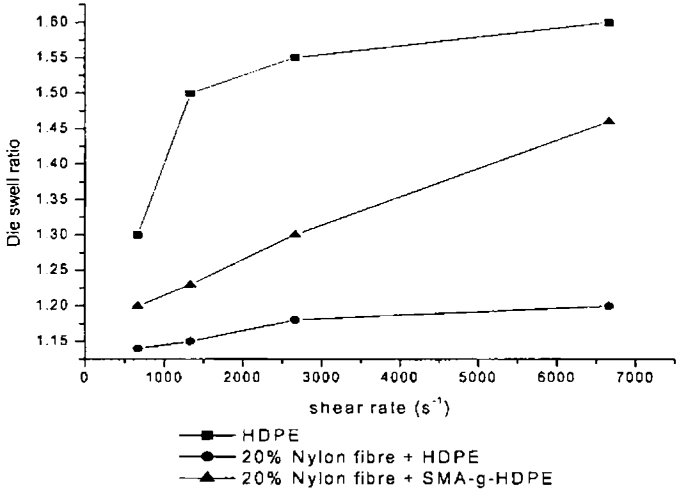


Figure 4b.7 Variation of die swell ratio of Nylon fibre/HDPE composites at different shear rates at 180 °C

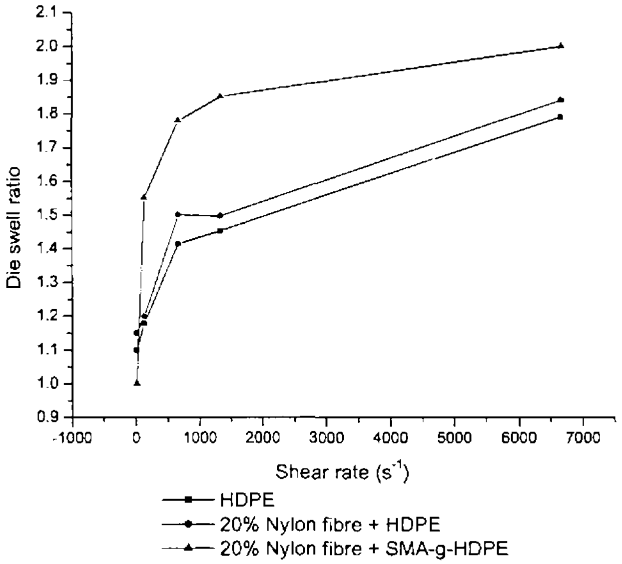


Figure 4b.8 Variation of die swell ratio of Nylon fibre/HDPE composites at different shear rates at 220 °C

b) Effect of temperature

Figure 4b.8 gives the variation of die swell ratio of HDPE, Nylon/ HDPE composite and Nylon/SMA-g- HDPE composite at different shear rates at a constant temperature of 220 °C. There is an increase in the die swell ratio upon the addition of fibre as observed in the case of nylon fibre/PP composite.

4b.3.6 Activation energy

The variation of melt viscosity with reciprocal of absolute temperature of nylon fibre/PP composites at two different shear rates 1333 and 6666 s^{-1} are reported. Activation energies of HDPE, nylon fibre/ HDPE composite and nylon fibre/SMA-g- HDPE composite are given in Table 4b.2. Activation energies were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates. As in the case of the nylon fibre/PP composite, the activation energy increases with chemical modification of the matrix. However the increase is not very pronounced at higher shear rate.

Table 4b.2 Activation energies (kJ/mol) of flow of nylon fibre/HDPE composites at two shear rates

Sample	Activation energy (kJ/mol)	
	at 1333 (s^{-1})	at 6666 (s^{-1})
0% Fibre + HDPE	0.90	0.58
10% Fibre + HDPE	2.23	1.47
20% Fibre + HDPE	1.66	1.14
30% Fibre + HDPE	2.08	1.6
10% Fibre + SMA-g-HDPE	2.77	1.38
20% Fibre + SMA-g-HDPE	3.66	1.49
30% Fibre + SMA-g-HDPE	3.25	1.29

4b.4 Rheological measurements using Torque Rheometer

4b.4.1 Effect of fibre loading and shear rate (rpm) on viscosity (torque)

Figure 4b.9 shows the plot of log torque Vs log rpm for various fibre loading. The family of straight lines obtained is parallel showing that the power law indices for the parent polymers and their composites are more or less the same. The rheological interpretation of the measurements was based on the analysis of Blyler and Daane. Goodrich and Porter considered the torque rheometer measuring head as two adjacent rotational viscometers with irregular concentric cylinders [13-19]. They succeeded in converting torque rheometer data into fundamental rheological units for materials that exhibit Newtonian viscosity. Blyler and Daane extended this work to Non-Newtonian materials and derived the equation

$$M= C(n)KS^{n}$$

where M is the torque, K and n are parameters of the famous power law equation.

Table 4b.3 shows the power law indices (n) for different fibre loading and these n values can be used for predicting the behaviour of the composites at lower shear rate. The constant n value agrees with the parallel straight line obtained in the log melt viscosity Vs log rpm plot.

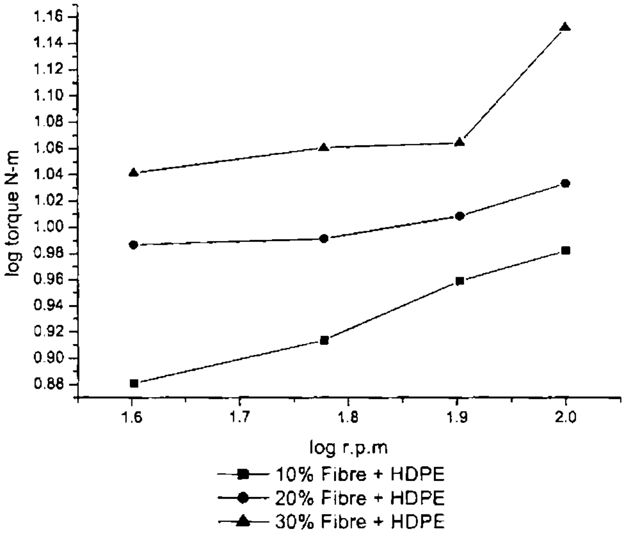


Figure 4b.9 Flow curves from torque rheometer

Table 4b.3 Power law index values for Nylon fibre/HDPE composites

	10% Fibre + HDPE	20% Fibre + HDPE	30% Fibre + HDPE
Power law index (n value)	0.26	0.21	0.23

4b.4.2 Effect of matrix modification on melt viscosity

Figure 4b.10 shows the plot of log torque Vs log rpm for various fibre loading in which the matrix is modified. The torque value remains almost constant. Table 4b.4 shows the power law indices (n) for different fibre loading and these n values can be used for predicting the behaviour of the composites at lower shear rate.

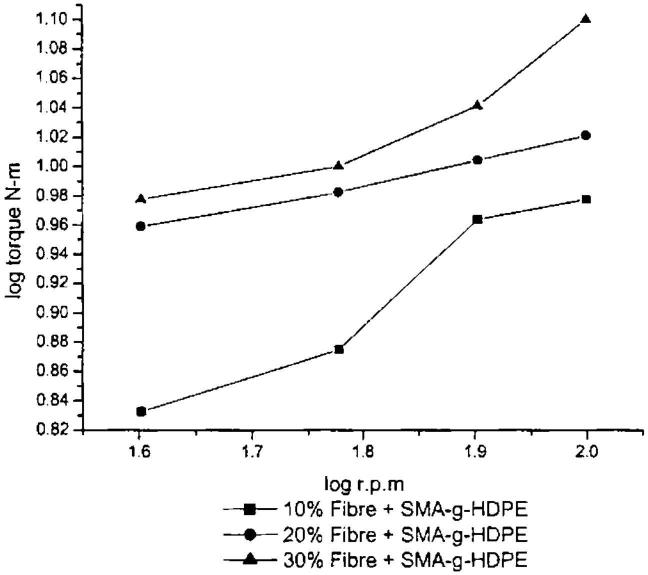


Figure 4b.10 Flow curves from torque rheometer

Table 4b.4 Power law index values for Nylon fibre/ SMA-g-HDPE composites

	10% Fibre + SMA-g-HDPE	**20% Fibre + SMA-g-HDPE**	**30% Fibre + SMA-g-HDPE**
Power law index (n value)	0.39	0.25	0.31

4b.4.3 Energy required for processing

The energy required for processing the composites at different rpm for a period of 8 min is given in Table 4b.5. The energy needed is found to be increasing with the fibre loading and also with the increase in rpm as expected.

Table 4b.5 Energy required for processing of Nylon fibre/HDPE composites at different rotor speeds

Rotor speed (r.p.m)	Energy required (kJ) for processing at different fibre content		
	10% Fibre	20% Fibre	30% Fibre
40	15.3	21.7	28.5
60	29.1	29.6	31.8
80	36.6	41.7	46.3
100	41.2	48.7	58.3

Chapter 4

Rheology and Processing Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part C. Simulation studies of recyclable short nylon fibre reinforced polypropylene composites.

4c.1 Introduction

In the continuing demands for materials with improved performance including reduced weight, increased strength, faster productivity and lower cost, thermoplastics and thermoset polymers are both classes of materials that cannot be ignored. The former have thus attracted much interest for structural applications. Polypropylene is one of the most commonly used thermoplastic polymers. Fibre reinforced composite materials have recently been adapted to improve upon the mechanical properties of plastic materials. Accordingly, PP reinforced with synthetic fibres is now widely used in automobile applications.

Reinforced thermoplastics are commonly manufactured by injection moulding, a process which has the benefits of a short production cycle, yielding excellent surfaces and the ease of moulding complex shapes. However, mixing short fibres with the polymer matrix can greatly change the mechanical properties, in a manner strongly dependent on the orientation and distribution of the fibres. Selecting and identifying injection moulding process parameters that affects proper fibre orientation, is thus of major concern to the plastics industry.

The orientation of short fibres in injection moulding has been investigated. Some researchers have focused on the simulation of fibre orientation Hirari *et al.* [20] predicted the distribution of fibre orientation in thin injection moulded parts, for a flow of molten resin considered to exhibit two dimensional isothermal properties. Greene *et al.* [21-23] also developed computer programs to predict the two dimensional fibre orientations in thin, composite parts. Other researchers have been interested in three dimensional simulation of fibre orientation. Friedl *et al.* [24] proposed a model to predict three dimensional fibre orientation distribution in injection mouldings.

Bay and Tucker [25] simulated fibre orientation in simple injection moulding using a three-dimensional second rank tensor function. The finite element method was employed by Kabenemi *et al.* [26] to calculate the flow behaviour and fibre orientation during the filling of injection moulded parts.

Most studies on fibre orientation address the correlation of processing conditions with both fibre orientation and mechanical properties in different materials, to help in optimizing processing conditions to yield desired properties. Wilson *et al* [27] examined the effects of moulding variables on the mechanical properties of short fibre reinforced thermoplastic polyurethane; the properties were evaluated both parallel and perpendicular to the polymer flow. Bright and Darlington, and Xavier *et al.* [28-29] similarly examined the influence of injection moulding parameters on the fibre orientation distribution, and the mechanical properties of glass fibre reinforced polypropylene. The observed mechanical properties were explained with reference to fibre orientation. Barbosa and Kenny [30] statistically elucidated the relationships among processing conditions, fibre distribution and mechanical behaviour. The correlation between fibre orientation and mechanical properties for other materials was considered by Delpy and Fischer [31].

4c.2 Experimental

The standard tensile specimens (ASTM D 638) were moulded in a semiautomatic reciprocating injection moulding machine, with a maximum injection pressure of 60 MPa. Mold Flow Software was used to predict the parameters like fill time, tensile modulus along the principal direction, air traps, and the fibre orientation and distribution in the polymer matrix. The properties feed to the software are listed below (Table 4c.1).

Table 4c.1Physical properties of PP and nylon fibres

Melt flow rate

Melt Flow Index of PP : 20 g/10 min (230 °C/2.16kgf)

Thermal properties of PP

Processing temperature : 200 °C
Specific heat : 3064 J/kg-C
Heating/Cooling rate : -0.1667 °C/s
Thermal conductivity : 0.15 W/m-C

PVT properties of PP

Melt Density : 0.738 g/cc
Solid Density : 0.907 g/cc

Mechanical properties of PP

Elastic Modulus (First Principal Direction) : 900 MPa
Poisson's Ratio : 0.392

Properties of nylon fibre

Density : 0.98 g/cc
Specific Heat : 1047 J/Kg-C
Thermal Conductivity : 0.24 W/m-C

4c.3 Results and discussion

4c.3.1 Fill Time

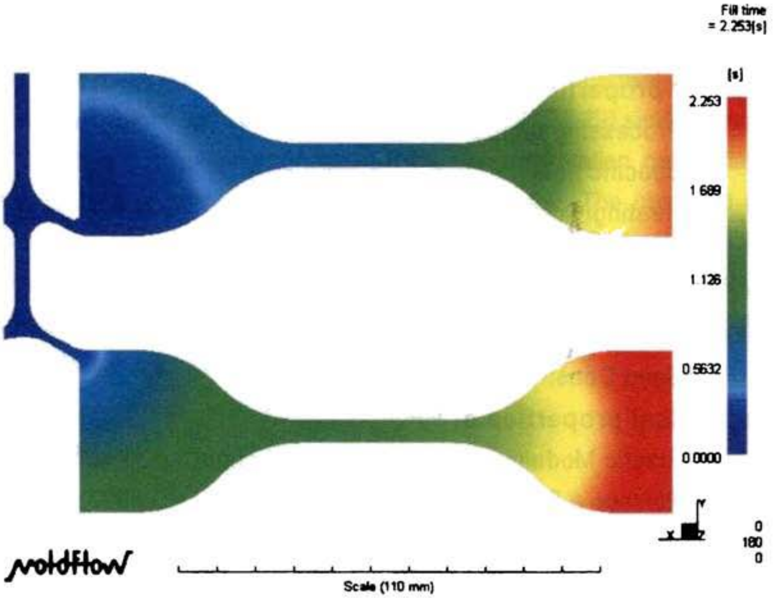


Figure 4c.1

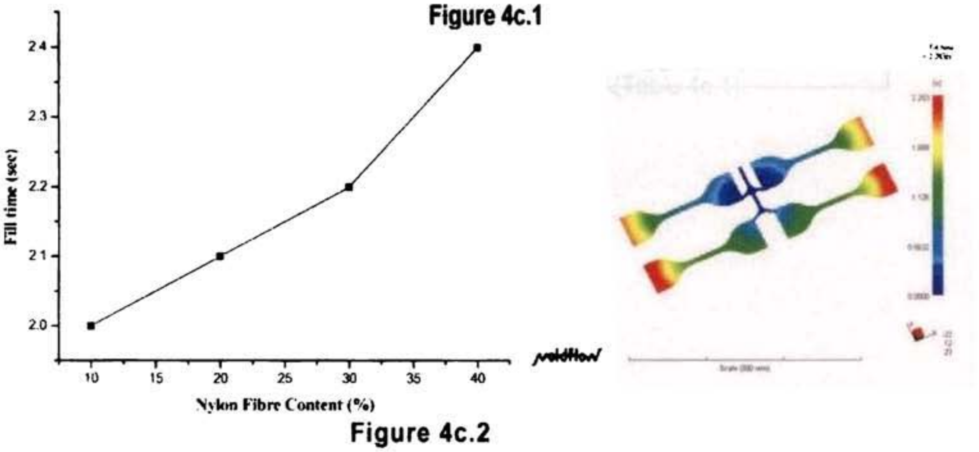
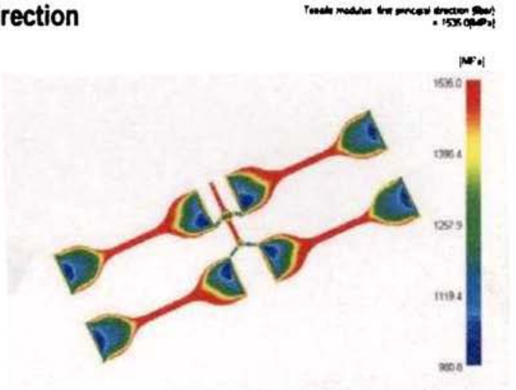


Figure 4c.2

Figure 4c.1 shows the mold filling characteristics of 30 % nylon fibre/PP composite obtained by simulation with an approximate fill time of 2 sec (as observed experimentally). The actual fill times obtained by simulation are shown in the figure 4c.2. Similar results are obtained with other composites having fibre contents of 10, 20 and 40 %. It may be observed that the fill time marginally increases with fibre content obviously due to the increased resistance to flow with increase in fibre content.

4c.3.2 Tensile Modulus along Principal Direction



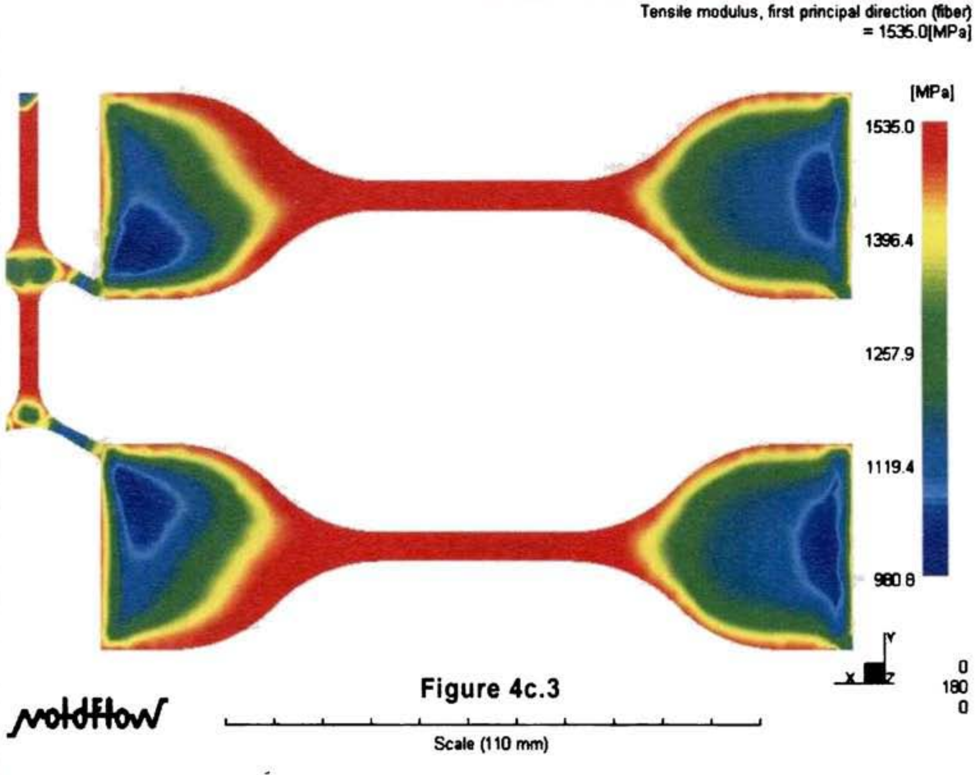


Figure 4c.3

Figure 4c.3 shows the simulated result of tensile modulus along the principal direction of nylon fibre/PP composite. The predicted maximum modulus is 1535 MPa for 30% fibre loading. Experimental value observed is 1400 MPa (Chapter 3a), which is within the experimental limits.

4c.3.3 Average Fibre Orientation

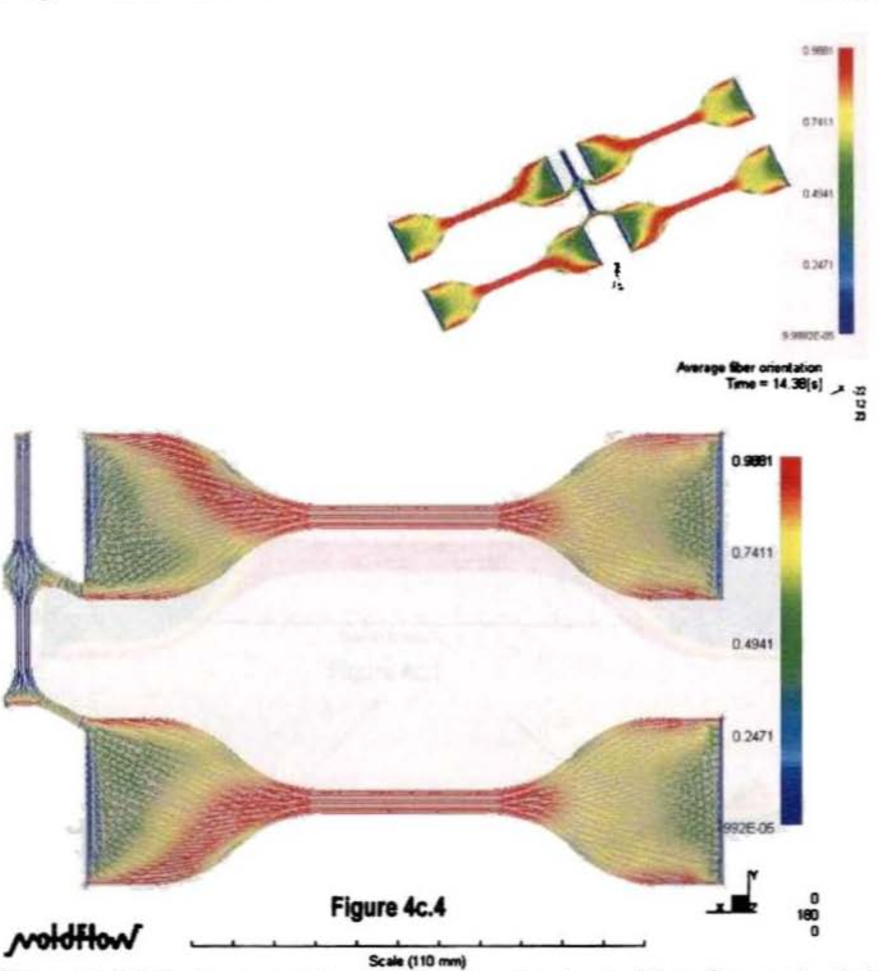


Figure 4c.4

Fibre orientation is a very important parameter in deciding the mechanical properties of composite. In injection-molded composites, the fibre alignment (or orientation) show a layered nature, and are affected by the filling speed, the processing conditions and the material behavior, plus the fibre aspect ratio and concentration. Figure 4c.4 shows the simulated result of average orientation of nylon fibres in a 30 % nylon fibre/PP composite. The maximum orientation of the fibres is along the principal direction where maximum strength is expected. There can be a significant variation in mechanical properties with different mold geometry and fibre content.

4c.3.4 Air Trap

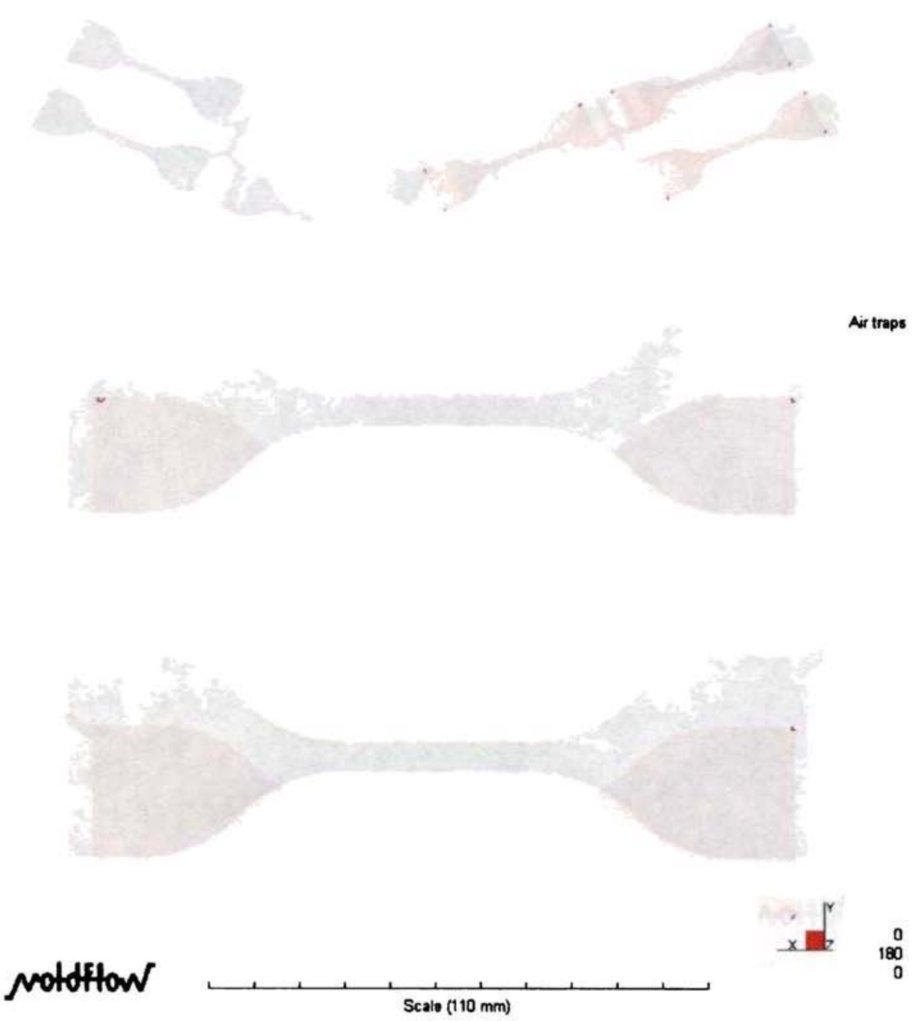


Figure 4c.5

An air trap is an air or gas bubble that has been trapped by converging flow fronts or trapped against the cavity wall. This causes a surface blemish on the part. In our specimen the air traps are found to be at the corners of the sample and hence the mechanical properties are not much likely to be adversely affected (Figure 4c.5).

4c.3.5 Volumetric Shrinkage at Ejection

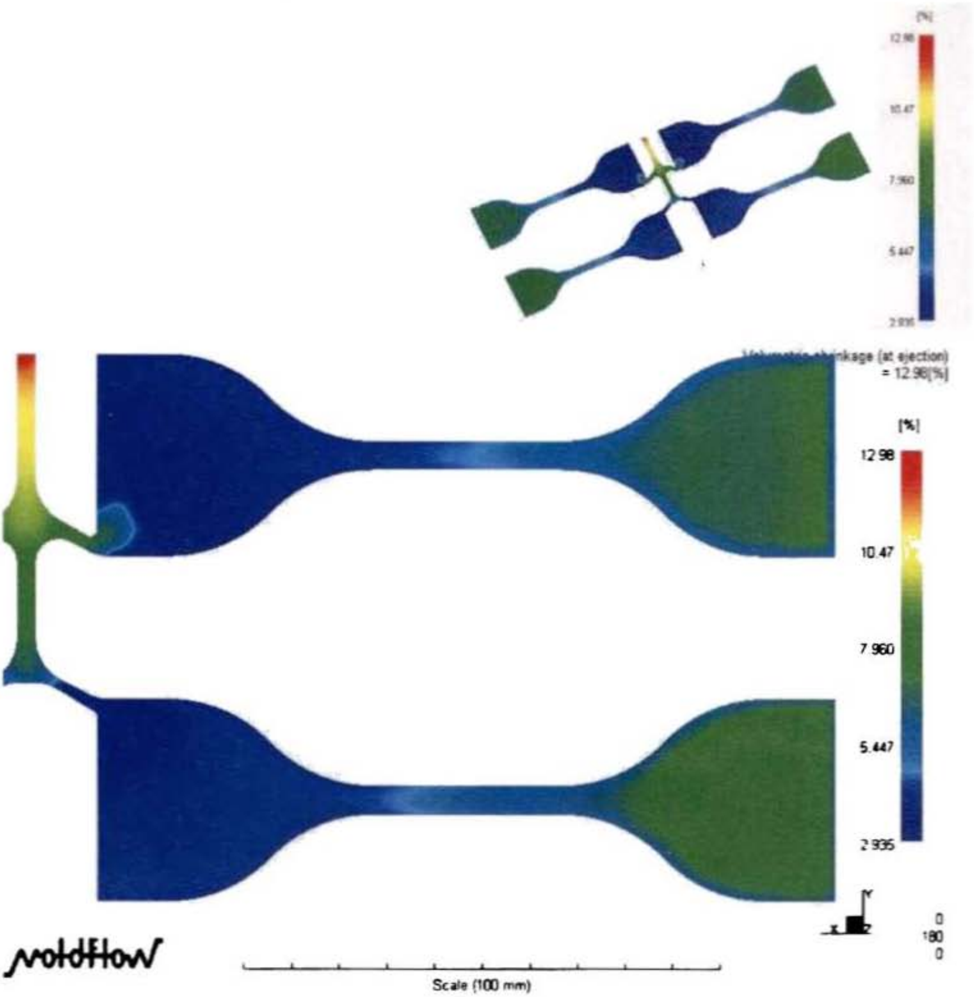


Figure 4c.6

The volumetric shrinkage result is a 3D flow analysis result from mold flow simulation. Volumetric shrinkage should be uniform across the whole part to reduce warpage. The maximum shrinkage observed for 30 % nylon fibre/PP composites is 5 % as shown in Figure 4c.6.

4c.3.6 Bulk Temperature (End of Filling)

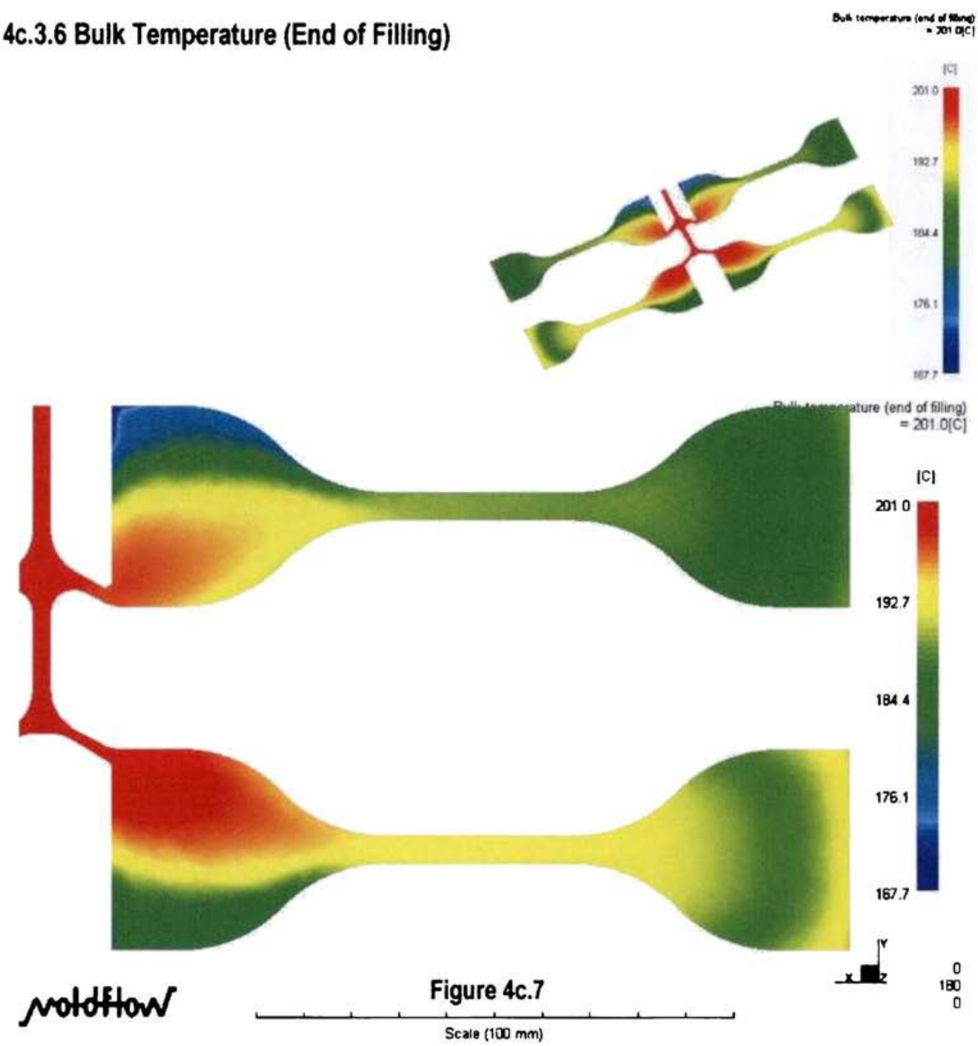


Figure 4c.7

Bulk temperature is used to indicate the weighted average temperature across the thickness. It represents the energy that is transported through a particular location. The temperature of polymer melt changes not only with time and location, but with thickness during the entire injection molding cycle as well. From the figure it is observed that the maximum temperature occurs in the melt injecting zone as expected. In the case of nylon fibre/PP composites it should be ensured that the high temperature zones do not affect the reinforcing fibres. From the figure 4c.7 maximum temperature recorded is 200 °C and hence it may be concluded that the temperatures involved are with in the limits.

4c.3.7 Time to Freeze

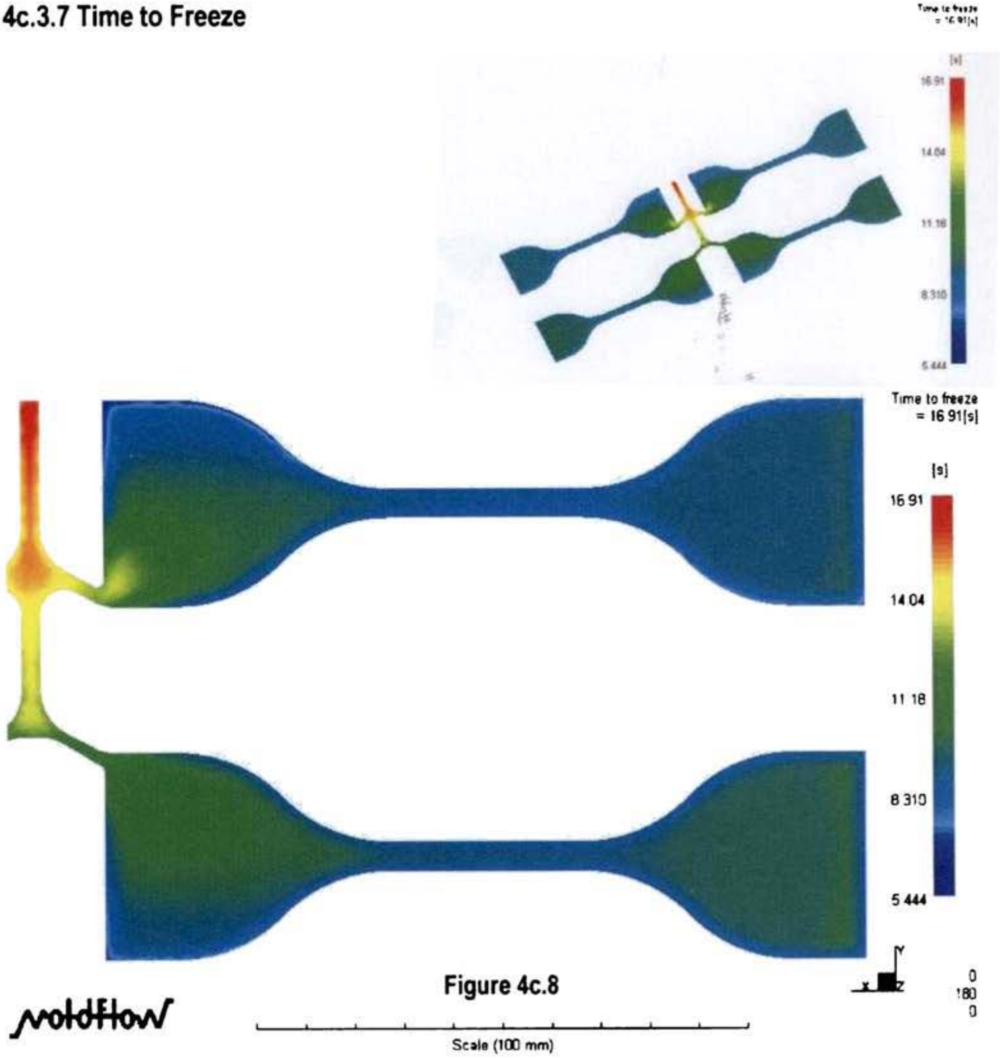


Figure 4c.8

The Freeze time result is generated from a 3D flow analysis, and shows the time for the part to cool down to ejection temperature, measured from the start of the cycle. The freeze time at several locations varies across the surface of the specimen as shown in Figure 4c.8.

4c.3.8 Temperature at flow front

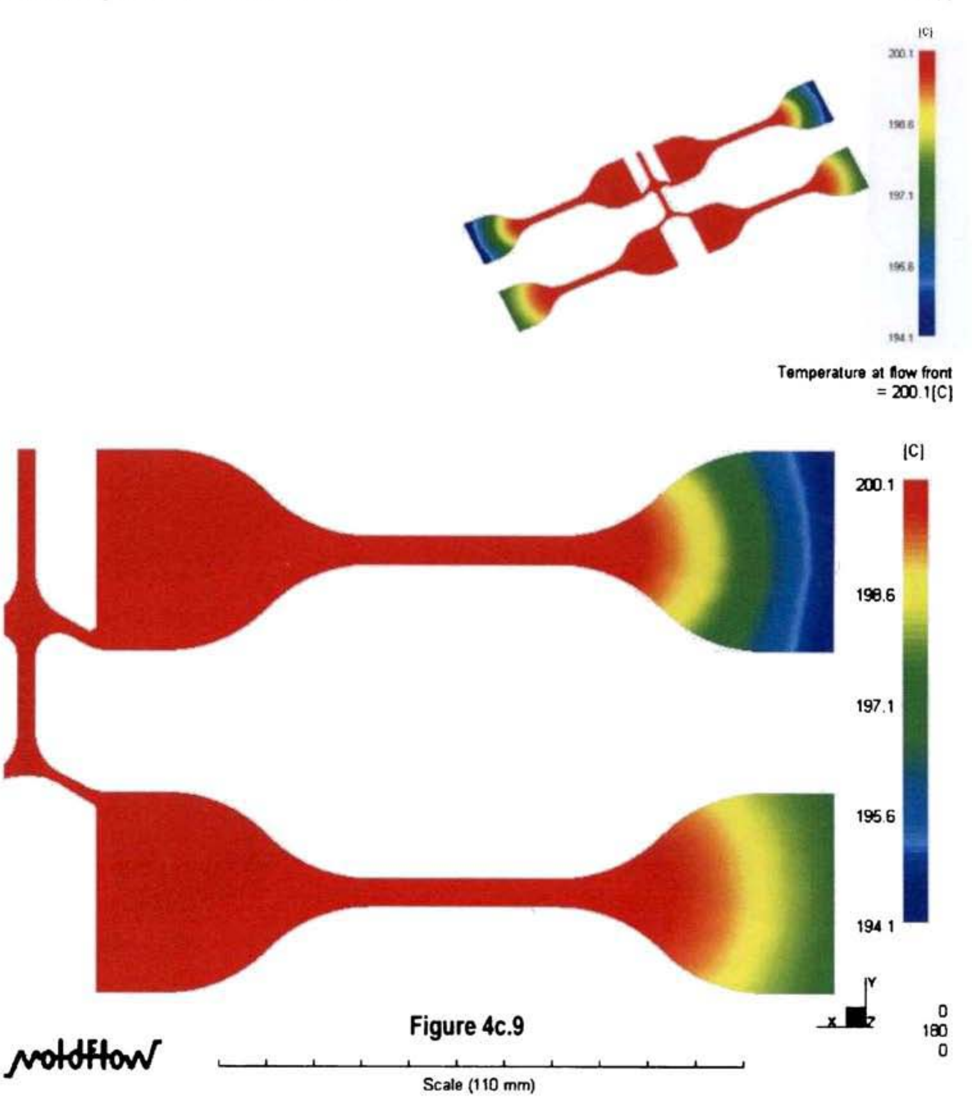


Figure 4c.9

Figure 4c.9 shows the temperature of the polymer flow front at the end of the analysis. It predicts that there will not be any short shot or material degradation since the temperature is neither too high nor too low.

4c.3.9 Sink Index

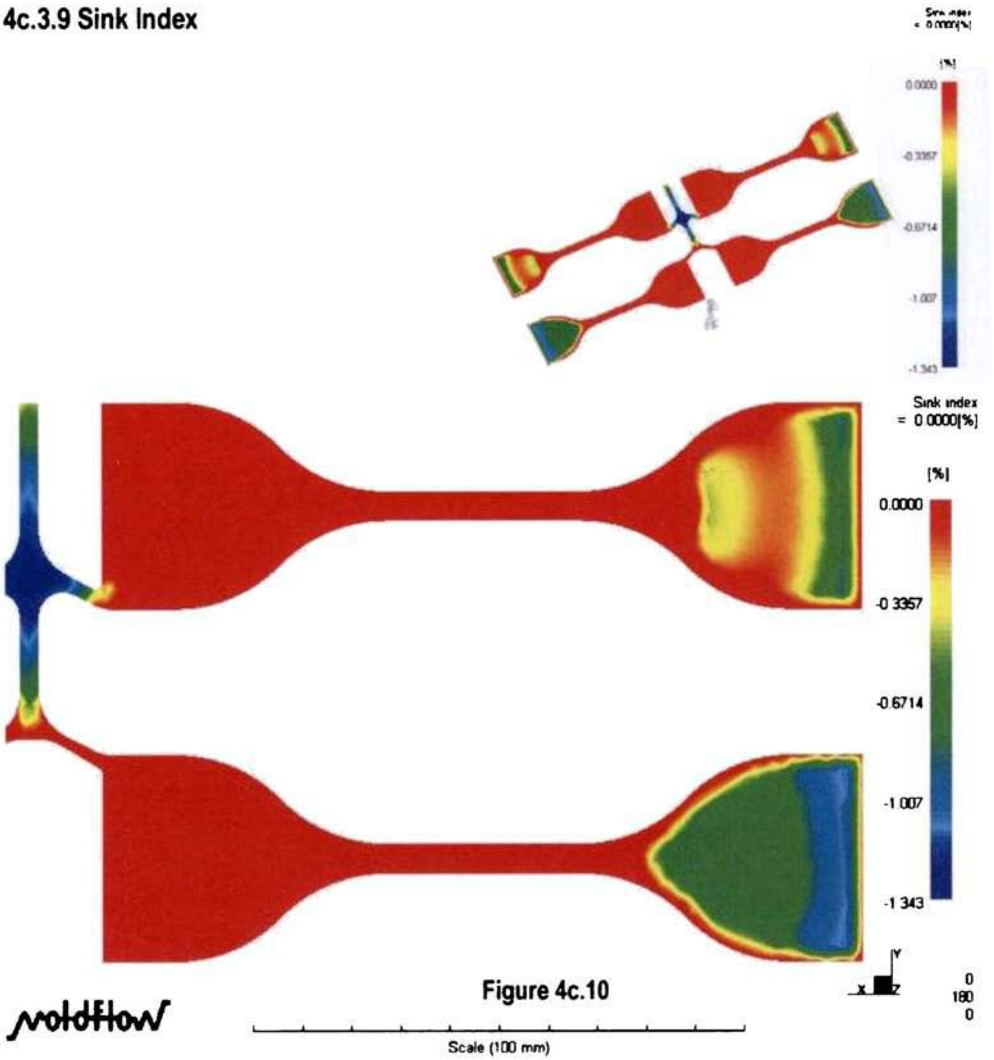


Figure 4c.10

The sink index shows potential shrinkage due to a hot core. It is calculated for each location at the instant when local pressure has decayed to zero during the packing stage, and reflects how much material is still in molten form and left unpacked. As can be observed from the Figure 4c.10, potential areas where sink marks can occur are at the upstream end of the sample where the packing may not be efficient to compensate the shrinkage. Also the runner area is prone to shrinkage since there is no packing to compensate shrinkage in this area. However this does not affect the dimensional stability of the sample.

4c.3.10 Frozen Layer Fraction

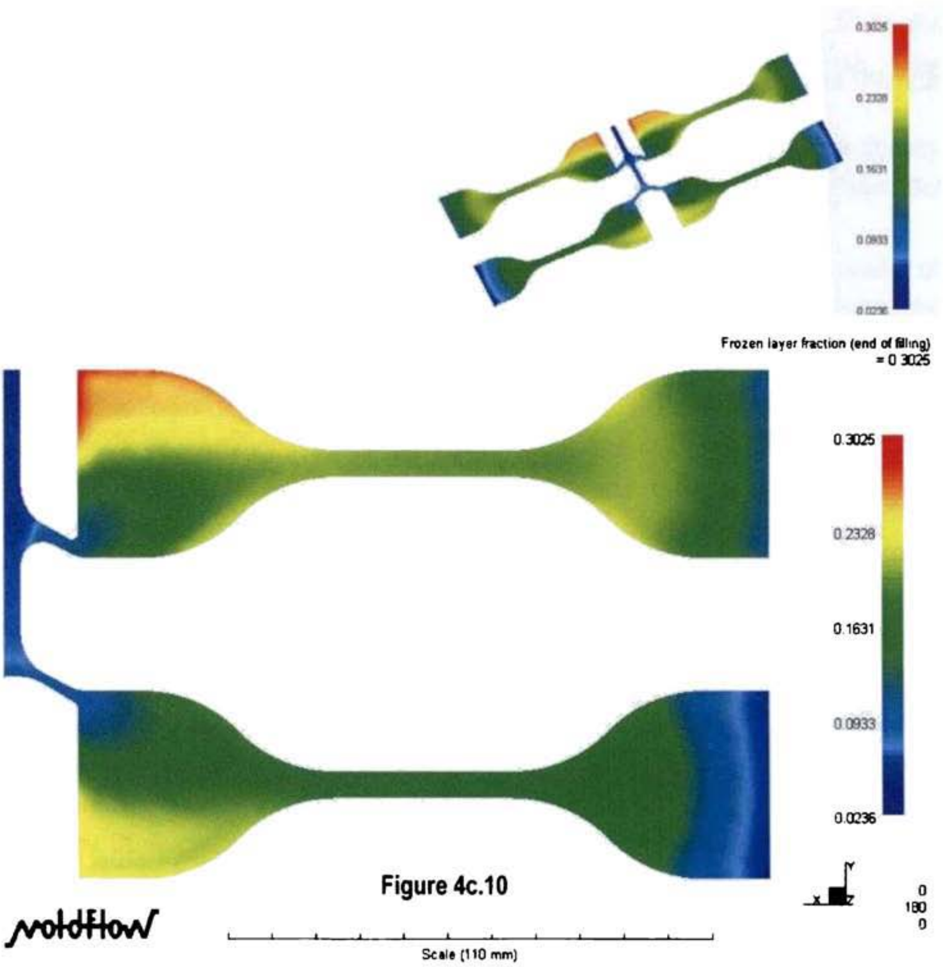


Figure 4c.10

Frozen layer fraction shows the thickness of the frozen layer as a fraction at the end of the filling phase. Frozen layer thickness has very significant effects on the flow resistance. The viscosity exponentially increases with decreasing temperature. The thickness of the flow layer is also reduced as the thickness of the frozen layer increases. The least frozen layer thickness is shown at the extreme end of the sample (Figure 4c.11).

Conclusions

The following conclusions can be drawn from the rheological behaviour of nylon fibre/PP and nylon fibre/HDPE composites.

- Viscosity increases with fibre content. However, this effect is significant only in the lower shear range. In the higher shear range the increase in viscosity is only marginal when the fibre content increases from 10 to 30 %. The viscosity further reduces with chemical modification. At higher shear rate the viscosity of modified composite is close to that of matrix polymer.
- As expected, the melts are pseudoplastic in nature and the viscosity decreases with increase in temperature. It can be observed that the composite becomes less pseudoplastic with the addition of fibres. The strongest pseudoplastic nature is obtained at 220 °C when the composite gets converted into a blend.
- The die swell behaviour is also widely different at the two processing temperatures. At 180 °C the die swell decreases with addition of fibre while at 220 °C the die swell increases with fibre addition.
- The activation energy of flow increases with fibre addition and matrix modification. However, the activation energy marginally decreases with increase in shear.
- The moldflow software can be used for determining the fibre orientation, tensile modulus, temperature profile, fill time, shrinkage etc.

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Chapter 5

Thermal Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. Thermal behaviour of recyclable short nylon fibre reinforced polypropylene composites

5a Introduction
5a.1 Experimental
5a.2 Results and discussion
5a.2.1 Thermo Gravimetric Analysis (TGA)
5a.2.2 Differential Scanning Calorimetry (DSC)
5a.2.3 Dynamic Mechanical Analysis (DMA)

Part B. Thermal behaviour of recyclable short nylon fibre reinforced high density polyethylene composites

5b Introduction
5b.1 Experimental
5b.2 Results and discussion
5b.2.1 Thermo Gravimetric Analysis (TGA)
5b.2.2 Differential Scanning Calorimetry (DSC)
5b.2.3 Dynamic Mechanical Analysis (DMA)

Chapter 5

Thermal Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. Thermal behaviour of recyclable short nylon fibre reinforced polypropylene composites

5a Introduction

Thermal analysis of polymers is an important subject as it covers a broad field, ranging from the development of thermoresistant polymers and ablation problems to the stabilisation of thermolabile polymers. Thermal analysis is an important analytical method in understanding the structure-property relationship and mastering the technology for molecular design and industrial production of different polymeric materials, especially fibre reinforced composites. Moreover, it is a useful technique to determine the thermal stability of the materials. In addition, it is possible to quantify the amount of moisture and volatiles present that can cause deterioration in the composites.

One of the accepted methods for studying the thermal properties of polymeric materials is thermogravimetry (TG). Thermogravimetric data indicate a number of stages of thermal breakdown, weight loss of the material in each stage, threshold temperature etc. [1]. Both TG and derivative thermogravimetry (DTG) will provides information about the nature and extent of degradation of the material.

It is generally known that physical and mechanical properties of a semi crystalline polymer are dictated by morphology, which in turn, is influenced by crystallization behaviour of the polymer. Many fillers have been incorporated into PP matrix for cost reduction and it was later discovered that those fillers contributed functionality to the composites, such as improving the stiffness and mechanical properties and modifying the crystallization of the polymer [2-8]. The structure and properties of the composites were affected by the source and structure of fillers and the interaction between the filler particles and with the polymeric matrix. Hamdan *et al.* [9] reported that PP and sago starch were not compatible after noting that the tensile properties of the PP/sago starch blends decreased with increasing sago starch content even though sago starch granules were well dispersed in the PP matrix. To improve the compatibility between PP and starch, Weil [10] proposed use maleated PP instead of PP and the resultant PP/starch composites exhibited improved tensile strength. Li *et al.* and Bagheri [11-12] reported that starch had interactions with PP under processing conditions, thus inhibiting thermal degradation of PP and improving the flame retardant properties of PP. Hence it is interesting to study the effect of molecular characteristics on crystallization kinetics of a semi-crystalline polymer, which is a key to determine the final properties of a polymeric product. In differential scanning calorimetry (DSC), the heat flow rate associated with a thermal event is measured as a function of time and temperature allowing us to obtain quantitative information regarding melting and phase transitions of the composite system.

With the advent of different thermoplastic composites for different applications for which dynamic data are directly relevant (machinery, transport, buildings, domestic appliances, acoustic devices etc.), it is worthwhile to study the polymer composite structure to investigate the dynamic mechanical thermal properties, particularly the dynamic modulus and internal friction, over a wide range of temperatures. When internal molecular motion occurs, the material responds in a viscoelastic manner and the strain response lags behind the stress. The tangent of this phase lag is expressed as tan δ and is also known as the damping factor. The damping properties of a material represent its capacity to reduce the transmission of vibration caused by mechanical disturbances to its structure. The dynamic mechanical characteristics are mostly depends upon the amount of fibre, additives like compatibilizers, fibre orientation and mode of testing. In this section, the fibres were randomly placed and our aim was to compare different parameters at different levels of the fibre within the experimental range.

5a.1 Experimental

Thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) was done using TGA Q 50 (TA Instruments) at a heating rate of 10 °C/min from room temperature to 600 °C with 10-12 g of sample, in a nitrogen environment. Differential Scanning Calorimetry DSC Q100 (TA Instruments) equipped with a RCS cooling system was used to study thermal transitions in the samples at different cooling rates. the sample weight was approximately 5 mg. A dynamic mechanical analyzer DMA Q800 (TA Instruments) was made use of for measuring the storage modulus and mechanical damping (tan δ).

5a.2 Results and discussion

5a.2.1 Thermogravimetry (TG)

The TG and DTG curves of neat PP, nylon fibre and nylon fibre/PP composite [13] are given in Figures 5a.1& 5a.2. Thermal decomposition of each samples take place in a programmed temperature range of 30-600 °C. The temperature of onset of degradation (T_i), the temperature at which rate of decomposition is 50 %, the temperature at which the rate of decomposition is maximum (T_{max}), the peak degradation rate and the residue at 600 °C are given in Table 5a.1. PP degrades in a single step. The degradation starts at a temperature of 348 °C and the peak rate of degradation is 2.914 %/min at corresponding (T_{max}) 470 °C. Neat nylon fibre also degrades in a single step with peak rate of degradation 2.058%/min and corresponding temperature is 464 °C. Residue at 600 °C is 0.35 % for the fibre. It is seen that both the matrix and fibre follows single step degradation and also having comparable T_{max}. Hence nylon fibre/PP composite also show similar degradation pattern. The onset of degradation of nylon fibre/PP composite increases from 348 to 382 °C, indicating improved thermal stability of the composites. The temperature of 50% degradation of the modified nylon fibre/PP composite is increased from 452 to 461 °C, the peak rate of decomposition decreased from 2.914 to 1.915 %/min and the corresponding temperature (T_{max}) increases from 470 to 477 °C.

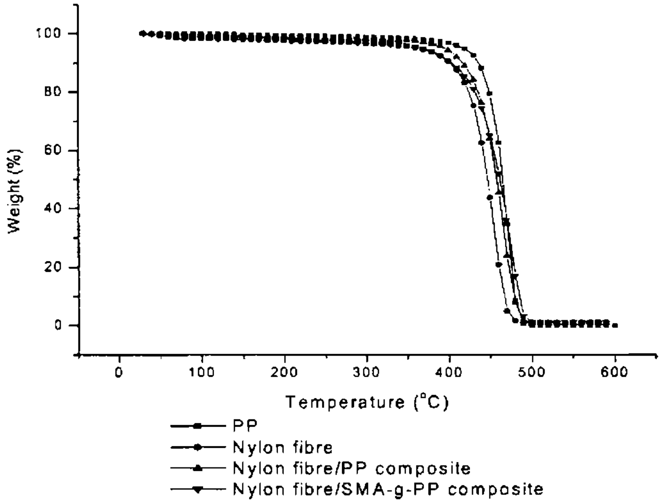

Figure 5a.1 Thermogravimetric traces of PP, nylon fibre, nylon fibre/PP composite & nylon fibre/SMA-g-PP composite

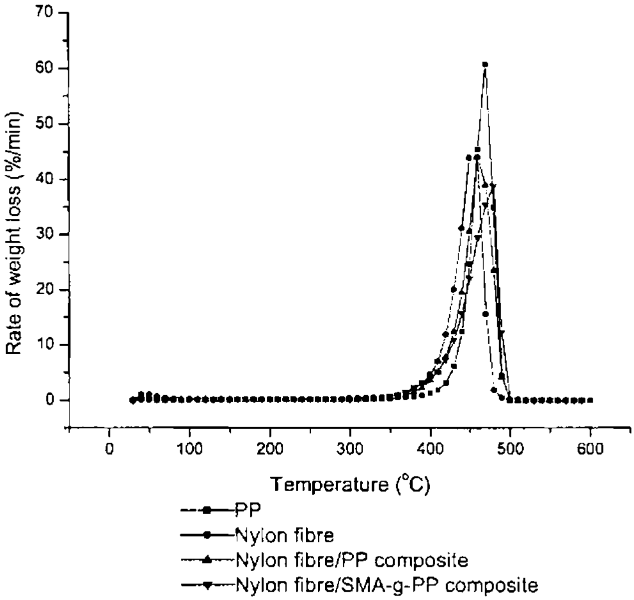

Figure 5a.2 Differential thermogravimetric traces of PP,nylon fibre, nylon fibre /PP composite & nylon fibre/SMA-g-PP composite

Table 5a.1 Degradation characteristics of PP, nylon fibre & nylon fibre/PP composites.

Sample	T_i (°C) Onset	Temp 50% Loss (°C)	Residue at 600 °C (%)	Peak rate of decomposition (%/min)	Peak Temp. (T max) (°C)
PP	348	454	0.348	2.914	470
Nylon Fibre	368	454	0.355	2.058	464
PP/Nylon Composite	382	457	0.394	2.172	462
SMA-g-PP/Nylon Composite	347	461	1.266	1.915	477

The order of degradation was calculated by Freeman-Carroll [14] method using the equation,

$$\Delta \log(dW/dt) = n.\log W_r - \left(\Delta E/2.3R\right)\Delta\left(1/t\right) \quad \text{..................(1)}$$

where dW/dt is the rate of reaction, n is the order of reaction, Δ E is the activation energy of the reaction, R is the gas constant, T is the absolute temperature and W_r is proportional to the amount of reactant remaining. The above equation can be rearranged to,

$$\frac{\Delta \log(dW/dt)}{\Delta \log W_r} = n.- \frac{\left(\Delta E/2.3R\right)\Delta\left(1/t\right)}{\Delta \log W_r} \quad \text{..................(2)}$$

The order of the reaction and the activation energies can be obtained from the intercept and gradient of the plot of the left hand side of equation (2) versus Δ(1/T)/ Δ log W_r and such plots are given in Figure 5a.3. The intercepts show that the degradation of PP and composites follow the second order kinetics.

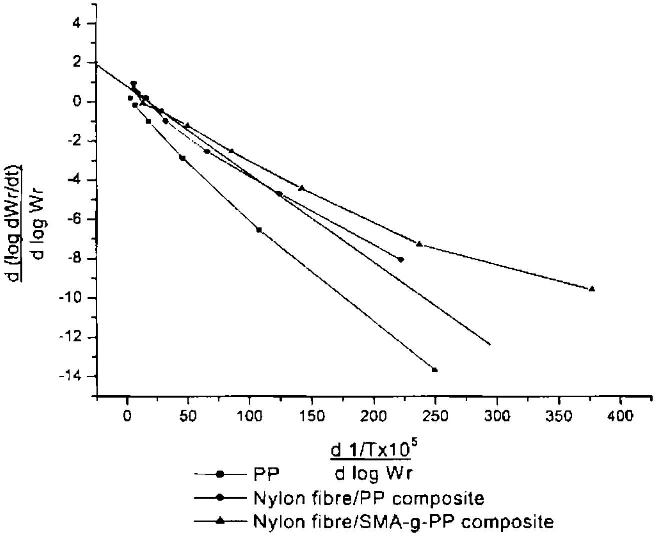

Figure 5a.3 Freeman-Caroll plots for PP, nylon fibre/PP & nylon fibre/SMA-g-PP

5a.2.2 Differential Scanning Calorimetry (DSC)

The DSC curves of PP, nylon fibre/PP composites and nylon fibre/SMA-g-PP composites at different cooling rates are depicted in Figure 5a.4, 5a.5 & 5a.6. These curves provide important parameters on the crystallization behaviour of the composites, such as peak temperature denoted as crystallization temperature (T_c), corresponding peak time t_{max}, degree of crystallinity at X_c, crystallization enthalpy (ΔH) etc. The effect of the different cooling rates is following: the faster the cooling rate, the lower the temperature range at which the crystallization occurs, at slower cooling rate, there is sufficient time to activate nuclei at higher temperature. On contrary, at faster cooling rates, the activation of nuclei occurs at lower temperature. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at a slower scanning rate. The peak temperature T_c shifts to lower temperature with an increasing cooling rate for PP, nylon fibre/PP composite and also for nylon fibre/SMA-g-PP.

For a given cooling rate, T_c of the nylon fibre/PP composite is slightly higher than PP, indicating that the addition of nylon fibre into PP increases the crystallization rate of PP [15-16]. T_c of the nylon fibre/SMA-g-PP composite is shifted to higher value than PP, again indicating the increase in crystallization rate of PP due to the matrix modification. The crystallization enthalpy (ΔH) shifts to lower values as the cooling rate increases. This means that the crystallization of nylon fibre/PP composites become more imperfect than PP (Table 5a.2).

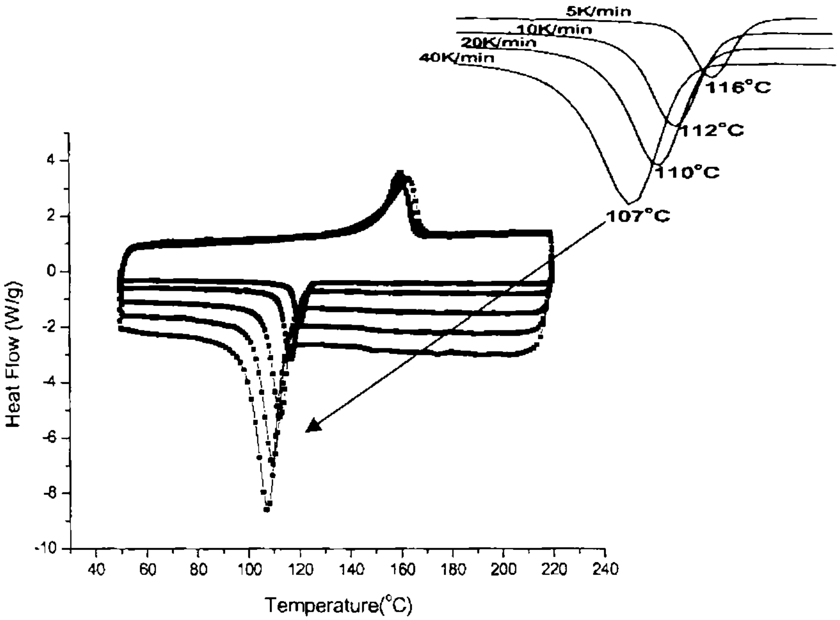

Figure 5a.4 DSC scans at different cooling rates for PP

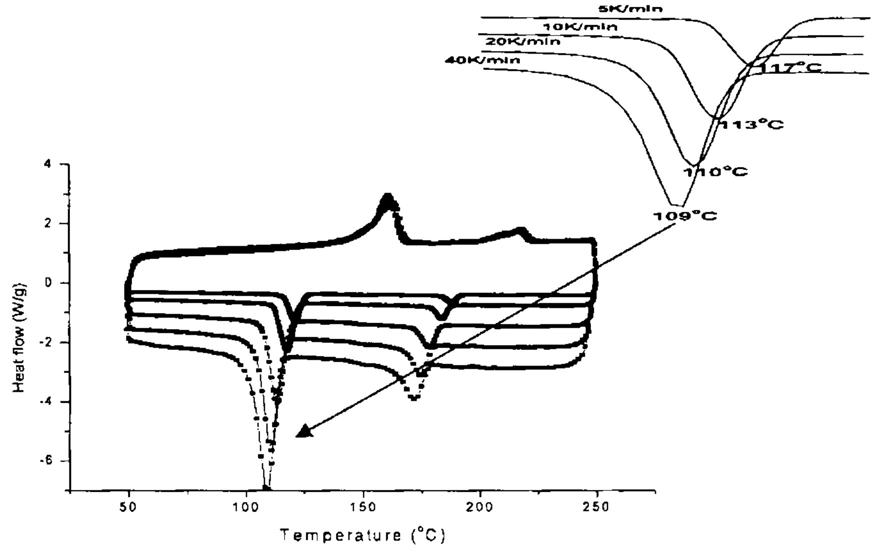

Figure 5a.5 DSC scans at different cooling rates for nylon fibre/ PP composite

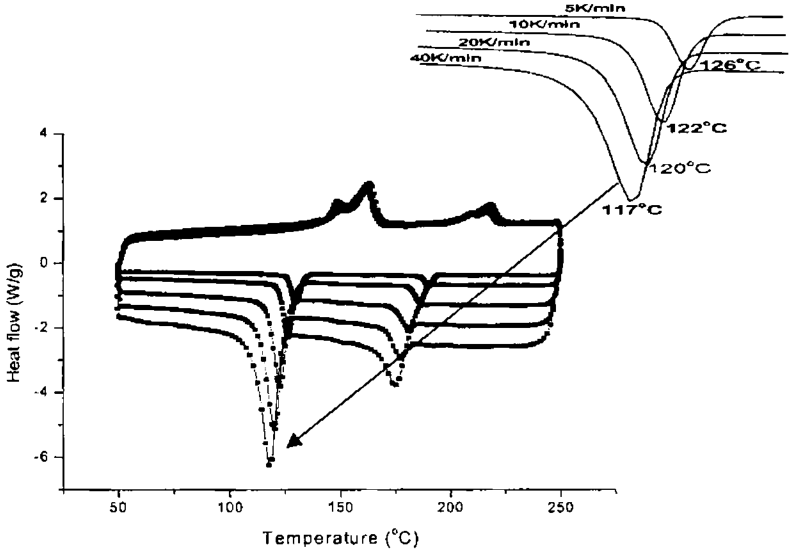

Figure 5a.6 DSC scans at different cooling rates for nylon fibre/SMA-g-PP composite

Table 5a.2 Crystallization parameters of PP & nylon fibre/PP composites

Sample	p (°C/min)	T_c ($_o$C)	X_c (%)	ΔH (J/g)
PP	40	107.2	53	85
	20	112.6	55	84
	10	116.7	56	86
	5	120.3	58	88
Nylon fibre / PP composite	40	109.5	52	57
	20	113.1	54	59
	40	118.3	55	60
	5	121.8	55	62
Nylon fibre/ SMA-g-PP composite	40	117.9	46	49
	20	122.8	47	51
	10	125.3	48	52
	5	129.6	50	53

P,cooling rate during nonisothermal crystallization; T_c, crystallization temperature; X_c, degree of crystallinity ; ΔH, crystallization enthalpy.

5a.2.3 Dynamic Mechanical Analysis (DMA)

Figures 5a.7 & 5a.8, show the variation of storage modulus of nylon fibre/PP composites as a function of temperature. Even with 10% addition of fibres there is an improvement in storage modulus showing the superior load bearing capacity of the composite under dynamic conditions. However the storage modulus decreases with further addition of fibres.

Figures 5a.9 & 5a.10 show the variation of loss factor with temperature for various weight fractions of the fibre. It is found that the introduction of fibres reduces the loss factor. Hence 10 % nylon fibre/PP composite is found to display all-round properties.

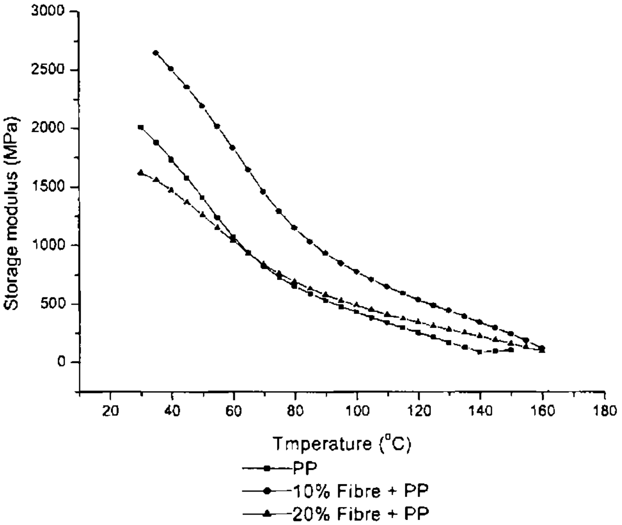

Figure 5b.7 Variation of storage modulus of nylon fibre/PP composite with temperature at different fibre content

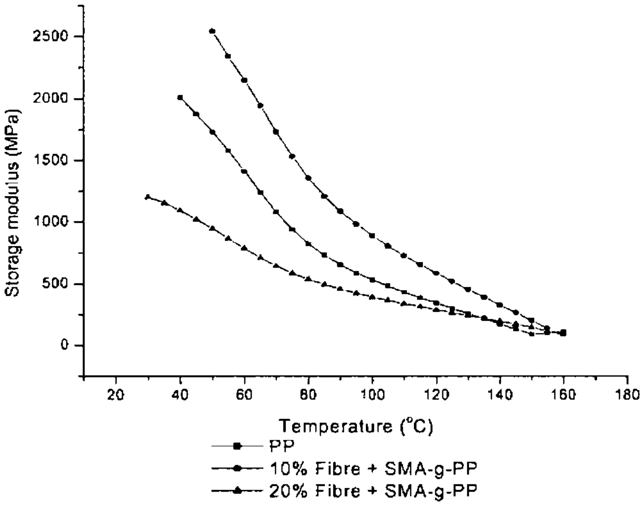

Figure 5a.8 Variation of storage modulus of nylon fibre/SMA-g-PP composite with temperature at different fibre content

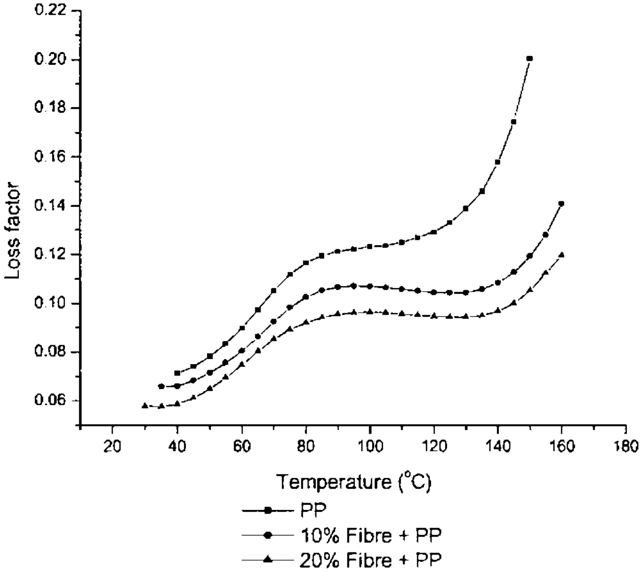

Figure 5a.9 Variation of loss factor of nylon fibre/PP composite with temperature at different fibre content

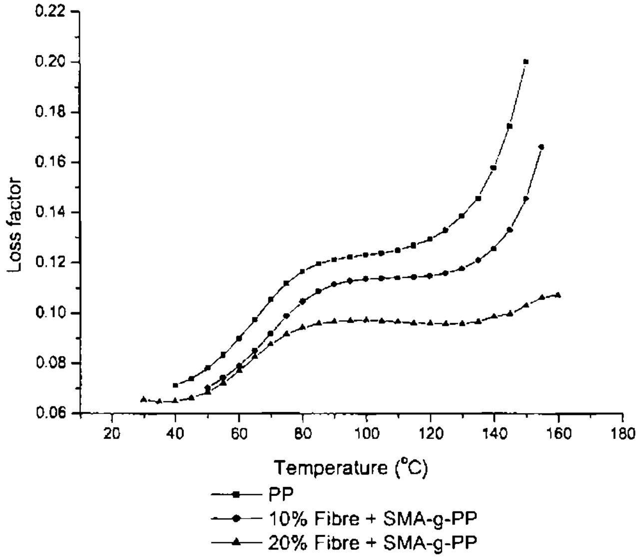

Figure 5a.10 Variation of loss factor of nylon fibre/SMA-g-PP composite with temperature at different fibre content

Chapter 5

Thermal Behaviour of Recyclable Short Nylon Fibre Reinforced Thermoplastic Composites

Part B. *Thermal behaviour of recyclable short nylon fibre reinforced high density polyethylene composites*

5b Introduction

This section describes thermal degradation behaviour of nylon fibre/HDPE composite and nylon fibre/SMA-g-HDPE.

5b.1 Experimental

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) was done using TGA Q50 (TA Instruments) at a heating rate of 10 °C/min from room temperature to 600°C with 10-12 g of sample, in a nitrogen atmosphere. Differential Scanning Calorimetry DSC Q100 (TA Instruments) equipped with a RCS cooling system was used to study thermal transitions in the samples at different cooling rates. the sample weight was between 7 and 10 mg. A dynamic mechanical analyser DMA Q800 (TA Instruments) was made use of for measuring the storage modulus and mechanical damping (tan δ).

5b.2 Results and discussion

5b.2.1 Thermo Gravimetric Analysis (TGA)

The TG and DTG curves of neat HDPE, nylon fibre and nylon fibre/HDPE composites [19] are given in Figures 5b.1 & 5b.2. Thermal decomposition of each samples takes place in a programmed temperature range of 30-600 °C. The temperature of onset of degradation (T_i), the temperature at which rate of decomposition is 50 %, the temperature at which the rate of decomposition is maximum (T_{max}), the peak degradation rate and the residue at 600 °C are given in Table 5b.1. HDPE degrades in a single step. The degradation starts at a temperature of 337 °C and the peak rate of degradation is 2.283 %/min at corresponding (T_{max}) of 481 °C. Neat nylon fibre also degrades in single step with peak rate of degradation 2.058 %/min and corresponding temperature of 464 °C. Residue at 600 °C is 0.35 % for the fibre. From the figure it can be seen that nylon fibre/HDPE composite also shows almost similar degradation pattern as that of the matrix alone as in the case of nylon fibre/PP composite. The onset of degradation of nylon fibre/HDPE composite increases from 337 to 358 °C, indicating improved thermal stability of the composites.

The temperature of 50 % degradation of the modified nylon fibre/HDPE composite is decreased from 471 to 458 °C, the peak rate of decomposition decreased 2.283 to 2.114 %/min and the corresponding temperature (T_{max}) increases from 481 to 487 °C.

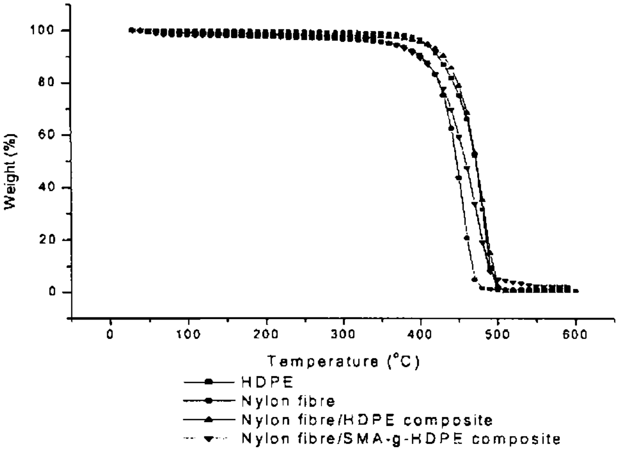

Figure 5b.1 Thermogravimetric traces of HDPE, nylon fibre, nylon fibre/HDPE composite & nylon fibre/SMA-g-HDPE composite

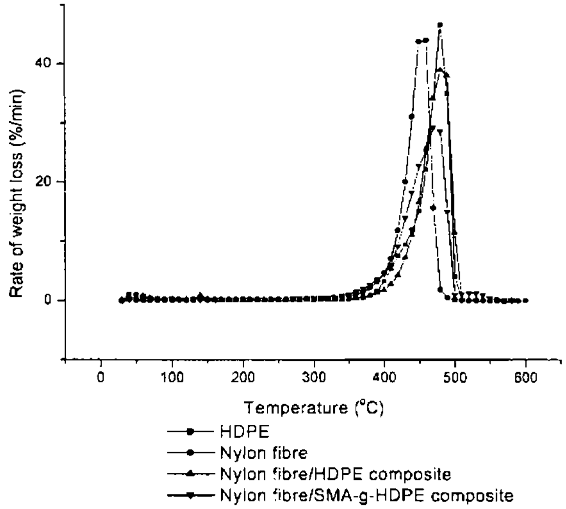

Figure 5b.2 Differential thermogravimetric traces of HDPE, nylon fibre, nylon fibre/HDPE composite & nylon fibre/SMA-g-HDPE composite

Table 5b.1 Degradation characteristics of HDPE, nylon fibre & nylon fibre/ HDPE composites.

Sample	T_i (°C) Onset	Temp at 50% Loss (°C)	Residue at 600 °C (%)	Peak rate of decomposition (%/min)	Peak Temp. (Tmax) (°C)
HDPE	337	471	0.504	2.283	481
Nylon Fibre	368	454	0.355	2.058	464
HDPE/Nylon Composite	358	471	0.552	2.045	487
SMA-g-HDPE/Nylon Composite	344	458	2.37	2.114	487

The order of degradation was calculated by Freeman-Carroll method using the equation (5a.1)

The order of the reaction and the activation energies can be obtained from the intercept and gradient of the plot of the left hand side of equation (2) versus $\Delta(1/T)/\ \Delta \log W_r$ and such plots are given in Figure5b.3. The intercepts show that the degradation of HDPE and composites follow the second order kinetics as in the case of nylon fibre/PP composites.

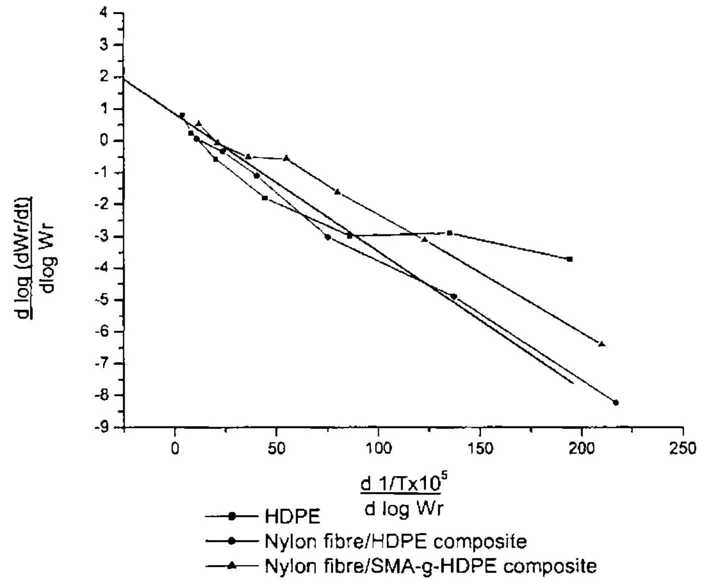

Figure 5b.3 Freeman-Caroll plots for HDPE, nylon fibre/HDPE & nylon fibre/SMA-g-HDPE

5b.2.2 Differential Scanning Calorimetry (DSC)

The DSC curves of HDPE, nylon fibre/HDPE composites and nylon fibre/SMA-g-HDPE composites at different cooling rates are depicted in Figure 5b.4, 5b.5 & 5b.7. These curves provide important parameters on the crystallization behaviour of the composites, such as peak temperature denoted as crystallization temperature (T_c), degree of crystallinity at X_c, crystallization enthalpy (ΔH). The crystallization temperatures of HDPE and nylon fibre/HDPE composites shifted to lower temperatures with increasing cooling rates as in the case of nylon fibre/PP composites [20]. At a given cooling rate, crystallization enthalpy of nylon fibre/HDPE composites were higher than that of HDPE, indicating that the addition of nylon fibre into PP increases the crystallization rate of PP (Table5b.2).

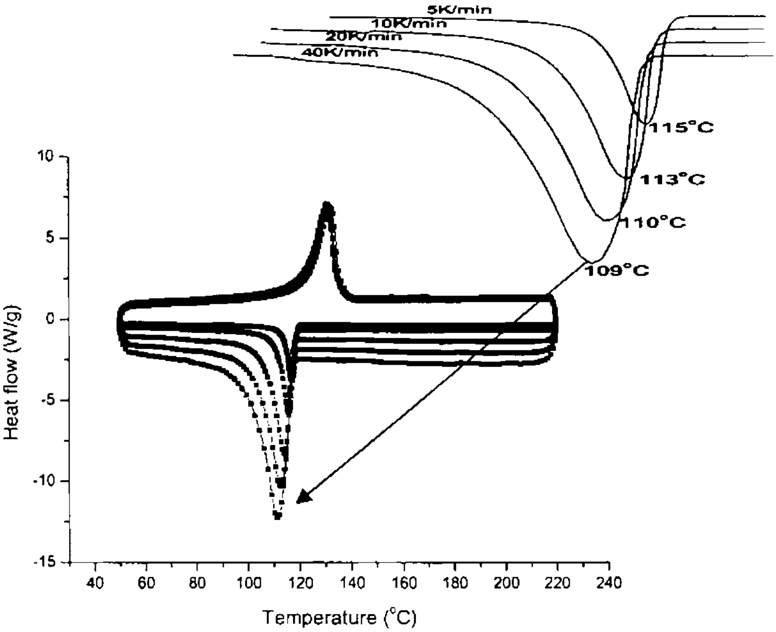

Figure 5b.4 DSC scans at different cooling rates for HDPE composite

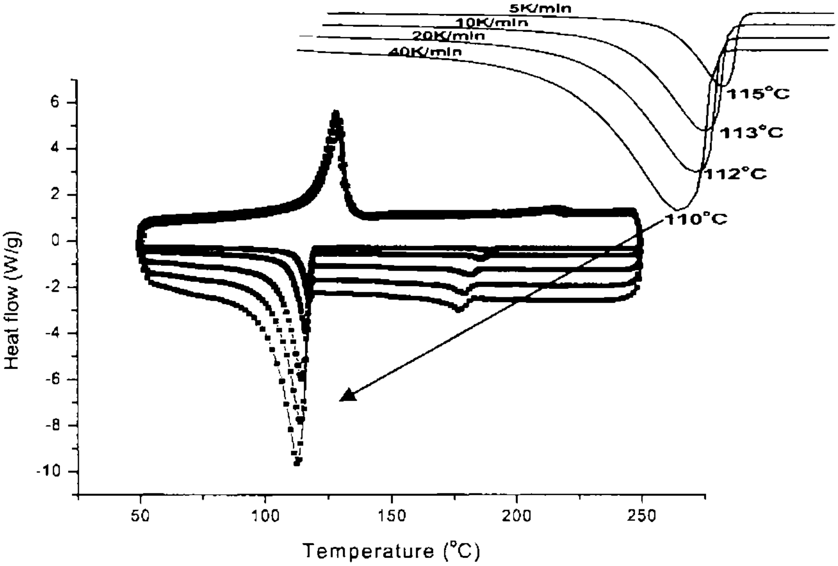

Figure 5b.5 DSC scans at different cooling rates for Nylon Fibre/HDPE Composite

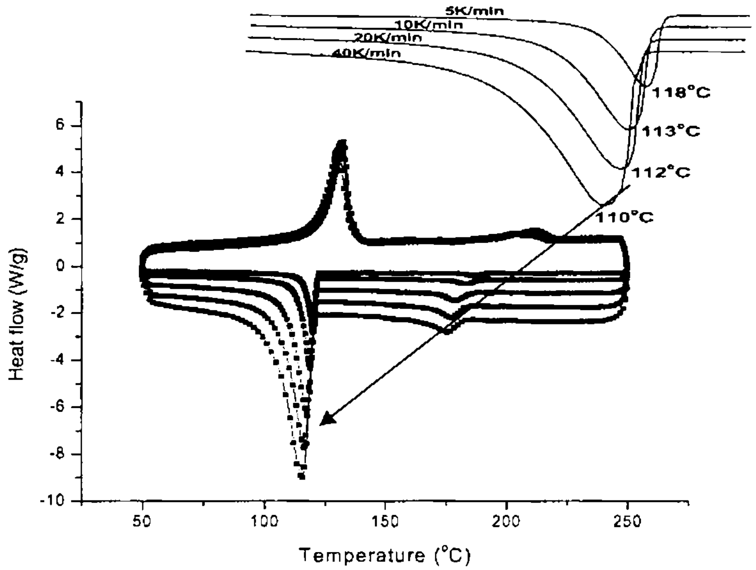

Figure 5b.6 DSC scans at different cooling rates for Nylon/SMA-g-HDPE composite

Table 5b.2 Effect of Nylon fibre on the crystallization parameters of HDPE

Sample	p (°C/min)	T_c (°C)	X_c (%)	ΔH (J/g)
HDPE	40	109.0	67	197
	20	112.0	63	185
	10	115.1	59	174
	5	117.0	57	169
Nylon fibre/HDPE composite	40	110.2	50	151
	20	113.4	47	140
	40	115.3	46	137
	5	117.6	45	134
Nylon fibre/SMA-g-HDPE composite	40	112.2	47	139
	20	115.0	47	138
	10	118.4	46	137
	5	120.4	44	130

p, cooling rate during nonisothermal crystallization;T_c, crystallization temperature; X_c, degree of crystallinity ;ΔH, crystallization enthalpy.

5b.2.3 Dynamic Mechanical Analysis (DMA)

In figures 5b.7 & 5 b.8 the variation of storage modulus (E') at different weight fractions of the fibre is shown as a function of temperature. It can be seen from the figure that the E' of HDPE is lower than that of the nylon fibre/HDPE composite. With the addition of the nylon fibre, the E' values are also increased. This is due to the reinforcement imparted by the fibre that allows stress transfer from the matrix to the fibre. The E' value of the composite is found to be decreased after the addition of 20% fibre as in the case of nylon fibre/PP composite.

Figures 5b.9 & 5b.10 shows the variation of loss factor with temperature for various weight fractions of the fibre. It is seen that the introduction of fibres reduces the value of loss factor. The composite containing 10% fibre is most efficient for carrying dynamic loads as in the case of the nylo fibre/PP composites.

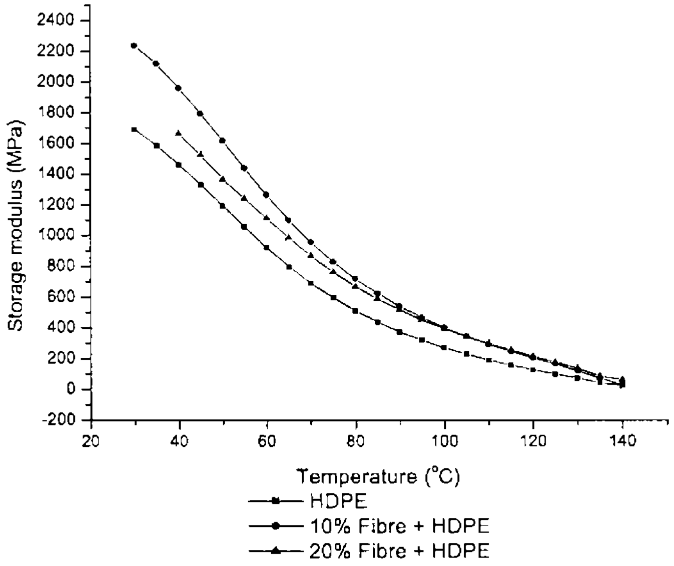

Figure 5b.7 Variation of storage modulus of nylon fibre/HDPE composite with temperature at different fibre content

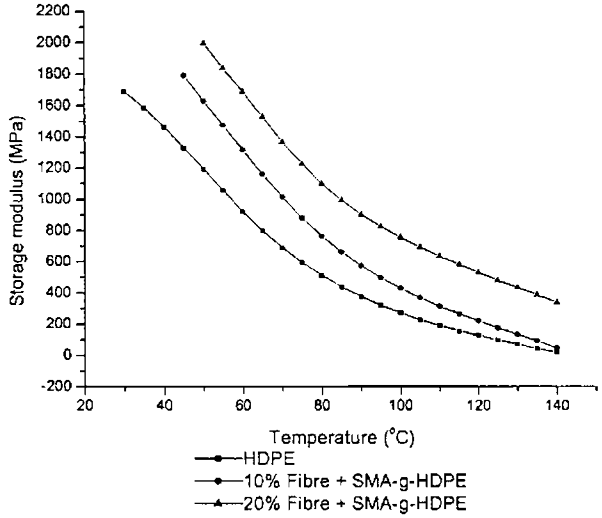

Figure 5b.8 Variation of storage modulus of nylon fibre/SMA-g-HDPE composite with temperature at different fibre content

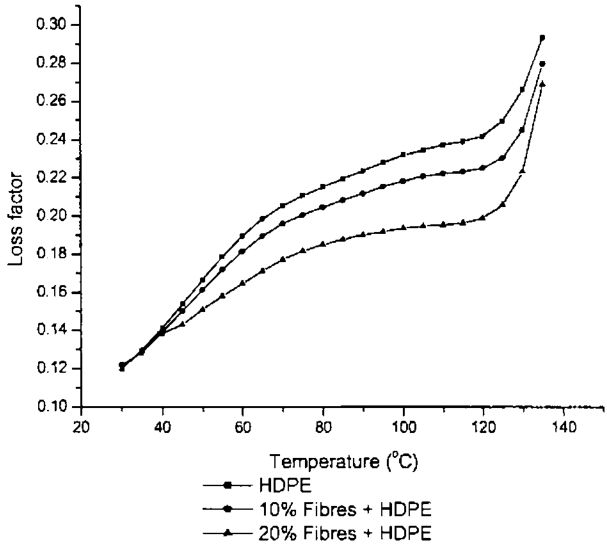

Figure 5b.9 Variation of loss factor of nylon fibre/HDPE composite with temperature at different fibre content

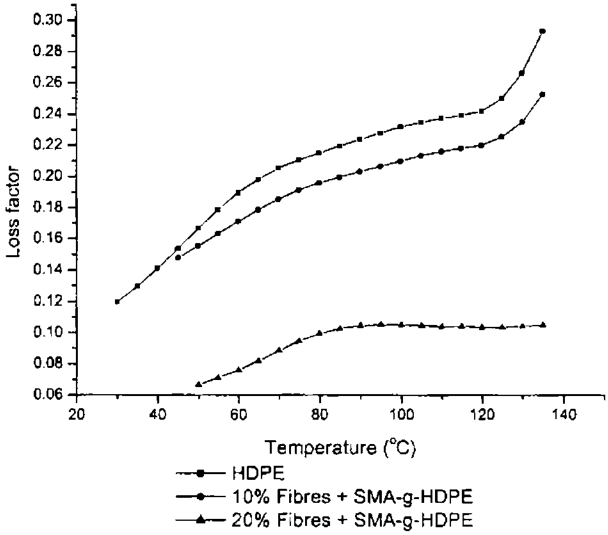

Figure 5b.10 Variation of loss factor of nylon/SMA-g-HDPE composite with temperature at different fibre content

Conclusions

The following conclusions can be drawn from the thermal behaviour of nylon fibre/PP and nylon fibre/HDPE composites.

- Thermogravity shows that matrix and fibre have similar single step degradation behaviour and the same differential thermogravimetric peaks. The thermal degradation behaviour of the composite follows that of matrix and fibre even though the onset of thermal degradation marginally increase with fibre addition.
- The DSC curve shows the nucleating effect of nylon fibres. While there is only marginal increase in the crystallization temperature of the matrix in the unmodified composite, there is a moderate increase in the crystallization temperature with chemical modification.
- DMA of the composite shows that the composite containing 10 % fibre to be capable of taking higher dynamic stress than the matrix with increase in storage modulus and decrease in loss factor.

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Chapter 6

Recyclability of Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. ***Recyclability of short nylon fibre reinforced polypropylene composites***

6a.1 Introduction
6a.2 Low temperature recycling
6a.2.1 Experimental
6a.2.2 Results and discussion
6a.2.3 Effect of low temperature recycling on tensile properties
6a.3 High temperature recycling
6a.3.1 Experimental
6a.3.2 Results and discussion
6a.3.3 Effect of high temperature recycling on tensile properties
6a.3.4 Thermo Gravimetric Analysis of the recycled sample
6a.4 Effect of using process-waste nylon fibres on the mechanical properties of the nylon fibre/PP Composite
6a.4.1 Experimental
6a.4.2 Results and discussion

Part B. ***Recyclability of short nylon fibre reinforced high density polyethylene composites***

6b.1 Introduction
6b.2 Experimental
6b.3 Results and discussion
6b.3.1 Effect of low temperature recycling on mechanical properties
6b.3.2 Effect of high temperature recycling on mechanical properties
6b.3.3 Thermo Gravimetric Analysis of the recycled sample

Chapter 6

Recyclability of Short Nylon Fibre Reinforced Thermoplastic Composites

Part A. *Recyclability of short nylon fibre reinforced polypropylene composites*

6a.1 Introduction

Composites, consisting of an association of a polymeric matrix and a synthetic filler (e.g., glass fibre, silicium carbide, carbon, or aramid) as reinforcement have been used increasingly in all material fields (automotive, packaging, construction etc.) because of the combination of their high performance and great versatility. Fibre reinforced polymer composites are very attractive because of their ease of fabrication, economy and superior mechanical properties [1]. Extrusion, compounding and injection moulding processes are frequently employed to make polymer composites [2]. The effect of fibre content on the mechanical properties of polymer composites is of particular interest and significance. It is often observed that the increase in fibre content leads to an increase in the strength and modulus [3-4]. However, current environmental problems caused by a concentration of these products in waste areas, their partial combustibility, and the increasing demand for techniques for recycling made a remarkable drop in the projected growth rate of glass reinforced thermoplastic composite [5-13]. Studies of blends and composites using recycled PET have been carried out with several polymeric materials, like polyethylene and polystyrene [14-15]. Blends of PET and PP-co-MA are also reported [16].

In this section, recyclability of the composites described in earlier chapter is considered. Two modes of recycling are proposed.

- Recycling of the matrix without melting the fibres at a temperature above the melting point of matrix, but below that of the fibre (low temperature recycling).
- Recycling of both the matrix and fibre at a temperature above the melting point of both the matrix and fibre (high temperature recycling).

The effect of using process-waste nylon fibres to reinforce the polypropylene matrix were also investigated.

6a.2 Low temperature recycling

6a.2.1 Experimental

The composites were again mixed in the Thermo Haake Rheocord 600. This time temperature was kept at 180 °C. The tensile properties of the samples were determined using dumb-bell shaped samples using universal testing machine (Shimadzu) at a crosshead speed of 50 mm/min according to ASTM-D-638. The morphology of the tensile fractured surfaces were investigated using Scanning Electron Microscope (SEM).

6a.2.2 Results and discussion

6a.2.3 Effect of recycling on tensile properties

Figures 6a.1 & 6a.2 show the tensile strength of the nylon fibre/PP composites after three times recycling. It can be observed that tensile strength remains constant even after three times of recycling [17]. There is also marginal increase in the tensile strength in some cases, which may be due to improved orientation of fibres. In the case of modified polypropylene composites there is a decrease in the strength especially during third recycling. The higher values of tensile strength in both cases indicates that the nylon fibres are not melted and still acts as reinforcement for the polypropylene matrix. Scanning electron micrographs (Figures 6a.3 & 6a.4) of the tensile fractured surfaces prove that the nylon fibres are not melted at low temperature recycling.

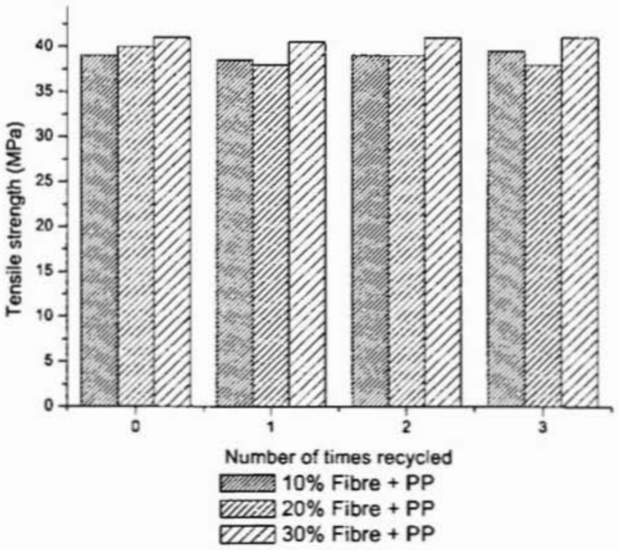


Figure 6a.1 Variation of tensile strength on recycling

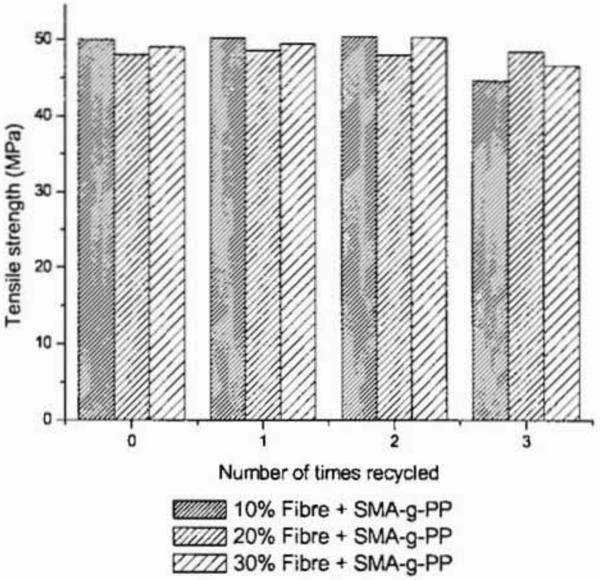


Figure 6a.2 Variation of tensile strength on recycling

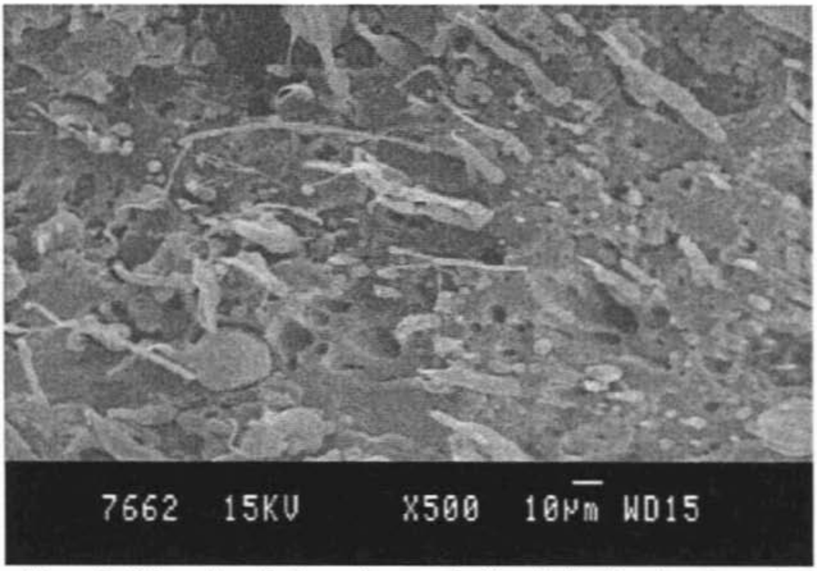


Figure 6a.3 Scanning electron micrograph of tensile fractured surface of Nylon fibre/PP composite recycled at low temperature

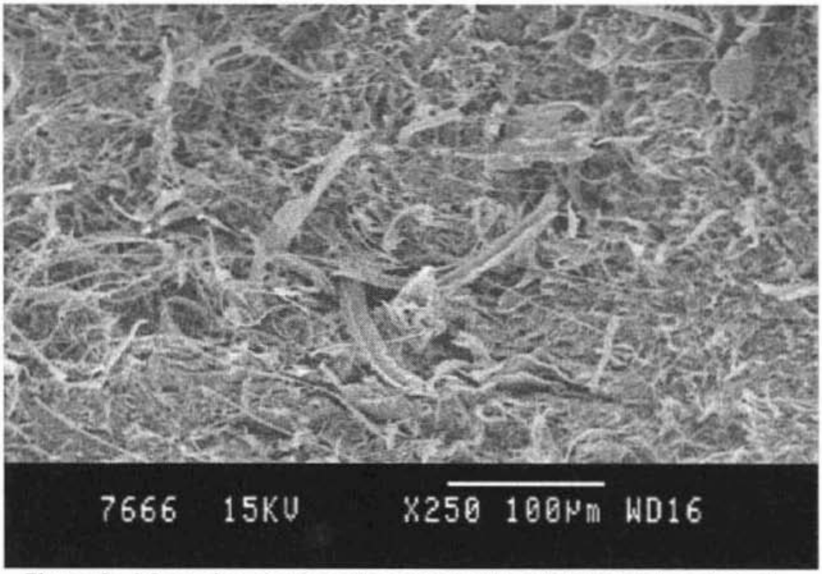


Figure 6a.4 Scanning electron micrograph of tensile fractured surface of Nylon fibre/SMA-g-PP composite recycled at low temperature

6a.3 High temperature recycling

6a.3.1 Experimental

The composites were again mixed in the Thermo Haake Rheocord 600. This time temperature was kept at 220 °C which is sufficient to melt the nylon fibres at the shear employed. The tensile properties of the samples were determined using dumb-bell shaped specimens using the universal testing machine (Shimadzu) at a crosshead speed of 50 mm/min according to ASTM-D-638. The morphology of the tensile fractured surfaces were investigated using Scanning Electron Microscope (SEM). Thermal degradation of the recycled samples were measured by Thermo Gravimetric Analysis (TGA).

6a.3.2 Results and discussion

6a.3.3 Effect of recycling on tensile properties

Figures 6a.7 & 6a.8 show the tensile strength results of the nylon fibre/PP composites after three times recycling. In the case of high temperature recycling the nylon fibre also gets melted resulting in the formation of nylon/PP blend. So in the first cycle there is drastic reduction in strength due to the disintegration of the fibre. However, there is not much reduction in strength in subsequent recycling showing that matrix is not severely affected by recycling. It can be clearly understood from the figure that tensile strength remains constant even after three times recycling. In the case of modified polypropylene composites there is a more drastic reduction in the first cycle due to the large drop in strength from modified fibre composite to a blend. However, there is no considerable decline in strength during subsequent recycling as in the case of the unmodified composites. SEM photographs (Figures 6a.9 & 6a.10) of the tensile fractured surfaces prove that the nylon fibres were melted at high temperature recycling. The difference in the morphology of the unmodified and modified blend is also evident from the Scanning electron micrographs of the fracture surfaces.

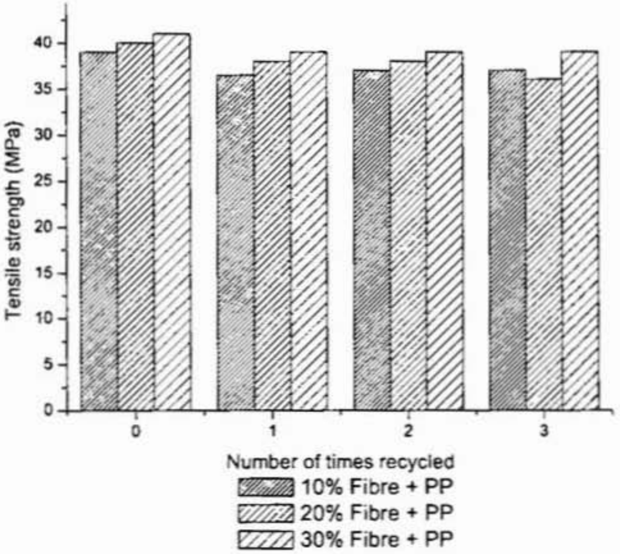


Figure 6a.7 Variation of tensile strength on recycling

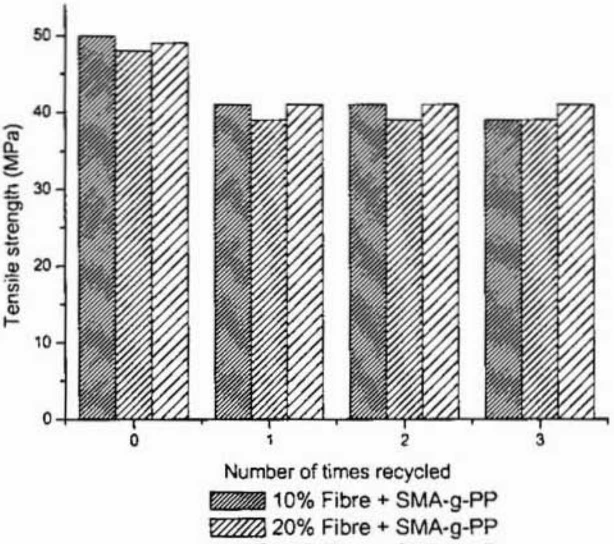


Figure 6a.8 Variation of tensile strength on recycling

6a.3.4 Thermo Gravimetric Analysis of the recycled sample

Figure 6a.12 shows the DTG curves of nylon/ fibre/PP composites compared with recycled nylon fibre/PP composite. From the figure it is clear that the rate of weight loss of the recycled composite remains same indicating that recycling does not affect thermal stability.

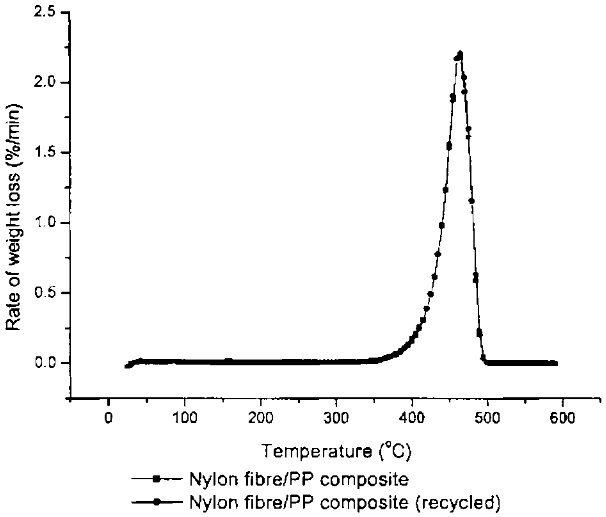


Figure 6a.12 Differential thermogravimetric traces of Nylon fibre/PP composite & Nylon fibre/PP composite (Recycled)

Figure 6a.13 shows the DTG curves of nylon fibre/SMA-g-PP composites compared with recycled nylon fibre/SMA-g-PP composite. The rate of weight loss of the recycled composite is lower than that of the composite without recycling. This indicates that the thermal stability of the modified composite gets lowered during recycling at higher temperature.

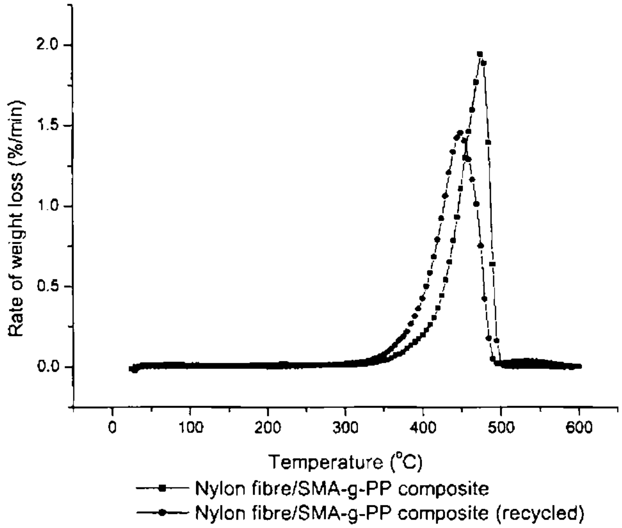


Figure 6a.13 Differential thermogravimetric traces of Nylon fibre/SMA-g-PP composite & Nylon fibre/SMA-g-PP composite (Recycled)

Table 6a.2 Degradation characteristics of recycled composites

Sample	T_i (°C) Onset	Temp. 50% Loss(°C)	Residue at 600 (°C)	Peak rate of decomposition (%/min)	Peak Temp. (°C)
PP/Nylon Composite	382	457	0.394	2.172	462
SMA-g-PP/Nylon Composite	347	461	1.266	1.915	477
PP/Nylon Composite (Recycled)	365	457	0.509	2.138	463
SMA-g-PP/Nylon Composite (Recycled)	349	442	1.623	1.428	448

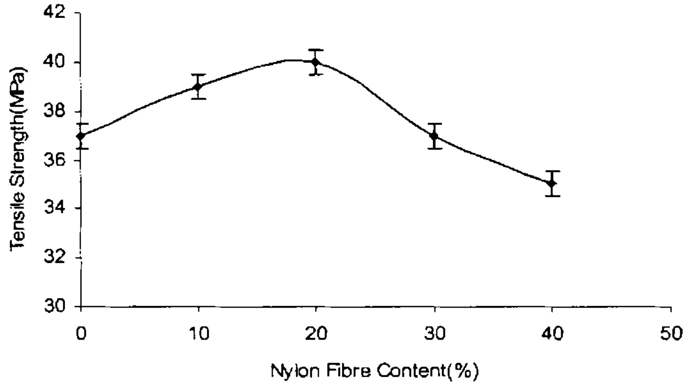
6a.4 Effect of using process-waste nylon fibres on the mechanical properties of the Nylon/PP Composite

6a.4.1 Experimental

Composites were prepared using polypropylene homopolymer (PP) (REPOL H200MA, Reliance Industries Ltd), with a melt flow index of 20 g/10 min (230 °C/2.16 kgf) and nylon fibres of diameters 0.25 mm from Covema Industries, CSEZ, Kochi. Styrene-maleic anhydride (SMA) grafted polypropylene was also prepared in accordance with the procedures given in US Patent 4,753,997. The continuous nylon fibres were cut into staples, so that the fibres used as reinforcement had an average length of 8+/- 2 mm. The tensile properties of the samples were determined using dumb-bell shaped specimens on a universal testing machine (Shimadzu) at a crosshead speed of 50 mm/min according to ASTM-D-638. The flexural properties were determined at a crosshead speed of 5 mm/min (ASTM-D-790) using the universal testing machine. The composites were again mixed in the Thermo Haake Rheocord 600. This time temperature was kept at 220 °C which is sufficient to melt the nylon fibres at the shear provided.

6a.4.2 Results and discussion

Figures 6a.11 & 6a.12 show the variation of tensile strength of PP reinforced with process-waste nylon fibres. There is a slight increase in the tensile strength up to the addition of 20 % nylon fibre. In the case of the flexural strength also, composites containing 20% nylon fibre shows maximum improvement.



Fiaure 6a.11 Variation of tensile strenath with fibre content

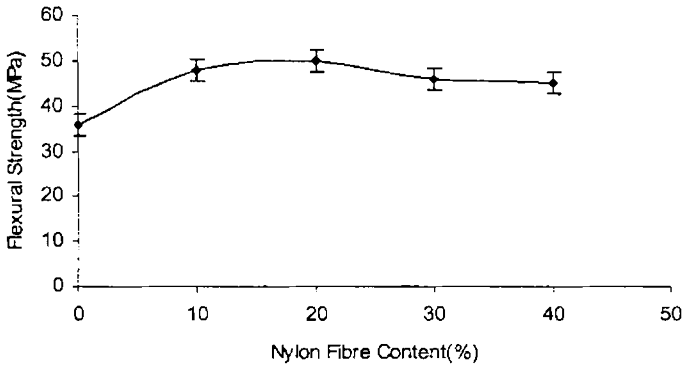


Figure 6a.12 Variation of flexural strength with fibre content

Table 6a.1 shows the improvement in the tensile and flexural properties of the composite as a result of the matrix modification. There is a significant improvement in the mechanical properties after matrix modification. The mechanical properties of the recycled samples also show superior properties than that of matrix alone.

Table 6a.1 Mechanical properties of recycled process- waste nylon fibres/PP composite

Property	PP	PP+20% fibre	SMA-g-PP +20% fibre	SMA-g-PP +20% fibre (Recycled)
Tensile strength (MPa)	37	40	45	38
Flexural strength (MPa)	36	51	60	54

Chapter 6

Recyclability of Short Nylon Fibre Reinforced Thermoplastic Composites

Part B. *Recyclability of short nylon fibre reinforced high density polyethylene composites*

6b.1 Introduction

Recyclability is the major attraction of these composites having both the matrix and reinforcement based on polymers. For checking the recyclability of the composites the tensile and flexural samples were mixed again in the Thermo Haake Rheocord 600. Samples remoulded at a temperature below the melting point of nylon (low temperature) show mechanical properties higher than those of virgin HDPE indicating that fibres continue to reinforce the matrix. Samples remoulded at a temperature higher than the melting point of nylon(high temperature) also show mechanical properties higher than those of virgin HDPE due to the formation of HDPE/nylon blends.

6b.2 Experimental

The tensile properties of the samples were determined using dumb-bell shaped specimens on a universal testing machine (Shimadzu) at a crosshead speed of 50 mm/min according to ASTM-D-638. The morphology of the tensile fractured surface was investigated using Scanning Electron Microscope (SEM). Thermal stability of the recycled samples was measured by Thermo Gravimetric Analysis (TGA).

6b.3 Results and discussion

6b.3.1 Effect of low temperature recycling on tensile properties

Figures 6b.1, 6b.2, 6b.3 & 6b.4 show the tensile strength and tensile modulus results of the nylon fibre/HDPE composites after three times recycling at a temperature of 180 °C. It can be observed from the figure that tensile strength remains constant even after three times of recycling [18]. In the case of modified high density polyethylene composites there is a decrease in the strength during third recycling. These observations are similar to nylon fibre/PP composite. Scanning electron micrographs (Figures 6b.5 to 6b.8) of the tensile fractured surfaces prove that the nylon fibres were not melted at low temperature recycling.

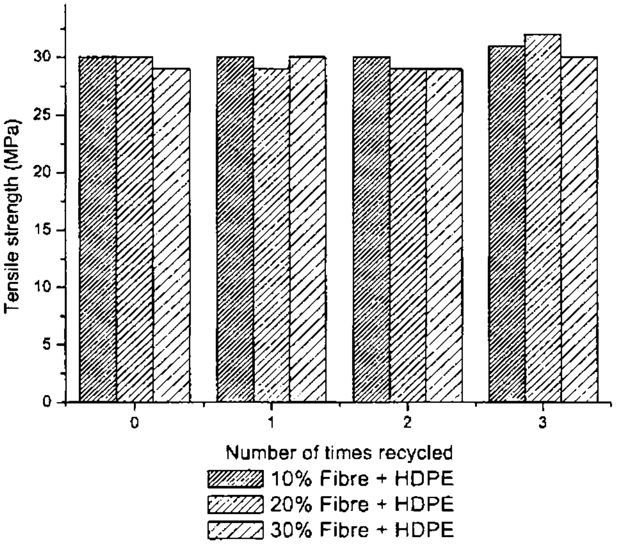


Figure 6b.1 Variation of tensile strength on recycling

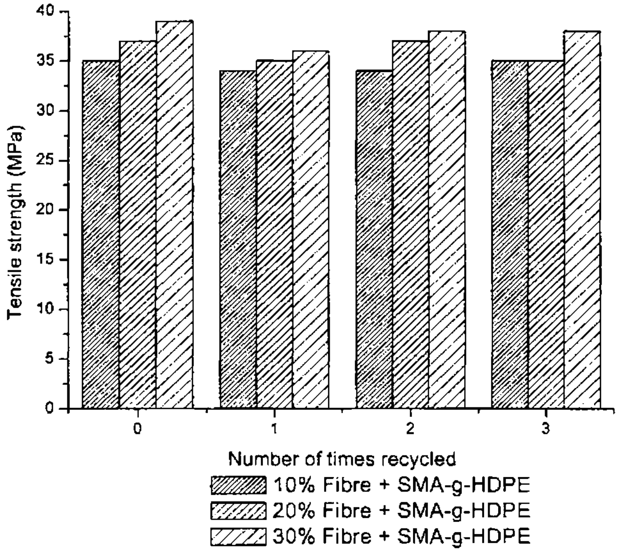


Figure 6b.2 Variation of tensile strength on recycling

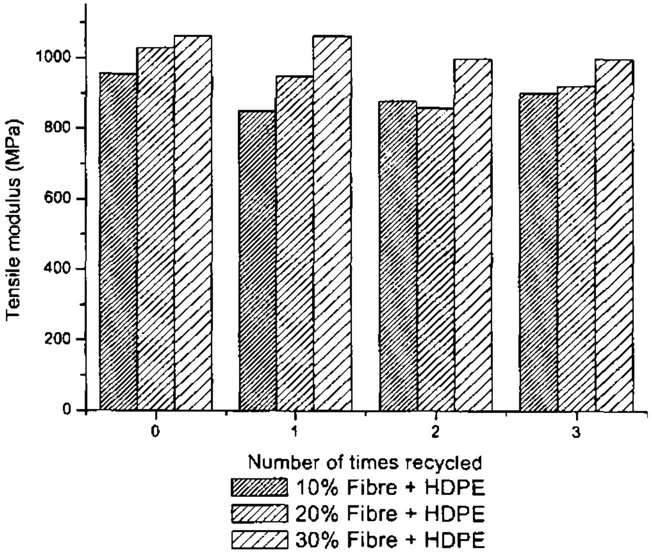


Figure 6b.3 Variation of tensile modulus on recycling

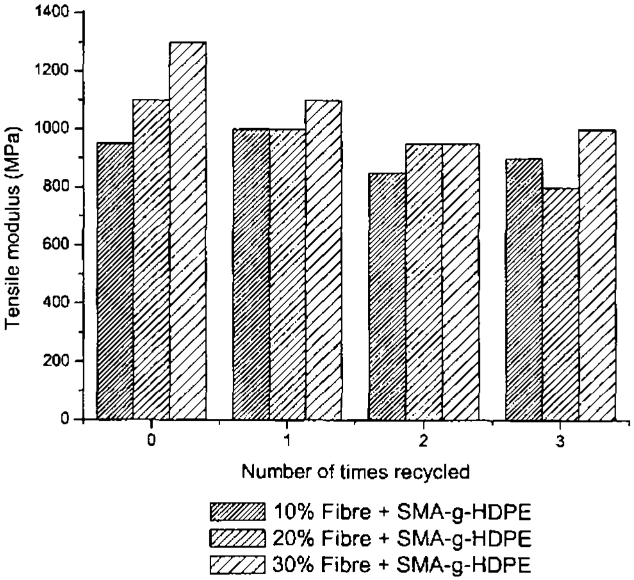


Figure 6b.4 Variation of tensile modulus on recycling

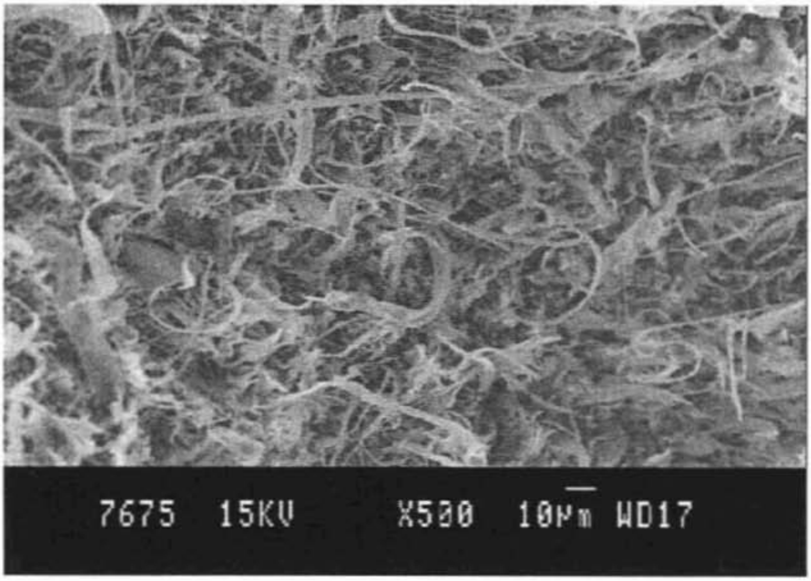


Figure 6b.5 Scanning electron micrograph of tensile fractured surface of nylon fibre/ HDPE composite recycled at low temperature (Higher magnification)

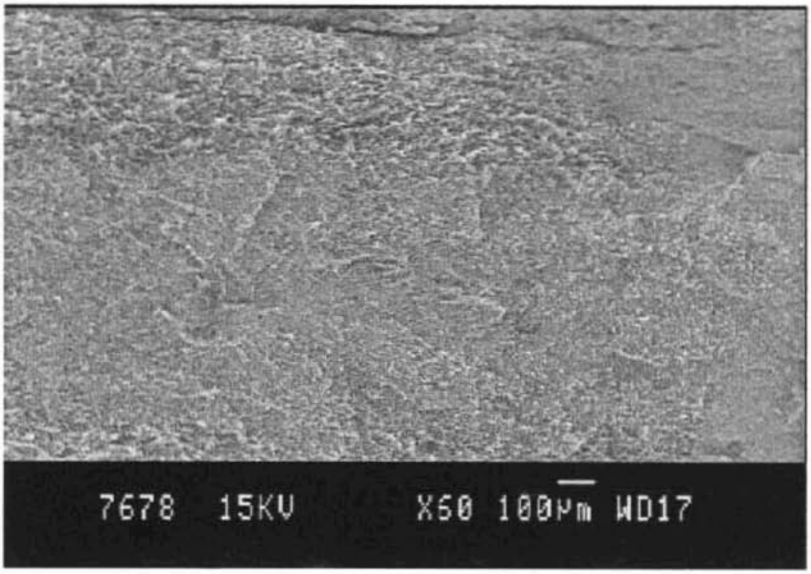


Figure 6b.6 Scanning electron micrograph of tensile fractured surface of nylon fibre/HDPE composite recycled at low temperature (Lower magnification)

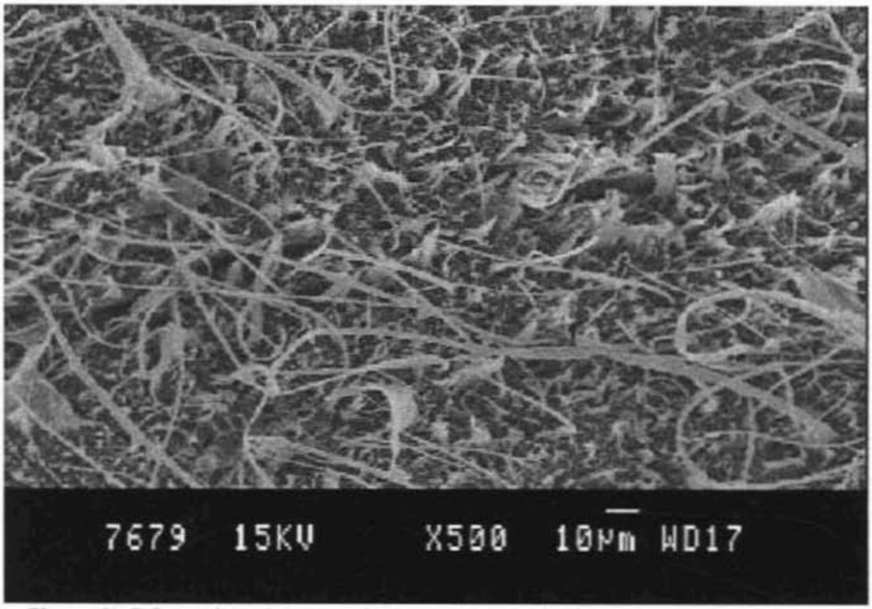


Figure 6b.7 Scanning electron micrograph of tensile fractured surface of nylon fibre/ SMA-g-HDPE composite recycled at low temperature (Higher magnification)

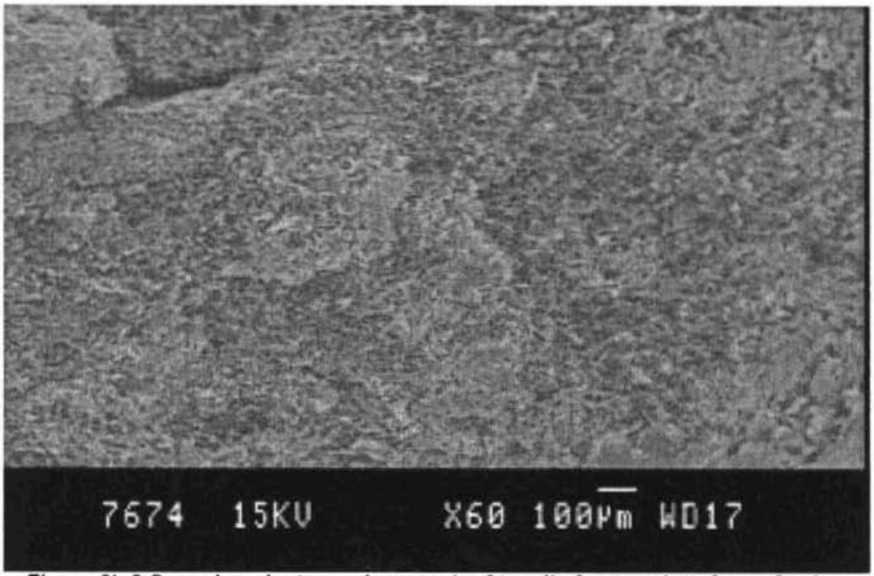


Figure 6b.8 Scanning electron micrograph of tensile fractured surface of nylon fibre/ SMA-g-HDPE composite recycled at low temperature (Lower magnification)

6b.3.2 Effect of high temperature recycling on tensile properties

Figures 6b.9, 6b.10, 6b.11 & 6b.12 show the tensile strength results of the nylon fibre/HDPE composites after three times recycling at a temperature of 220 °C. In the case of high temperature recycling the nylon fibre also gets melted resulting in the formation of nylon fibre/HDPE blend. The strength of nylon fibre/HDPE blend is lower than nylon fibre/HDPE composite. This may be due to the melting of the reinforcing fibre. The strength of the Nylon/HDPE blend is found to be remaining constant during continuous moulding. In the case of modified HDPE composites also there is decrease in the strength during recycling. These observations are the same as in the case of nylon fibre/PP composite. SEM photographs (Figure 6b.13 to 6b.16) of the tensile fractured surfaces confirm that the nylon fibres were melted and the formation of nylon/HDPE blends at high temperature recycling.

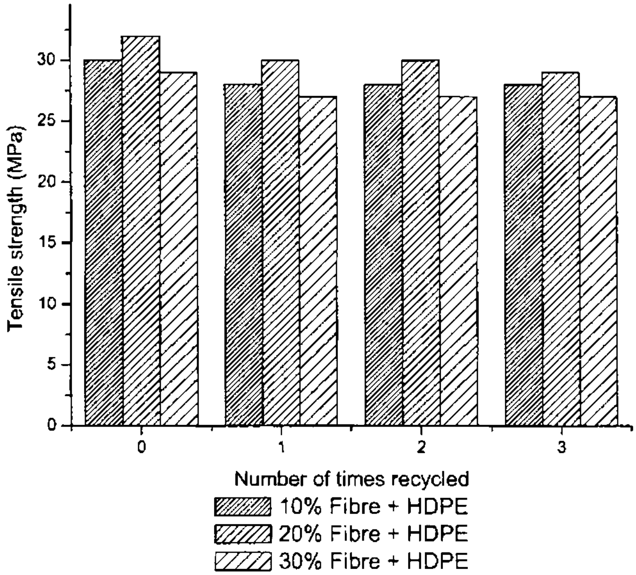


Figure 6b.9 Variation of tensile strength on recycling

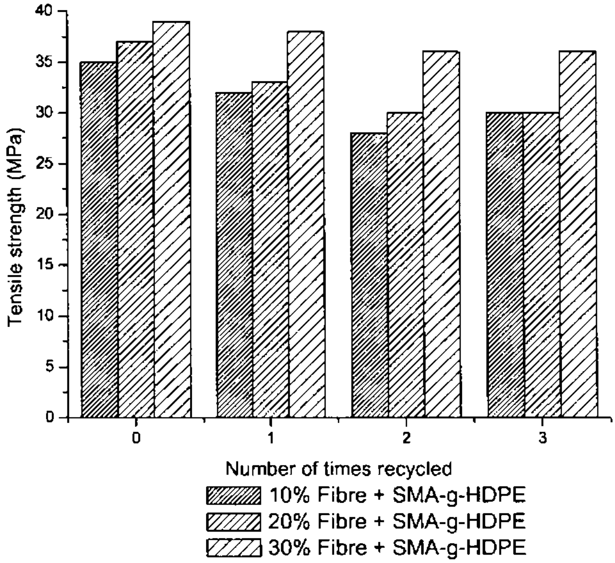


Figure 6b.10 Variation of tensile strength on recycling

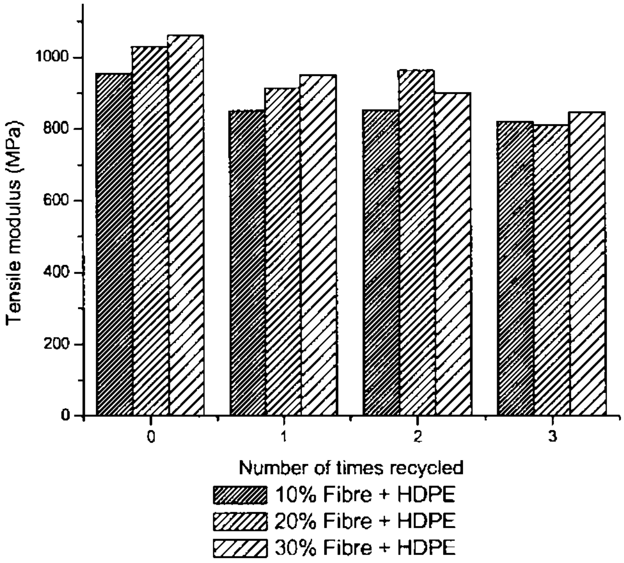


Figure 6b.11 Variation of tensile modulus on recycling

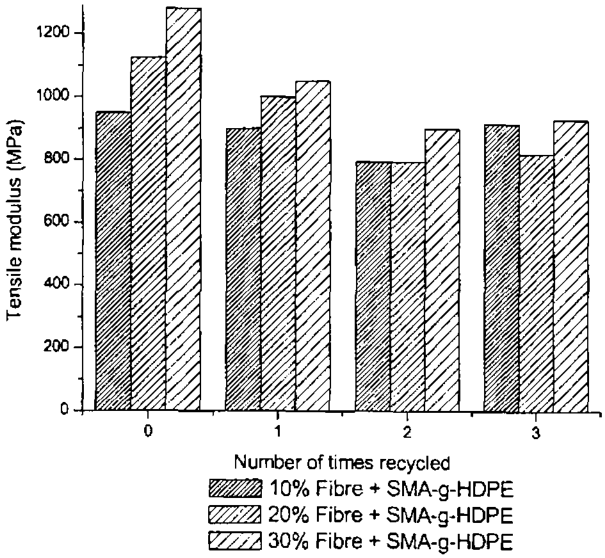


Figure 6b.12 Variation of tensile modulus on recycling

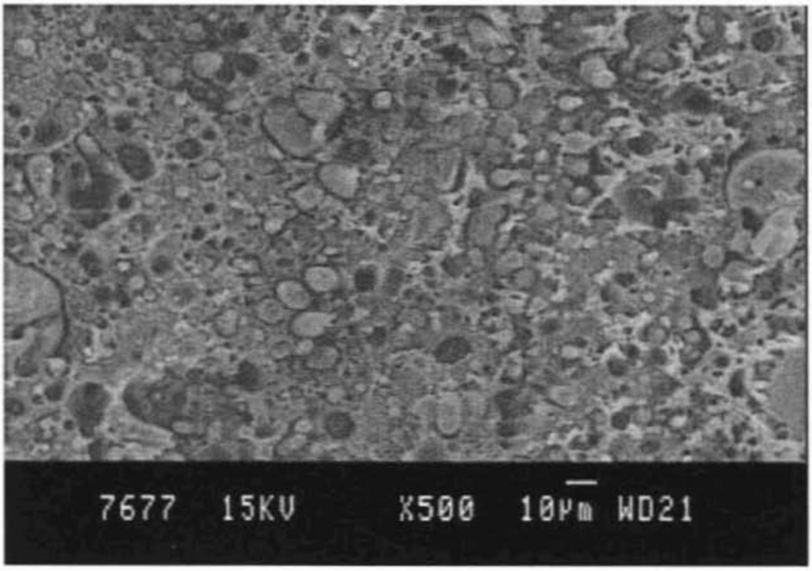


Figure 6b.13 Scanning electron micrograph of tensile fractured surface of nylon fibre/HDPE composite recycled at high temperature (Higher magnification)

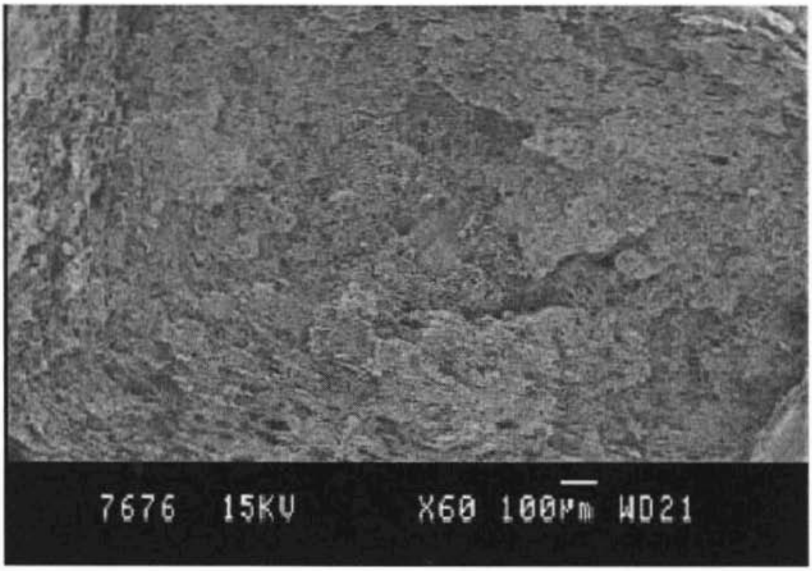


Figure 6b.14 Scanning electron micrograph of tensile fractured surface of nylon fibre/HDPE composite recycled at high temperature (Lower magnification)

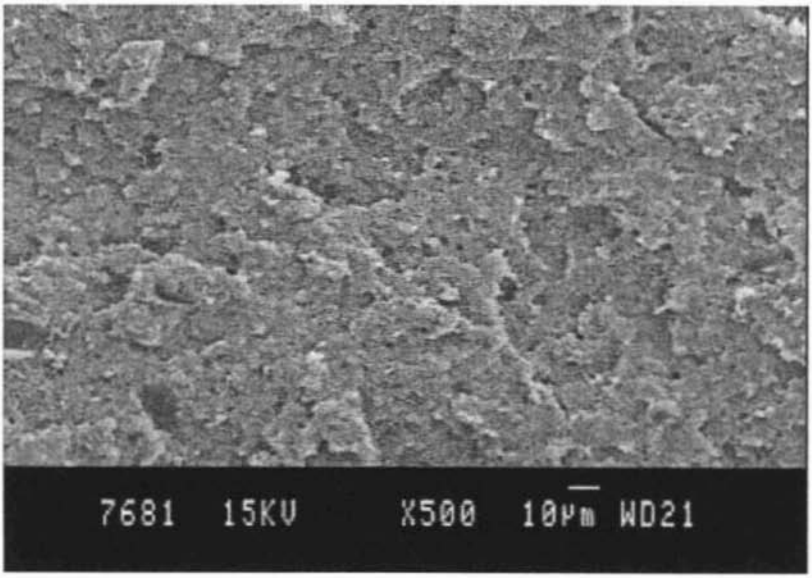


Figure 6b.15 Scanning electron micrograph of tensile fractured surface of nylon fibre/SMA-g-PP composite recycled at high temperature (Higher magnification)

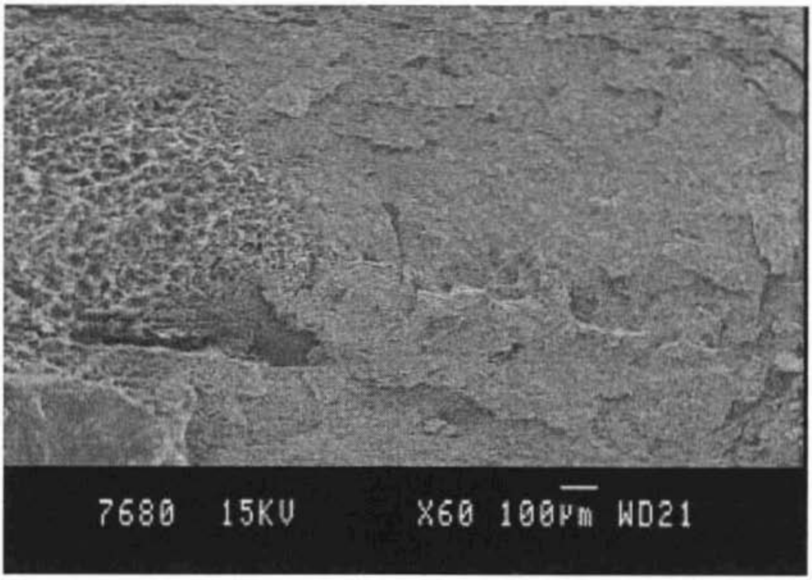


Figure 6b.16 Scanning electron micrograph of tensile fractured surface of nylon fibre/SMA-g-PP composite recycled at high temperature (Lower magnification)

6b.3.3 Thermo Gravimetric Analysis of the recycled sample

Figure 6b.17 shows the thermo gravimetric curves of nylon fibre/HDPE composite and recycled nylon fibre/HDPE composite. From the figure it is clear that rate of weight loss of the recycled composite is remaining the same indicating the fine thermal stability same as in the case of nylon fibre/PP composite.

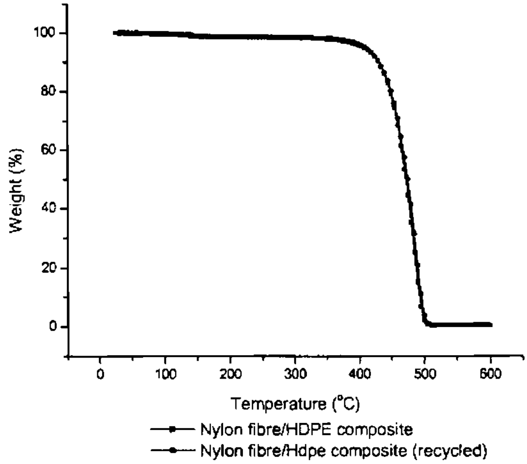


Figure 6b.17 Thermograms of Nylon fibre/HDPE & Nylon

Figure 6b.18 shows the thermo gravimetric curves of nylon/SMA-g-PP composite compared with recycled nylon/SMA-g-PP composite. The rate of weight loss of the recycled composite is lower than that of the composite without recycling. This indicates that the thermal stability of the modified composite gets lowered during recycling at higher temperature.

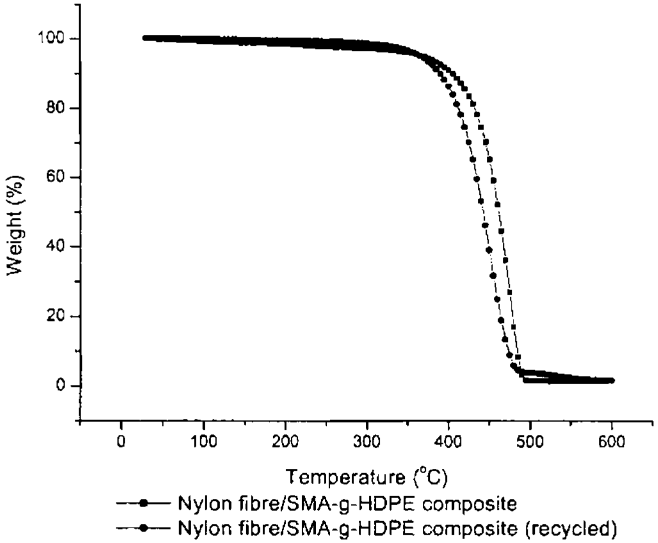


Figure 6b.18 Thermograms of Nylon fibre/SMA-g-HDPE & Nylon fibre/ SMA-g-HDPE (Recycled)

Table 6b.1 Degradation characteristics of recycled composites

Sample	T_i (°C) Onset	Temp. at 50% Loss(°C)	Residue at 600 (°C)	Peak rate of decomposition (%/min)	Peak Temp. (°C)
HDPE/Nylon Composite	365	466	0.5183	1.806	468
SMA-g-HDPE/Nylon Composite	335	489	1.425	1.873	485
HDPE/Nylon Composite (Recycled)	332	475	0.4914	2.045	487
SMA-g-HDPE/Nylon Composite (Recycled)	341	476	1.319	2.114	489

Conclusions

The recyclability is a major advantage of these composites. It is observed that,

- The strength of the composite remains the same or marginally increases with repetitive recycling at lower temperatures.
- The strength of the composite marginally decreases with repetitive recycling at higher temperatures. However, the strength of the recycled composite is superior to that of the matrix polymer.
- The scanning electron micrographs confirm that the fibre remains intact at the lower temperature recycling while they are melted at the higher temperature recycling.
- Polypropylene can be reinforced with process-waste nylon fibres as well.

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Chapter 7

Conclusions

The study shows that standard plastics like polypropylene and high density polyethylene can be reinforced by adding nylon short fibres. Compared to the conventional glass reinforced thermoplastics this novel class of reinforced thermoplastics has the major advantage of recyclability. Hence such composites represent a new spectrum of recyclable polymer composites. The fibre length and fibre diameter used for reinforcement are critical parameters. While there is a critical fibre length below which no effective reinforcement takes place, the reinforcement improves when the fibre diameter decreases due to increased surface area.

While the fibres alone give moderate reinforcement, chemical modification of the matrix can further improve the strength and modulus of the composites. Maleic anhydride grafting in presence of styrene was found to be the most efficient chemical modification. While the fibre addition enhances the viscosity of the melt at lower shear rates, the enhancement at higher shear rate is only marginal. This shows that processing of the composite can be done in a similar way to that of the matrix polymer in high shear operations such as injection moulding. Another significant observation is the decrease in melt viscosity of the composite upon grafting. Thus chemical modification of matrix makes processing of the composite easier in addition to improving the mechanical load bearing capacity.

For the development of a useful short fibre composite, selection of proper materials, optimum design with regard to the particular product and choosing proper processing parameters are most essential. Since there is a co-influence of many parameters, analytical solutions are difficult. Hence for selecting proper processing parameters 'mold flow' software was utilized. The orientation of the fibres, mechanical properties, temperature profile, shrinkage, fill time etc. were determined using the software.

Another interesting feature of the nylon fibre/PP and nylon fibre/HDPE composites is their thermal behaviour. Both nylon and PP degrade at the same temperature in single steps and hence the thermal degradation behaviour of the composites is also being predictable. It is observed that the thermal behaviour of the matrix or reinforcement does not affect each other. Almost similar behaviour is observed in the case of nylon fibre/HDPE composites. Another equally significant factor is the nucleating effect of nylon fibre when the composite melt cools down. In the presence of the fibre the onset of crystallization occurs at slightly higher temperature.

When the matrix is modified by grafting, the onset of crystallization occurs at still higher temperature. Hence it may be calculated that one reason for the improvement in mechanical behaviour of the composite is the difference in crystallization behaviour of the matrix in presence of the fibre.

As mentioned earlier, a major advantage of these composites is their recyclability. Two basic approaches may be employed for recycling namely, low temperature recycling and high temperature recycling. In the low temperature recycling, the recycling is done at a temperature above the melting point of the matrix, but below that of the fibres while in the high temperature route, the recycling is done at a temperature above the melting points of both matrix and fibre. The former is particularly interesting in that the recycled material has equal or even better mechanical properties compared to the initial product. This is possible because the orientation of the fibre can improve with successive recycling. Hence such recycled composites can be used for the same applications for which the original composite was developed. In high temperature recycling, the composite is converted into a blend and hence the properties will be inferior to that of the original composite, but will be higher than that of the matrix material alone.

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Curriculum Vitae

Thomas N Abraham was born in Kadayiruppu, Kerala, India on June 1st 1978. He took his bachelors degree (B.Sc) in Chemistry in 1999, and masters degree (M.Sc) in Chemistry with specialization in Polymer Science in 2002 from Mahatma Gandhi University. In September 2002, he joined the Polymer Recycling group at the Polymer Science and Rubber Technology Department of Cochin University of Science and Technology for his Ph.D under the supervision of Prof. Dr K.E. George.