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KENAF - REINFORCED POLYPROPYLENE
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KENAF - REINFORCED POLYPROPYLENE COMPOSITES

By

Rajeev Karnani

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ABSTRACT

KENAF-REINFORCED POLYPROPYLENE COMPOSITES

By

Rajeev Karnani

Natural fibers have an outstanding potential as a reinforcement in thermoplastics. This study deals with the preparation of kenaf reinforced polypropylene composites by reactive extrusion processing in which good interfacial adhesion is generated by a combination of fiber modification and matrix modification methods. PP matrix was modified by reacting with maleic anhydride and subsequently bonded to the surface of the modifried lignocellulosic component. The fiber surface was modified by reacting it with a silane in a simple and quick aqueous reaction system, similar to that employed for glass fibers. The modified fibers are then extruded with the modified polymer matrix to form the compatibilized composite. The various reactions between the kenaf fiber and maleated polypropylene (MAPP) chains, is expected to improve the interfacial adhesion significantly as opposed to simple mixing of the two components, since new covalent bonds between the fiber surface and matrix are created in the former case. Typical mechanical tests on strength, toughness and Izod impact energy were performed and the results are reported. These findings are discussed in view of the improved adhesion resulting from reactions and/or enhanced polar interactions at phase boundaries.

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Chapter 1

Introduction

In recent years there has been mounting interest in the use of renewable, environmentally friendly materials in place of plastics based on non-renewable petroleum resources. The combined environmental problems of overflowing landfills, inefficient incineration of traditional fillers, excessive dependence on petrochemical based plastics, and environmental pollution along with adverse public opinion has further necessitated an acceleration of effort in this direction. The driving forces behind the utilization of natural fiber reinforced composites are low cost, biomass utilization, environmental benefits, and process benefits, all of which are achieved without compromising performance properties. In this regard, new biobased reinforcement/filler materials and matrix resins offer advantages such as good mechanical properties, biodegradability, recyclability and easy incineration. These materials offer a value added outlet to the low cost agricultural products.

The advantages of natural fibers over traditional reinforcing materials such as glass fibers, talc, and mica are: acceptable specific strength properties, low cost, low density, high toughness, good thermal properties, reduced tool wear, reduced dermal and respiratory irritation, ease of separation, enhanced energy recovery, and biodegradability. It has been demonstrated that wood fiber reinforced polypropylene composites has properties similar to traditional glass fiber reinforced polypropylene composites [1]. Lignocellulosic-polymer composites have been recently reviewed by Rowell, Youngquist, and Narayan [2].

The main bottlenecks in the wide scale use of these fibers in thermoplastics have been the poor compatibility between the fibers and the matrix and the inherent high moisture sorption, causing dimensional changes in the lignocellulosic based fibers. The efficiency of a fiber reinforced composite depends a great deal on the fiber-matrix interface and the ability to transfer stress from the matrix to the fiber. This stress transfer efficiency plays a dominant role in determining the mechanical properties of the composite and also in the material's ability to withstand environmentally severe conditions. Additionally, it is important to maintain a good stiffness to impact strength balance, in order to expand the applicability of these natural fiber-reinforced composites.

1.1 Objective

This work is a part of ongoing intensive research aimed at developing new natural fiber reinforced thermoplastic composites. The bast fiber of a plant called kenaf (ke naf), an annual hibiscus fiber plant, was used as the reinforcement. The goal was to develop kenaf fiber reinforced polypropylene composites with properties tailored to suit applications where it could be a potential low-cost substitute to the expensive glass-reinforced composites. It was also necessary to understand and optimize the processing parameters, composition and interfacial adhesion in order to improve the mechanical properties of the composites.

1.2 Structure of the Thesis

The following paragraphs give a brief outline of the contents in each chapter of this thesis :

Chapter 2 provides a simple background on polymer composites especially short-fiber reinforced thermoplastics, their mechanics and role of interfacial adhesion in influencing their mechanical properties. The chapter also deals with natural fiber reinforced thermoplastics and their advantages and disadvantages over the conventional composites. This is followed by a discussion on the causes of poor fiber-matrix adhesion in such systems, and the methods and approach adopted by some researchers to overcome this problem.

Chapter 3 provides information on the constituent materials. Some natural fibers, their composition and properties in comparison to kenaf fiber are discussed. It also includes a description on polypropylene, its characteristics, and experimental evaluation of its Power Law parameters. This is followed by a short introduction to silane coupling agents, their chemistry and role in improving the fiber-matrix adhesion.

Chapter 4 describes the method of preparing the composites by extrusion and further processing by injection molding. The setup and operating conditions of both the equipment are discussed in detail. Since processing is a major factor influencing the mechanical properties of the composites, an understanding of the processing variables and their optimization is the focus of this chapter.

Chapter 5 discusses in detail the methods and instruments used in the characterization of the composites. It deals with tensile, flexural and impact tests for mechanical characterization; differential scanning calorimetry and thermogravimetric analysis for thermal characterization; and scanning electron microscopy for morphology study.

Chapter 6 contains data, results and discussion on the characteristics of the various kenaf reinforced polypropylene composites. The experimental approach and the rationale are clearly stated in this chapter. An effort has been made to explain the differences in the mechanical properties of the coupled and uncoupled composites.

Chapter 7 covers the maleation study on polypropylene. The role of maleated polypropylene (MAPP) in improving the mechanical properties of the composites is explained. For better understanding of the maleation chemistry, experimental study was conducted in which the degree of maleic anhydride (MA) grafted onto polypropylene (PP) was varied by controlling the feed ratio of MA to the initiator. The amount of MA incorporated was determined by both titration and FT-IR spectroscopy. An attempt is made to correlate the rheological behavior (studied on rheometrics mechanical spectrometer) of maleated polypropylenes with their different degree of MA grafting.

Chapter 8 presents the conclusions from the thesis and some recommendations for future work.

Chapter 2

Background

2.1 Polymeric Composites

Composite materials can be defined as a system consisting of two or more physically distinct and mechanically separable materials, which can be mixed in a controlled manner to have a dispersion of one material in another to achieve optimum properties. The properties are superior and unique in some respects to the properties of individual components [3]. Composites in structural applications can be classified under one of the following: ceramics, metals and alloys and polymeric composites. One or more of these materials can be used to make various kinds of composites.

The discussion in this work will be restricted to polymeric composites only. The polymeric composites can be subdivided into the following categories: fibrous composites (consisting of fibers embedded in polymer matrix), laminated composites (consisting of fibrous composites in one or more than one different planes of orientation), particulate composites (consisting of particles of reinforcing medium in polymer matrix).

Fibrous composites are composed of fibers, which are either continuous and aligned or short and randomly dispersed in a polymer matrix medium. The fibers themselves can be of various types, prominent among them being carbon, glass and polymer fibers. The polymer matrix can be either a thermoset or a thermoplastic.

2.2 Fiber Reinforced Thermoplastics

The importance of fiber- reinforced thermoplastics arises largely from the fact that such materials can have unusually high strength and stiffness for a given weight of material. When polymer composites are compared to the unfilled polymers, the improvements they offer are spectacular. Thermoplastic matrices offer many advantages over thermosetting resins. They have higher temperature resistance, very good fracture toughness, good neat resin strengths, shorter molding cycles, reduced storage and handling problems, infinite shelf life of intermediate prepegs, capability to fusion bond, recyclability, and repairability [4].

Difficulties in processing have hampered the use of thermoplastic composites on a wider scale. The intractability of these matrices due to their high viscosities even at elevated processing temperature give rise to a host of problems such as stiff and boardy prepegs due to high resin content, poor fiber wetting, solution devolatilization during casting leading to formation of voids and loss of mechanical strength.

Thermoplastic polymers such as isotactic polypropylene (iPP) are often reinforced by using glass fibers in order to increase the stiffness, tensile strength and dimensional stability at elevated temperatures. A strong interface between fibers and thermoplastic is extremely important to develop thermoplastic composites with improved physical and mechanical properties.

2.3 Mechanics

In reinforcing a thermoplastic or a thermoset with fibers the aim is to exploit the load bearing capability of the fibers to yield a composite which has higher strength [5]. There are two important rules for fiber composites: first, the modulus of the fiber should be greater than the modulus of the matrix and second, the elongation of the fiber should be less than the elongation of the matrix [6]. Usually, fibers have good strength and stiffness but are very brittle. The improvement in the mechanical properties of a fiber reinforced composite is due to its ability to withstand a higher load than the matrix it replaces [7]. The strong and stiff fiber bear most of the load and the polymer matrix protects the fibers and transfers the load to them [8].

It is usual to establish a critical aspect ratio (length to diameter ratio) for the polymer-fiber composite, and for effective load transfer short fibers must exceed a certain critical length. Generally speaking, the greater the aspect ratio of the fiber, the better the reinforcing effect, in terms of increased tensile strength and stiffness [9]. To achieve maximum reinforcing efficiency, the fibers must be at least 10 times longer than the critical length [10].

2.4 Fiber - Matrix Adhesion

The level of adhesion of reinforcing fibers to the polymer matrix is an important factor in the determination of composite mechanical properties. Mechanical strength can only be achieved by the uniform efficient transfer of stress between matrix and fibers, via a strong interfacial bond [6]. The strength of the interfacial bond is also responsible for promoting good environmental performance even when the composite is loaded. The role of the matrix is to bind the fibers together and protect them from environmental conditions. With these factors in mind, many fibers and reinforcing agents are pre-treated before they are incorporated into the composite. A common pretreatment uses a coupling agent that acts as a bridge between the fiber and the matrix, thus creating a stronger bond between the two. Research has shown that very small additions of a coupling agent are sufficient to promote good bonding and improve mechanical properties.

Also, it is believed that it is essential to have good "wetting" of the fibers in order to increase adhesion and produce a strong composite [11]. With increased dispersion, the fibers will be "wetted out" or totally enclosed by the matrix. Absorption alone can produce increased adhesion between the fibers and matrix. Upon examining the surface wettability of a composite, it is seen that improved surface wettability is an important concern in improving fiber/matrix bonding.

When producing a composite material it is very difficult to simultaneously improve properties such as stiffness, mechanical strength, and toughness. In order to achieve high mechanical strength one must obtain uniform stress transfer between matrix and fibers while producing a strong bond at the interface. An entire field of research has been devoted to understanding the mechanism involved in resolving the tensile strength/toughness dilemma.

2.5 Natural Fiber Reinforced Thermoplastics

Synthetic fibers like glass, aramid, and carbon fibers are the most widely used reinforcements in the polymeric composites industry. These materials are designed and engineered with respect to performance and cost, but with a limited concern about the ultimate disposability and environmental impact of the waste residues generated [12]. The use of natural fiber, to replace wholly or partly the conventional inorganic fibers like glass as a reinforcement, is presently receiving increasing attention primarily because of their low cost and environmental benefits. Several types of fibers are available depending on the climatic conditions and potential end use such as wood fibers/pulp, kenaf, flax, sisal, hemp, jute, ramie, coir, recycled newspaper/wood fibers, etc. These natural fibers constitute cellulose and hemicelluloses bound to lignin and associated with varying amounts of other natural materials; and are commonly termed as lignocellulosics. Section 3.1 covers natural fiber chemistry and their mechanical properties in more detail.

Traditionally, the natural fibers have been incorporated in polymer systems primarily as fillers. There use as reinforcement has been investigated over the last few years by many researchers. The range of commercial applications of these natural fiber composites has started broadening recently. Especially with thermoplastics, the range includes well established sheet molding compounds materials such as Woodstock, Lignotoc, etc.

There are number of benefits offered by natural fiber over glass fiber reinforced or mineral filled thermoplastics. These include [13,14] :

- low cost per unit volume basis.

- low density
- high specific stiffness and strength
- desirable fiber aspect ratio of the fiber
- good thermal properties
- flexibility during processing with reduction in tool wear
- value addition of a low cost agricultural product
- environmental attributes:
    - energy recovery with clean incineration
    - biodegradability
    - reduced dermal and respiratory irritation.

There are certain drawbacks associated with the lignocellulosic fiber composites which we need to overcome in order to promote their wide use. The drawbacks are [14] :

- poor interfacial adhesion
- poor stiffness/impact balance
- inherent high moisture sorption
- poor fiber dispersion
- surface defects (unaesthetic)
- poor water resistance.

The efficiency of a fiber reinforced composite depends a great deal on the fiber-matrix interface and the ability to transfer stress from the matrix to the fiber. This stress transfer efficiency plays a dominant role in determining the mechanical properties of the composite and also in the material's ability to withstand environmentally severe conditions.

Toughness and impact resistance of a composite are important properties in determining whether it can be used in specific applications. High flexural modulus and high toughness are favored structural properties but are often mutually exclusive characteristics of real materials. Natural fiber reinforced thermoplastics can match glass-fiber reinforced thermoplastics in elastic and flexural modulii but do not compare favorably in impact resistance as measured by the Izod test.

2.5.1 Causes of Poor Interfacial Adhesion

One of the main obstacles limiting the mechanical performance of these composites is the incompatibility of the lignocellulosic fibers and the thermoplastic. The lignocellulosic fiber is inherently polar and hydrophilic while many thermoplastics are non-polar and hydrophobic. Because of the two different polar characters, poor bonding results. The poor bonding becomes more remarkable when the different thermal shrinkage of fibers and matrix-polymer leave gaps between the two components [15]. A necessary condition for good fiber dispersion and good interaction and adhesion between the two components is the compatibility of the surface energies. Another difficulty encountered during the incorporation of these fibers into the thermoplastic matrix is the interfiber hydrogen bonding which tends to hold the fibers together.

2.5.2 Improving Interfacial Adhesion

Several studies aimed at improving dispersion of the lignocellulosic fibers in the on-polar matrix and increasing the stress transfer efficiency of the interface have been conducted in various laboratories. In general, it was found that enhanced interfacial adhesion can be achieved in one of the following ways [16]:

(i) fiber modification

(ii) use of interface-active additives

(iii) matrix modification.

Fiber Modification

Fiber modification involves grafting functional groups on the lignocellulosic fibers or coating fibers with additives that carry suitable functional groups, in order to make the fiber surface more compatible with that of the matrix material. The various reactive species that have been used for fiber modifications include one or more of the following - acetic anhydride, n-alkyl isocyanates, styrene, maleic anhydride, and silanes (Figure 2.1).

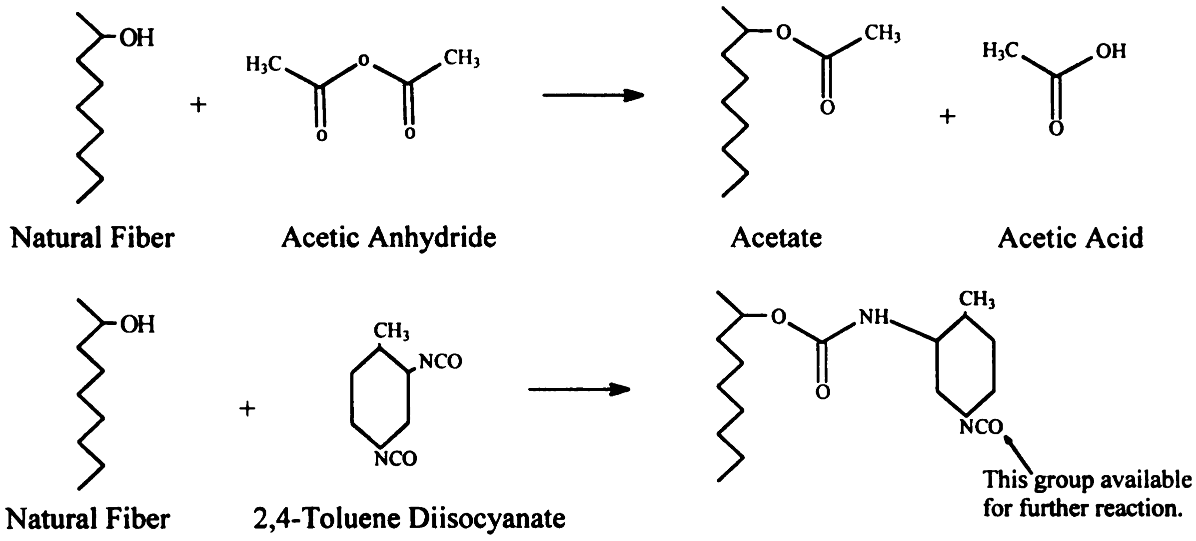


Figure 2.1 Fiber Modification Reactions [13].

Kokta and co-workers [17,18] employed a xanthate method of grafting to graft styrene on wood fibers that resulted in composites with improved mechanical properties as compared to composites with non-grafted fibers. Owen et al. [19] reacted n-alkyl isocyanates with wood and wood components to form carbamate derivatives which imparted hydrophobic qualities to wood. Rowell et al. [20-22] studied acetylation of wood and wood fibers to alter its hydrophobicity and thus enhanced the bonding characteristics with hydrophobic polymers. Felix and Gatenholm [23] surface coated cellulose fibers with a solution of a commercial low molecular weight propylene-co-maleic anhydride copolymer and studied the nature of adhesion in the composite with polypropylene. Klason et al.[24] prehydrolyzed cellulose fibers, before incorporating them in composites, in order to permit the fibers to finely comminute in the processing shear field. It resulted in homogeneous dispersion of fibers and improvement in mechanical properties.

Interface-active Additives

The second method of promoting interfacial adhesion involves the use of additives like coupling agents and compatibilizers. Sanadi and Rowell [25] used acrylic acid grafted (AAPP) and maleic anhydride grafted (MAPP) as coupling agents in composites of recycled newspaper fibers and polypropylene. They found the property improvements using MAPP to be better than AAPP, because of a greater possibility of acid-base interactions between the fiber surface and the carboxylic acid groups.

Karmaker et al. [26] reduced the water absorption of short jute fiber reinforced polypropylene by incorporating maleic anhydride polypropylene (MAPP) in the system. The maleic anhydride of MAPP promotes chemical bonding through esterification with hydroxyl group of cellulosic fibers. This chemical bonding eliminates the gap between lignocellulosic fibers and polypropylene caused by differential thermal shrinkage. The absence of gaps surrounding the fiber minimizes the spaces in the composite where water can locate.

Maldas et al. [27-29] studied the effect of coupling agents like poly[methylene(poly phenyl isocyanate)], maleic anhydride, and silanes on the properties of wood fiber-reinforced thermoplastic composites. They found that fiber coating followed by an isocyanate treatment yielded the greatest improvement in properties. Also, the isocyanate treatment combined with grafting resulted in improved properties.

Dalvag and co-workers [30] reported the use of a titanate compound and a low molecular weight propylene-co-maleic anhydride copolymer as a coupling agent. Coupling agents based on trichloro-s-triazine were synthesized and used to improve adhesion between cellulose fibers and an unsaturated polyester [31]. The authors suggest the formation of covalent bonds between the fiber and the matrix as opposed to just wetting of the fibers by the matrix material. As a result, these composites exhibited decreased water absorption as compared to the materials formulated without the coupling agents.

Myers and co-workers [32] studied the effect of a commercial additive, Epolene E-43, (low molecular weight propylene-co-maleic anhydride copolymer) on the mechanical properties of wood flour-polypropylene composites. The effect of Epolene E-43, wood flour concentration, residence time, and wood flour particle size on the mechanical properties were evaluated. Epolene E-43 exhibited a coupling behavior with improved properties. It was suggested that the high cost of Epolene E-43 could be offset by increasing the wood flour concentration in the composite.

Sapieha and co-workers [33] showed that the addition of dicumyl peroxide resulted in the direct grafting of polyethylene on cellulose fibers and improved mechanical properties of the composite. They proposed the existence of a critical peroxide concentration greater than which the grafting reaction was terminated, since the fiber surfaces were covered with grafted polyethylene.

Matrix Modification

Takase and Shiraishi [34] have modified a thermoplastic matrix by incorporating a maleic anhydride functionality and fabricated composites with wood pulp that exhibited good mechanical properties.

Krishnan and Narayan [16] performed reactive extrusion processing to modify polypropylene matrix with maleic anhydride and then subsequently generated in-situ grafts between the modified matrix and low-density hardwood residue by use of a suitable catalyst. They reported significant property improvements over the composites made without the compatibilizer.

Chapter 3

Constituent Materials

3.1 Natural Fibers

Plant fibers are conveniently classified according to the part of the plant where they occur and from which they are extracted, viz. leaf, bast, or seed. Kenaf, jute, flax and ramie fall under the group of bast fibers since they are obtained from the bast tissue or bark of the plant stem. These long, mutlicelled fibers can be readily split into finer cells which are manufactured into textile and coarse yarns. Sisal and cotton are examples of leaf and seed fibers respectively.

The strength of natural fibers is provided by cellulose, a rigid linear chain polymer composed of β-D-glucose units. Another major component is lignin, a highly cross linked polymer of substituted phenyl propene units, which plays the role of the matrix. Also present are the hemicelluloses, which are branched polymers of galactose, glucose, mannose, and xylose. Table 3.1 compiles the chemical composition data of some natural fibers. The increased use of lignocellulosic fiber reinforced composites has led to much research on new fillers, fibers, coupling agents, and compounding techniques.

Generally, among the various reinforcing fibers, the lignocellulosics have the highest elastic modulus and tensile strength approached only by a few of highly oriented fibers [35]. Specific tensile modulus and strength of the cellulosic fibers, which provide an indication of the characteristics of a void free fiber on a basis of equal mass, are

Table 3.1 Chemical Composition of some Natural Fibers, wt % [36].

Fiber	Botanical Name	Cellulose	Hemicellulose	Pectins	Lignin	Water soluble compounds	Fats and waxes
Cotton	*Gossypium sp.*	91.8	6.4	-	-	1.1	0.7
Flax	*Linium usitatissimum*	62.8	17.1	4.2	2.8	11.6	1.5
Jute	*Corchorus capsularis*	71.5	13.4	0.2	13.1	1.2	0.6
Kenaf	*Hibiscus cannabinus*	65.7	8.1	0.4	15.7	9.3	0.8
Ramie	*Boehmeira nivea*	76.2	14.6	2.1	0.7	6.1	0.3
Sisal	*Agave sisalana*	73.1	13.3	0.9	11.0	1.4	0.3
Wood		45.8	22.5	-	26.7	3.5	1.5

Table 3.3 Comparison of Kenaf with other synthetic fibers [35].

Material	Density (ρ), g/cm^3	Tensile Strength (σ), GPa	Specific Strength (σ/ρ)	Elastic Modulus (E), GPa	Specific Modulus (E/ρ)
Kenaf	0.45	11.9	26.44	60.0	133.3
E-Glass	2.54	3.5	1.38	72.4	28.5
Graphite	1.90	2.5	1.3	240.0	126.0
Kevlar 49	1.50	2.8	1.87	130.0	87.0
Steel	7.8	0.34 - 2.1	0.043 - 0.27	210.0	26.9
Polypropylene	0.9	up to 0.6	0.67	up to 6.5	7.2

equally high. Table 3.2 compiles mechanical properties data of some natural fibers. Their specific properties are close to those of glass fibers. Like glass fibers, the elongation at break of these fibers is low (2 to 5 %) but this is not a serious disadvantage in a reinforcing fiber. The length/diameter (l/d) of reinforcing fibers must be above a certain level which depends on the efficiency of fiber-matrix adhesion before the fiber strength is completely utilized. Lignocellulosic fibers are relatively short and coarse in comparison to most reinforcing fibers. Thus, bonding of matrix to fiber is likely to be important in determining whether the full strength of the fiber can be utilized in a composite. The relatively short fibers also place this type of materials at a disadvantage if toughness is required in the composite.

Table 3.2 Mechanical Properties of some Natural Fibers [36,13].

Fiber	Average Length	Dimensions Diameter	Ultimate Strain at break	Tensile Strength	Tensile Modulus
	L, mm	D, mm	%	GPa	GPa
Cotton	25	0.019	4 - 9	3.54	5.0
Flax	32	0.019	2 - 3	20.0	85.1
Jute	2.5	0.018	1 - 5	5.38	8.0
Kenaf	3.3	0.023	2 - 4	11.91	60.0
Ramie	120	0.040	2 - 7	13.25	76.0
Sisal	3	0.021	2 - 3	6.14	12.7

3.1.1 Kenaf

Kenaf (ke naf'), an annual hibiscus plant related to cotton, has been an important source of food, clothing, rope, sacking and rugs in central Africa and parts of Asia for several thousand years [37]. One of the major uses for kenaf is an alternative fiber for the pulp and paper industries. Kenaf fiber has great potential as a short-fiber reinforced thermoplastics because of its superior specific tensile strength compared to other fibers. See Table 3.3 for comparison of mechanical properties of Kenaf and other synthetic fibers. Successful development of useful and novel composites that contain a high percentage of kenaf will result in the increased utilization of kenaf fiber, thereby enhancing markets for U.S. farmers.

Kenaf has a bast fiber, which contains approximately 75% cellulose and 15% lignin, and offers the advantage of being biodegradable and environmentally safe. The bast fiber is actually a bundle of fibers bound by lignins and pectins. Chemical modification of the fiber has been studied by Rowell et al. [38] to make it more hydrophobic so as to improve its compatibility with non-polar thermoplastics.

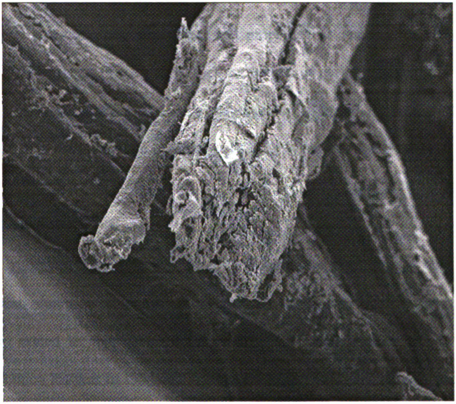


Figure 3.1 SEM image of kenaf bast fiber cross-section.

The kenaf fibers used in this work were obtained from Department of Agriculture, Mississippi State University, and were chopped into lengths of approximately 1.59 mm (1/16 in). The kenaf fiber cross-section (Figure 3.1) is unsymmetrical therefore the single fiber tests cannot be performed on it.

3.2 Matrix

Fibers, since they cannot transmit loads from one to another, have limited use in engineering applications. When they are embedded in a matrix material, to form a composite, the matrix serves to bind the fibers together, transfer load to the fibers, and protect them against environmental attack and damage due to handling. The matrix has a strong influence on several mechanical properties of the composite such as transverse modulus and strength, shear properties, and properties in compression. Physical and chemical characteristics of the matrix such as melting or curing temperature, viscosity, and reactivity with the fibers influence the choice of fabrication process. The matrix material for a composite system is selected, keeping in view all these factors.

3.2.1 Polypropylene

Polypropylene, the second largest volume thermoplastic - next only to polyethylene, continues to experience significant technological developments which promise to extend its applications dramatically. Total world capacity of polypropylene was 43.7 billion lbs/year in 1994 and is projected to grow to 51 billion lbs/year by 1998. Production gains will be fueled by increasing capacity and better prospects for end use markets such as fibers, packaging, and automotive parts [39].

The high production figures and diversity of applications reflect the many advantages of polypropylene. These include easy processability, lowest specific gravity of any thermoplastics, and resistance to most organic solvents, with the exception of very strong oxidizing agents such as fuming nitric acid or sulfuric acid. Polypropylene offers a wide variety of melt flow rates (from 0.3 to 800 g/10 min). Other advantages of the polymer includes its high melting temperature and its ease of recycling, an important consideration in many of the packaging and automotive application its use in.

Polymerization of propylene monomer under controlled conditions of heat and pressure in the presence of Ziegler Natta catalysts, which have multiple active sites, is the conventional method of producing polypropylene. The polypropylene produced by this method has a broad molecular-weight-distribution (MWD) and hence poor control over the resin properties.

Montell Polyolefins (formerly Himont Inc.) emphasized development of process and catalyst technology to broaden its polypropylene application base. It developed the Spheripol process that uses high activity, high selectivity catalysts to improve the impact/stiffness balance of traditional polypropylene products. An additional development of a rheological nature enhances strain-hardening behavior, thus providing high melt strength not normally present in linear polyolefins and expanding polypropylene's markets in thermoforming, high speed extrusion coating, foamed sheet, and large-part blow molding [40].

The recently introduced metallocene single-site catalyst (SSC) technology [41], heralded as a revolution in the olefin polymerization, offers narrow MWD polymers, which have numerous advantages over the broad MWD polymers: e.g. higher toughness, better optics, lower heat-seal-initiation temperatures, and higher crosslinking efficiency. The disadvantage of narrow MWD, however, is poor processability due to low shear sensitivity and low melt strength. But this problem has been offset by Insite technology, developed by Dow Plastics, which involves use of constrained-geometry (CG) homogeneous catalysts that produce highly processable polyolefins with a unique combination of narrow MWD and long-chain branches.

There are three basic types of polypropylene: isotactic, atactic, and syndiotactic. Each variety has a well-defined niche in the industrial sector. Isotactic polypropylene, which contains ordered monomer units inserted in the same configuration, is the most commercial polypropylene. Its molecular structure allows it to assume a helical and crystalline configuration, which makes the material stiff enough for use in a wide range of commercial applications.

In this work PROFAX 6501, an isotactic polypropylene homopolymer manufactured by Montell Polyolefins, was used. The properties of PROFAX 6501 are compiled in Table 3.4.

Table 3.4 Characteristics of PROFAX 6501.

Composition		Isotactic Polypropylene	
Manufacturer		Montell Polyolefins	
Melt Flow Rate (230°C, 2.16 kg)		5.8 g/10min	
Density		0.91 g/cc	
$M_w \times 10^{-3}$		365	
$M_n \times 10^{-3}$		39.5	
$M_z \times 10^{-4}$		386	
Complex Viscosity, η^* (Pa-s, T = 180°C)		Storage Modulus, G' (Pa, T = 180°C)	
~ 0.1 rad/s	25,990	~ 0.1 rad/s	1,034
~ 100 rad/s	895.3	~ 100 rad/s	78,860

3.2.2 Power-Law Model

Power law constitutive equation for non-newtonian polymer melts is:

$$\tau = -m\dot{\gamma}^{n-1}\dot{\boldsymbol{\gamma}} = -m\sqrt{\tfrac{1}{2}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})}^{\,n-1}\dot{\boldsymbol{\gamma}} \tag{3.1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate; m ($N.s^n/m^2$) and dimensionless n are parameters called the consistency and power law index, respectively. According to the model, the shear viscosity is linearly related to shear rate in the region $10<\dot{\gamma}<10^3\ s^{-1}$, and is given by :

$$\eta = m\dot{\gamma}^{n-1} \tag{3.2}$$

$$\log(\eta) = \log(m) + (n-1)\log(\dot{\gamma}) \tag{3.3}$$

A plot of $\log\eta$ vs $\log\dot{\gamma}$ (Figure 3.2) was generated for polypropylene (PROFAX 6501) by performing a shear rate sweep in steady mode on rheometric mechanical spectrometer (RMS-800) at 180°C. The parameter m is a sensitive function of temperature. It was experimentally determined that for PP (at 180°C): η_o (zero shear viscosity) = 26000 Pa-s, m = 1490 N.s^n/m^2, n = 0.18.

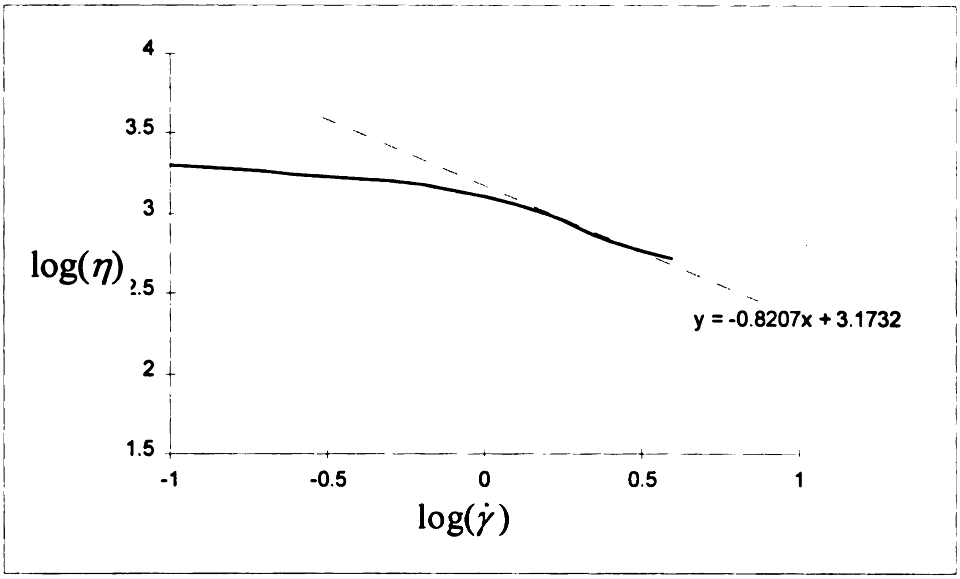


Figure 3.2 Plot of $\log\eta$ vs $\log\dot{\gamma}$ to determine power law parameters.

3.3 Coupling Agents

The coupling agents used in this work are: (i) Maleated polypropylene (MAPP) and (ii) Silane coupling agent. A detailed discussion on MAPP is presented in Chapter 7.

3.3.1 Silane Coupling Agents

Silane coupling agents are widely used to improve interfacial adhesion at the glass fiber or particulate filler-matrix interface. The coupling agent can be represented by the formula R_nSiX_3, where X is a hydrolyzable alkoxy group and R is a nonhydolyzable organic radical that possesses a functionality which enables the coupling agent to bond with the organic resins and polymers. Most of the widely used organosilanes have one organic substituent.

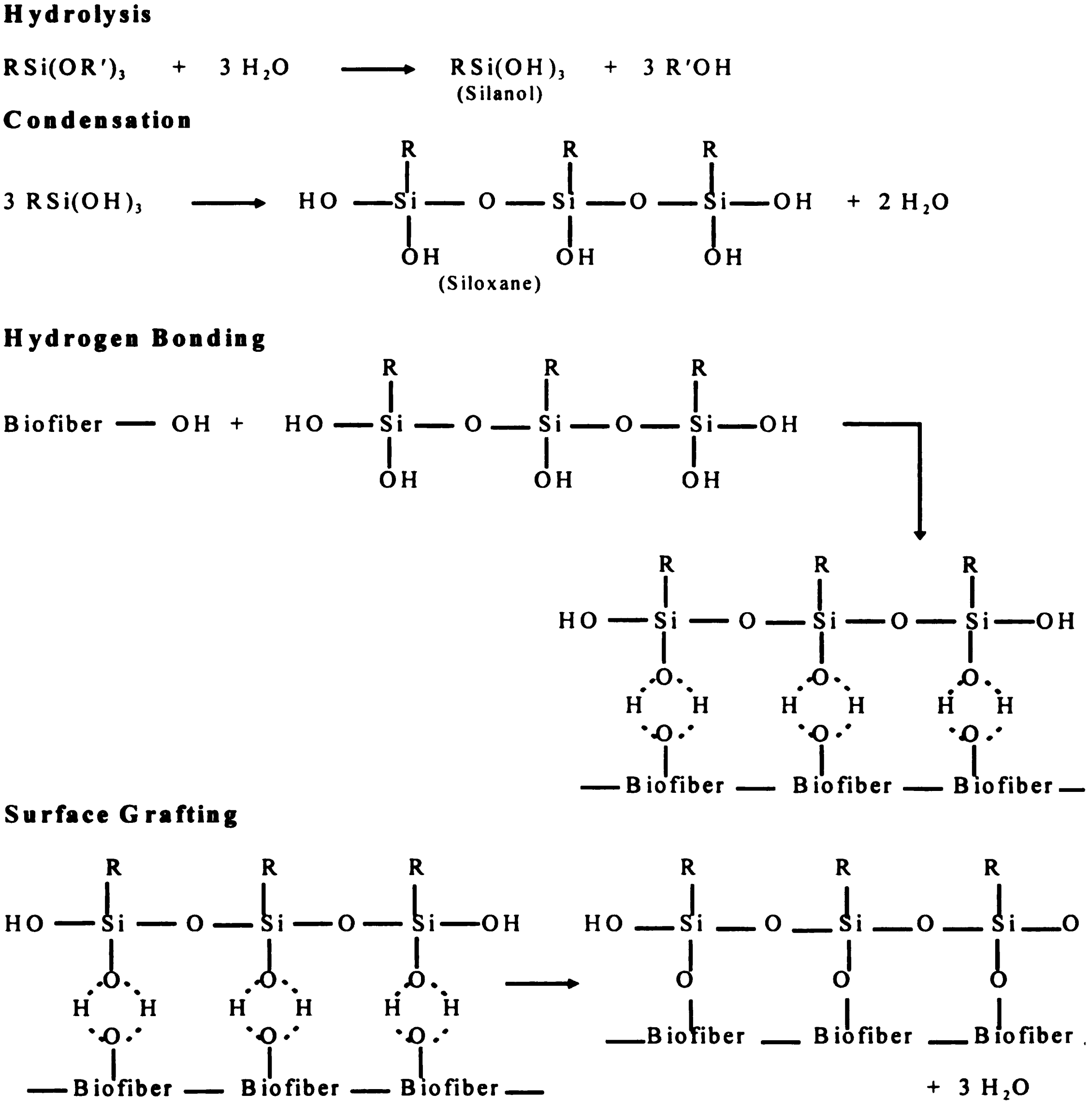


Figure 3.3 Reactions steps in the silane grafting of biofibers

Reaction of these silanes involves four steps (Figure 3.3). The natural fiber contains bound moisture which could hydrolyze the three labile X groups attached to silicon atom. Condensation to oligomer follows. The oligmers then hydrogen bond with OH groups on the natural fiber surface. Finally reaction of the functional organic group on R along with the polymer completes the bridge like structure between the fiber and the polymer [42].

The choice of chemical structure and the concentration of coupling agents play an important role in achieving the optimum mechanical properties of the composite. The most commonly used coupling agents are silanes and titanates. The dispersion of fiber in the matrix is one of the important factor to achieve a lower degree of variation in the ultimate properties of the composite.

Kenaf fibers were surface-grafted with siloxane chains using a 2 wt % silane solution in water. Amino-ethyl amino-propyl trimethoxy silane (Dow Corning Z6032) was used as the fiber surface modifying agent. The amount of silane necessary to obtain a minimum uniform multiyear coverage can be obtained by knowing the values of wetting surface of silane (ws) and the surface area of the filler.

$$amt.\ of\, silane = \frac{amt.\ of\, filler \times surface\ area\ of\, filler}{wetting\ surface\ (ws)} \tag{3.4}$$

Relative surface area of Kenaf was assumed to be 0.2 m^2/g. Wetting surface (ws) of Amino-ethyl amino-propyl trimethoxy silane = 353 m^2/g.

Chapter 4

Composites Processing

The processing of kenaf reinforced polypropylene composites involves two major steps: (i) extrusion and (ii) injection molding.

4.1 Extrusion

In extrusion the raw material passes from a hopper into a cylinder in which it is melted and dragged forward by movement of a screw. The screw compresses, melts, and homogenizes. When the melt reaches the end of the barrel, it is forced through the die that gives the desired shape with no break in continuity. The aim of the extrusion process in this work is to mix the matrix and the fiber so that samples taken from any portion of the extrudate show uniform properties.

Fibrous reinforcement of a polymer matrix demands a sophisticated mixing equipment which must provide extensive in take and conveying capabilities, polymer wetting, and dispersion of the reinforcement. The process should provide for controlled shear, temperature and residence time. This is to minimize material exposure to heat, prevent degradation, and to meet product requirements.

The extrusion process is a proven economical method for fiber reinforcement of polymers and co-rotating intermeshing twin screw extruders are particularly suited for these tasks [43]. Positive conveying, self wiping, and shear sensitive mixing characteristics provided by the screw mechanism satisfy requirements of reinforcement compounding. This mechanism results in interruption of streamline flow, which is needed to disperse both high and low aspect ratio reinforcing agents into a suitable polymer matrix.

Twin-screw extrusion is a complex process involving all forms of transport phenomena (momentum, heat and mass transfer). Modeling the flow of viscoelastic fluids in extruders has been an active area of study since long. White [44] has discussed the subject in great detail and has presented experimental results of many composite systems.

4.1.1 Extrusion Setup

A co-rotating, intermeshing twin screw extruder (Werner & Pfleidererer ZSK30) was used in this study (Table 4.1). The screw profile is designed so that the tip of the screw wipes the flank and root of the other screw, resulting in a self-cleaning action. This type of twin-screw mechanism provides efficient conveying, pressure build-up with close control over residence time distribution, shear input and temperature generation.

Modularity of screw design

Different screw elements or kneading blocks of varying profiles can be placed along the shaft to generate a controlled shear or mixing effect. The screw consist of continuous shafts on which screw-flighted components and special kneading elements are installed in any required order. The screw elements are available in various lengths, pitches, and pitch directions, and can be combined with kneading elements in many different ways. The kneading elements are made up of kneading discs which are staggered in relation to each other. The effect of the kneading elements can be altered by varying the width of the discs and/or the angle at which they are staggered.

Table 4.1 Characteristics of WP-ZSK 30 twin screw extruder.

Designation	Values
Screw outside diameter	30.7 mm
Screw root diameter	21.3 mm
Flight depth	4.7 mm
Center distance of screws	26.2 mm
Length of processing section	960 mm (30 D)
# of screw elements	27
# of kneading blocks	13

Table 4.2 Operating conditions for preparation of kenaf-PP composites.

Barrel Zone Temperatures (°C)	165,170,175,180,180,180
Screw Speed	150 rpm
Feed Rate	5 kg/h
Residence Time	~ 120 sec
Pressure Profile (P)	As shown in Figure 4.1
Fill Factor (f)	As shown in Figure 4.1

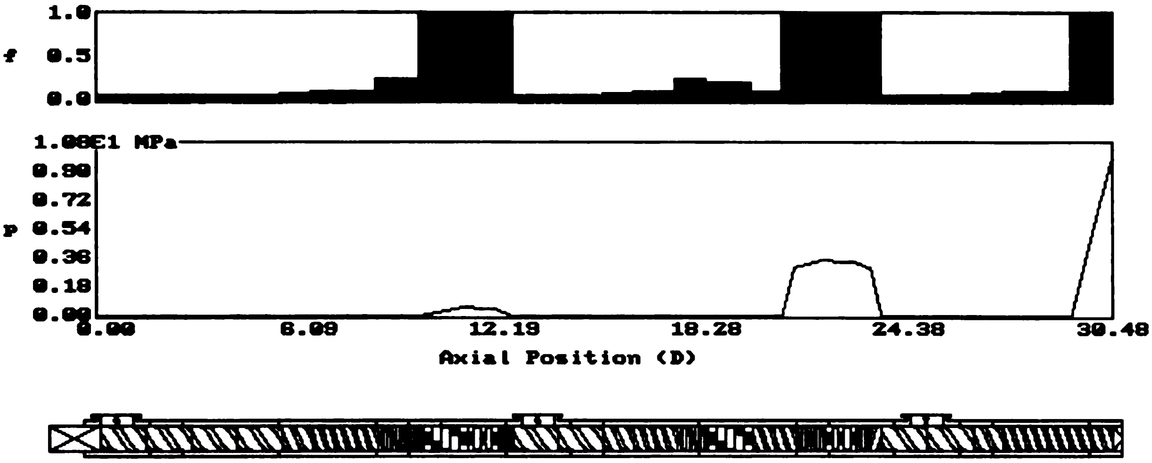


Figure 4.1 Screw configuration, pressure and fill factor profile along the screw.

4.2 Injection Molding

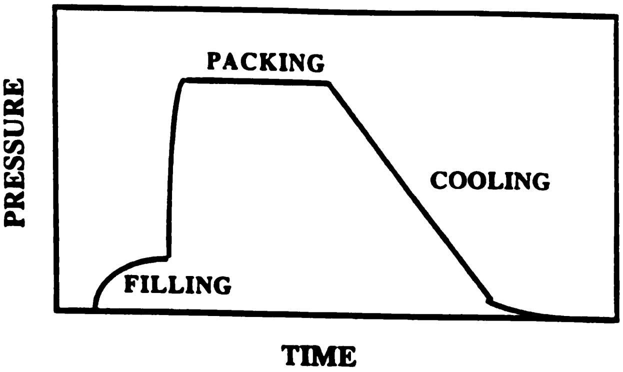
The aim of this process is to heat and masticate the extrudate into a melt, which is injected into a mold of desired shape. An injection molding cycle comprises plastication, injection, packing, cooling and ejection of a polymer (Figure 4.2).

A reciprocating-screw injection molding machine with a mold network is shown in Figure 4.3. A typical machine consists of a screw housed in a barrel which is provided with heater bands. Each machine has a hydraulic system which provides the power to close the mold. During injection, the polymer is transferred through a nozzle which is coupled to the mold block with a sprue bushing. The mold is made of runners which convey the hot polymer melt into cavities. Gates which act as restriction to the flow of the polymer connects runners to cavities.

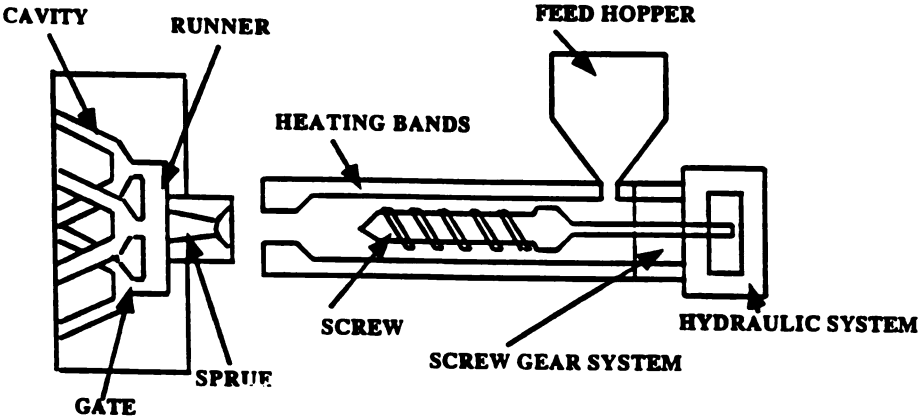
A few studies on the flow and molding behavior of fiber reinforced polymers have been published by Folgar and Tucker [45], Chan et al.[46] and Xavier et al [47]. Utracki [48] presents an excellent description of the issues to be resolved in the processing of fiber reinforced polymers in the light of their peculiar rheology.

Fiber Orientation

Goettler [49] found that the converging flow orients fibers in the flow (longitudinal) direction, while the diverging flow orients them perpendicular to the streamlines of flow (transverse). The overall structure of the specimen is a transversely oriented core surrounded by a longitudinally oriented skin. This type of skin/core pattern is formed only at very low fill times and causes non-uniformity of properties.



⟨ **Figure 4.2 Schematic representation of a injection molding cycle.**



⟨ **Figure 4.3 Schematic diagram of a reciprocating injection molding machine.**

4.2.1 Injection Molding Setup

The extrudate were injection molded on 350 kN Arburg Allrounder injection molding machine (Model 221-75-350). The machine contains a 33 mm single screw and a barrel which is provided with four heating zones inclusive of the one in the nozzle adapter section. Throughout the molding trials the processing conditions (Table 4.3) were held such that mold filling occurred in roughly 5 seconds and the average cycle time was about 35 seconds. The mold used produced a ASTM D-638 Type I tensile bar and a ASTM D-256 impact bar per cycle.

Table 4.3 Operating conditions for injection molding

Hopper to nozzle temperature profile (°C)			175,180, 200,200	
Injection Delay	Injection Time	Holding Time	Cooling Time	Die Opening Time
2.0 s	4.5 s	3.0 s	20 s	1.5 s
Screw back pressure			0.69 MPa	
Pack/Hold pressure			2.0 - 6.2 MPa	
Screw Speed			75 - 100 rpm	

4.3 Optimization

The processing of short-fiber reinforced thermoplastics requires the following considerations [50]:

1. control of rheological properties.
2. an efficient method of mixing.
3. control of mechanical/physical properties resulting from mixing.
4. control of the microstructure in the solid state.

A better understanding of the rheological behavior of the filled polymers would help in the choice of optimal processing conditions. Table 4.4 lists the elements of a composite structure and properties that depend on processing techniques.

Table 4.4 Elements of Composite Processing-Performance Relationships [49].

Process Parameters		Composite Structure		Composite Properties
Forming geometry Rate Temperature Pressure	→	Fiber concentration Fiber aspect ratio Fiber dispersion Fiber wet-out Fiber orientation	→	Modulus Strength Impact resistance Shrinkage

4.3.1 Extrusion - Process Parameters

It is important to understand the influence of extrusion process parameters on fiber length, fiber dispersion and fiber orientation in short-fiber reinforced thermoplastics. The optimum composite would comprise aligned long fibers that are well dispersed in the matrix.

Wall [51] has studied the effects of different mixing lengths and screw speed on the fiber/matrix bond and the degree of fiber length degradation :

i) as the mixing length is increased, there is a linear decrease in fiber length (Figure 4.4). The tensile strength of the extrudate increases initially with increasing mixing length until it reaches a maximum, beyond which there is no improvement (Figure 4.5).

ii) for a particular screw configuration, the screw speed has only a small effect on fiber length in the extrudate (Figure 4.6). As the screw speed was further increased to higher rates, there was a slight drop in fiber length. Increasing the screw speed increases the tensile strength until it reaches a maximum and decreases thereafter (Figure 4.7). With a proper temperature profile, there is a linear relationship between the throughput rate and screw speed.

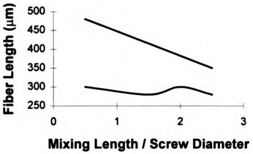


Figure 4.4 The effect of mixing length on fiber length.

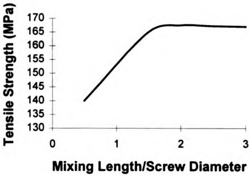


Figure 4.5 The effect of mixing length on product strength.

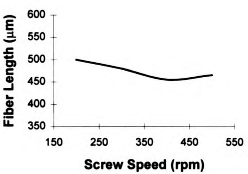


Figure 4.6 The relationship between screw speed and fiber length

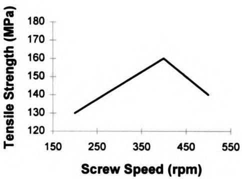


Figure 4.7 The relationship between screw speed and product strength.

4.3.2 Injection Molding - Process Parameters

There are four basic parameters in the injection-molding process: fill time, melt temperature, mold temperature, and peak cavity pressure. In turn, these parameters are dependent upon the machine variables, mold variables, and the polymer employed. Literature has many examples detailing the effect of these variables to the properties and morphology of the molded parts.

The effect of fill time on mechanical properties, surface appearance and dimensions of the injection molded specimens has been studied by Cox and Mentzer [52].

They attribute variations in mechanical properties and shrinkage on variations in molecular orientations. Melt temperature was found to be the most important parameter when related to residual stress. The importance of melt temperature was evinced by the fact that it affects melt flow time, melt pressure at the nozzle and the cavity and the cooling time. Mold temperature is manipulated during filling and cooling stage to reduce molecular orientation and residual (thermal) stresses. In order to minimize cycle time and to maintain correct gate freeze-off it is essential to monitor cavity pressure.

A typical fill pressure-fill time relationship for a hot polymer melt flowing into a cold mold has a minimum as shown in Figure 4.8 [52]. At very short fill times (fast flow rates), the fill pressure is very high and the flow is controlled by the viscous forces which resist the flow. In this region, the flow is completed very quickly, shear stresses are high, molecular orientation is high, and viscous heating occurs. As the fill time increases (slower flow rates), the viscous resistance decreases, resulting in a lower filling pressure. At some point, the fill pressure passes through a minimum and starts increasing with increasing fill time. This region is heat transfer controlled as the hot melt is filling the cold mold slowly with substantial heat transfer occurring. This lowers the temperature of the melt which in turn increases the viscosity and thus the pressure. From a processing viewpoint it is desirable to operate at the minimum in fill pressure because it is most stable portion of the curve.

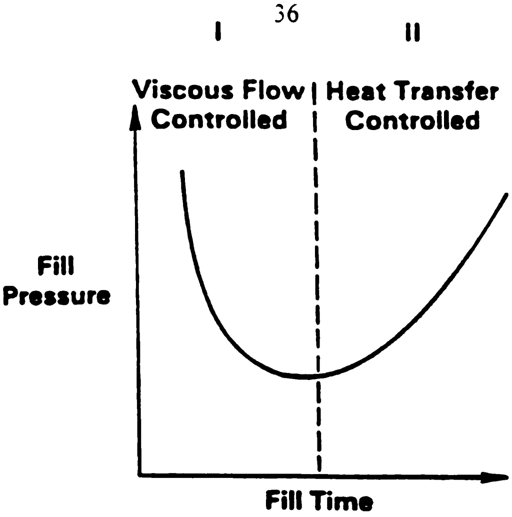


Figure 4.8 Typical fill pressure-fill time relationship.

4.4 Experimental Procedure

The raw materials - PROFAX 6501 (polypropylene) and kenaf bast fibers were fed into the extruder. Where necessary, they had to be mixed with compatibilizer (MAPP) or the fiber treated before being fed to the extruder. The extrudate was pelletized, dried and further processed by injection molding.

Before processing, kenaf fibers were dried in a convective oven at 100°C for 48 hours. Polypropylene and dried kenaf fibers were fed through a common feed port. Polypropylene was fed using a gravimetric feeder (Acrison Inc., Model 406). The product discharge is precisely regulated by the MD-II 2000 Controller (Acrison Inc.) on a weight loss basis. The feeder was operated in the internal gravimetric control mode (continuous) after calibration. This maintains the output rate constant according to the set feed rate. Dried kenaf fibers were fed by a volumetric feeder (K-Tron) after its calibration. The feed rates were set such that composites of various fiber weight fractions could be prepared.

The extruder was operated under the conditions specified in Table 4.2. Once the extrudate was free of purge material, strands of the extrudate were pulled out of the die into a water bath and were fed into a pelletizer. Since the pelletizer was not able to pinch or cut soft material, the strands were cooled in a quench tank filled with water. An arrangement was made to blow off water from the strands by using pressurized air, just before they entered the pelletizer. Pelletization of the material was stopped, when the load (torque) of the extruder, which was kept constant during extrusion, started decreasing.

The composite pellets were dried in an oven at 100°C for 30 hours, before they were injection molded. The injection molding machine was operated under conditions specified in Table 4.3, with a mold suitable for ASTM D638 specimens. Mold temperature, screw speed and injection speed were varied so as to produce samples with good surface appearance.

Since this study involves inter-comparison of different natural fiber composites, best efforts were made to maintain same conditions while carrying out processing of different blends. Purging of the extruder and injection molding machine was always conducted before and after a run. The purge resin was chosen (usually PS or HDPE) such that it is more viscous than the raw material under the operating conditions. The material handling equipment were maintained clean.

Chapter 5

Experimental Characterization

The injection molded specimens of kenaf reinforced polypropylene composites were characterized by mechanical tests (Tensile, Flexural and Impact) and thermal analysis tests (TGA and DSC). The melt flow properties were measured with a melt flow indexer. The morphology was studied by scanning electron microscopy. The data obtained from these tests are appropriately reduced to evaluate various material properties that can later be used for analysis and design of practical structures.

5.1 Mechanical Characterization

The specimens for these tests were conditioned for at least 48 hours at room temperature and 50% humidity prior to testing. At least five specimens were tested for each composite blend and property.

5.1.1 Tensile and Flexural Tests

These are static tests which are greatly dependent on the fiber orientation in the composites with respect to loading axis. Typical stress-strain curves obtained are as shown in Fig 6.1 (Chap. 6). In stress-strain tests the buildup of force (or stress) is measured as the specimen is being deformed at a constant rate. In these tests the stress can become non-homogeneous as it varies from region to region in the specimen as in cold-drawing or necking and in crazing. Also, since a polymer's properties are time dependent, the shape of the observed curve will depend on the strain rate and temperature.

In tensile test the specimen is exerted to tension in the longitudinal direction. A flexural test subjects the interface to a complex mixture of tension, compression and shear such that results are difficult to interpret in terms of mechanics, but the test is simple to run and relates well to composite performance. Both these tests were performed on a UTS of United Calibration Corporation (Model SFM 20) with the parameters as listed in Table 5.1, under ambient conditions.

The properties measured from these tests are: tensile and flexural strengths, elongation at yield and break, toughness, initial tensile and flexural modulus. All properties except the following can be directly obtained from the stress-strain plots.

Initial Tensile Modulus:

$$(E) = \left.\frac{d\sigma_T}{d\varepsilon}\right)_{\varepsilon\to 0} = \left.\frac{F/A}{(L-L_0)/L_0}\right)_{L\to L_0} \tag{5.1}$$

where F/A is the force per unit cross-sectional area,

L is the specimen length when a tensile force F is applied, and

L_0 is the unstretched length of the specimen.

Initial Flexural Modulus:

$$(E_{Flex}) = \left.\frac{PS^3}{4bt^3\delta}\right)_{\delta\to 0} = \frac{S^3 m}{4bt^3} \tag{5.2}$$

where P = load, S = span, δ = deflection, b = width , t = thickness, and

m = slope of the tangent to the initial straight line portion of the deflection.

Toughness is measured as the area under the stress-strain curve till the break point. Therefore, it is an indication of the energy that a material can absorb before breaking.

Table 5.1 Test Conditions for Tensile and Flexural Tests

	Tensile Test	3-point Flexural Test
ASTM	D638	D790
Temperature	30°C	30°C
Strain recorder	Laser Extensometer	Strain Gage
Loadcell Capacity, lb.	1000	1000
Test Speed	0.25 in/min	0.1 in/min
Sample Dimensions	Gage length - 2 in Width - 0.5 in Thickness - 1/8 in	Span - 2 in Width - 0.5 in Thickness - 1/8 in

5.1.2 Impact Tests

Impact tests measure resistance to breakage under specified conditions when the test specimen is struck at very high velocity. These properties are difficult to define and analyze in scientific terms, and hence it has been difficult to employ the results directly in designs.

Impact strengths quoted are critically dependent on specimen dimension and the geometry of notches. The notch in the Izod specimen serves to concentrate the stress, minimize plastic deformation, and direct the fracture to the part of the specimen behind the notch, scatter in energy-to-break is thus reduced.

Impact is the commonest way of measuring toughness of plastics and composites in industry. The toughness (area under stress-strain curve) and impact should be related in some manner. But the difference is due to the very high testing speed of impact tests compared to tensile tests.

The notch of depth 0.1in was made in the specimen on a TMI Notching Machine (Model 22-05). Then the test was conducted on a TMI Impact Machine (Model 43-02-00) with the parameters as listed in Table 5.2. The machine is programmed to give digital readout for the average impact strength and the standard deviation. Printed results were obtained from an on-line printer.

Table 5.2 Test Conditions for Izod Impact Test

ASTM	D256
Temperature	30°C
Izod Pendulum	5 lb.
Sample Dimensions	2.5 in X 0.5 in X 0.125 in

5.2 Differential Scanning Calorimetry (DSC)

DSC is an analytical technique in which the difference in heat flow between a sample and an inert reference is measured as function of time and temperature as both are subjected to a controlled environment of time, temperature, atmosphere and pressure. DSC is used to measure temperatures and heat of transition, specific heat, rate and degree of crystallinity, purity, rate of reaction, etc. Since the heating is controlled by a computer, it is possible to follow a complex heating algorithm.

5.2.1 Modulated DSC (MDSC)

A new technique, invented by Dr. Mike Reading, which provides the same information as conventional DSC plus additional benefits which significantly increase our understanding of the material properties. In MDSC heat flow is measured as a function of both a linear change and a sinusoidal change in temperature. The sinusoidal change permits the measurement of both the components of heat flow: reversing heat flow (heat capacity component) and non-reversing heat flow (kinetic component).

Temperature change in DSC is given by :

$$T(t) = T_o + \beta t \tag{5.3}$$

where T(t) = program temperature , T_o = starting temperature , t = time (min)

and β = linear heating rate (°C/min).

Temperature change in MDSC is given by :

$$T(t) = T_o + \beta t + A_T \sin(\omega t) \tag{5.4}$$

where A_T = amplitude of temperature modulation (±°C),

ω = 2π/P, the modulation frequency (sec^{-1}), and

P = period (sec).

DSC-Modulated DSC and Thermal Analyst 2200 System (TA Instruments) was used for determination of initial crystallinity of polypropylene with different level of maleation. Since the MDSC can separate the kinetic component from the total heat flow, it can measure the crystallization that occurs as the material is heated. When the enthalpy of crystallization (non-reversing) is compared to the enthalpy of melting (reversing), the excess melting enthalpy is due to the excess crystallinity. Another benefit of using MDSC is - increased resolution without loss of sensitivity.

5.3 Thermogravimetric Analysis (TGA)

TGA is performed by continuously measuring the mass of a material as a function of temperature or time in an instrument called thermobalance. The analytical result, or TGA curve, is a plot (as shown in Fig. 6.10) of the mass or the percentage of original mass remaining at the temperature or time depending on the objective of the experiment. The heated sample can be bathed in an inert environment using gases such as nitrogen or argon. TGA serves as a simple technique to obtain useful information about moisture, fiber or plasticizer content, degradation temperature, etc.

TGA was used for the determination of fiber content in kenaf polypropylene composites. Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) with Thermal Analyst 2200 System was used for TGA experiments.

5.4 Scanning Electron Microscopy (SEM)

The SEM (JEOL 6400) is employed to observe the surface morphology of a sample. The normal SEM image is formed when secondary electrons from the atoms of the sample are given out as a result of inelastic scattering by the electron beam. These secondary electrons are then detected by an Everhart-Thornley detector. The production of secondary electrons is very sensitive to the changes in topography of the sample. The projecting areas of the samples giving out a large number of these electrons and thus appear brighter. The electrons cannot escape from low lying areas like crevices and thus these appear dark in the final image. A resolution of 4 to 6 nm is possible with this technique.

Sample Preparation

The samples for SEM are typically 2 to 4 mm in diameter. The samples are mounted on Aluminum stubs and coated with gold in sputter coater. When a backscattered electron image is desired, the sample has to be coated with Carbon. A coating of about 20 nm thickness and the use of graphite paint was found to be sufficient to prevent charging of the sample with a 15 kV accelerating voltage.

5.5 Melt Flow Index

Melt flow indexer can be considered as a simple form of low shear capillary rheometer. It consists of a vertical cylinder bore with heating arrangement, a die at the bottom of the bore and a piston which fits on to the bore from the top. When the cylinder reaches the set temperature, it is charged with a weighed amount of sample and the piston is loaded with the specified weight. Melt flow index (MFI) is measured as the amount of material discharged through the die in 10 min.

Melt flow indexer is run under a constant stress but the shear rate is dependent on the melt viscosity. Actual shear rate of measurement is around 2.5 - 3 times the MFI. Melt flow index provides relative comparison of melt viscosities between different polymeric systems, though it does not provide any elastic information. The tests were conducted on a Ray-Ran Melt Flow Indexer with a melt temperature of 225°C and load of 2.16 kg (ASTM D1238-85).

Chapter 6

Mechanical Properties of Kenaf Reinforced Polypropylene Composites

The mechanical properties of composite materials are determined by the properties of the components, the morphology of the system, and the nature of the interface between the phases. Therefore a great variety of properties can be obtained by varying the structure of the system or interface properties. An important property of the interface is the degree of adhesion bonding between phases. Other parameters which influence the mechanical properties were discussed in section 4.3.

6.1 Selection of Fiber Length

The minimum fiber aspect ratio required for reinforcements is usually 20 times the critical fiber aspect ratio (l_c/d). Single-fiber tests are usually conducted to determine the critical fiber length (l_c) and interfacial shear strength (τ) using the equation :

$$\left(\frac{l_c}{d}\right) = \frac{\sigma_{fu}}{2\tau} \qquad (6.1)$$

where σ_{fu} is the fiber ultimate tensile strength.

There are certain limitations to the use of single fiber tests with kenaf fibers for determination of l_c. The non-uniform cross-section of kenaf fibers violate the basic assumption of the model equation (6.1), The average diameter of kenaf fiber is about 50 μm and it can be assumed that a minimum reinforcement length of 0.5 mm would be required. Therefore the kenaf fibers were chopped to a length of 1/16 in (1.58 mm) to start with. Further processing in an extruder and injection molder shortens the fiber thus decreasing its reinforcing efficiency. The burnt residue obtained from thermogravimetric analysis (TGA) of the sample were investigated under a microscope. It was found that more than 50 - 60 % of the fibers had a minimum length of 0.75 mm (aspect ratio of 15).

6.2 Experimental Approach

The objective of these experiments was to study the influence of the following factors on mechanical properties: (1) fiber fraction, (2) amount of compatibilizer - maleated polypropylene (MAPP), and (3) fiber modification by silane coupling agent. Based on the results an optimal composition for the composite can be determined.

The following kenaf based composites were prepared and investigated in this work. All percentages are in wt %.

1) Neat PP

2) Uncompatibilized composites (without MAPP)

20% Kenaf - 80% PP, 40% Kenaf - 60% PP, and 60% Kenaf - 40% PP.

3) Compatilbilzed composites (with MAPP)

With 2 % MAPP: 20% Kenaf - 78% PP, 40% Kenaf - 58% PP, and 60% Kenaf - 38% PP.

With 5 % MAPP: 20% Kenaf - 75% PP, 40 % Kenaf - 55%PP, and 60% Kenaf - 35% PP.

4) Silylated Composites - 20% Kenaf (treated with silane), 70% PP, 2% MAPP

The maleation of PP was performed by extruding a mixture of PP, maleic anhydride at 2 phr (parts per hundred resin) and 0.1 phr of an initiator, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane (Lupersol 101, Atochem). A detailed study on maleation of PP is presented in Chapter 7.

6.3 Results and Discussion

The composites were characterized by the tests mentioned in Chapter 5. At least five specimens were tested for each composite blend and property.The results presented are within a 5% confidence interval of the mean.

6.3.1 Tensile Properties

The stress-strain curves of the uncompatibilized and compatibilized composites are shown in Figure 6.1. The non-linearity in the curves is mainly due to the plastic matrix deformation. However, the distribution of fiber lengths present in the composite can also cause the slope of the stress-strain curve to decrease with increasing strain [3]. This is because the load taken up by the fibers and the efficiency of the fibers decreases as the strain increases.

Table 6.1 compiles the tensile test results for various kenaf reinforced polypropylene composite systems. It can be seen that the tensile modulus (stiffness) is strongly dependent on the fiber fraction (Figure 6.2) because the fiber stiffnesss contribution is dominant in the composite. There is a slight increase in stiffness with addition of MAPP to the composites.

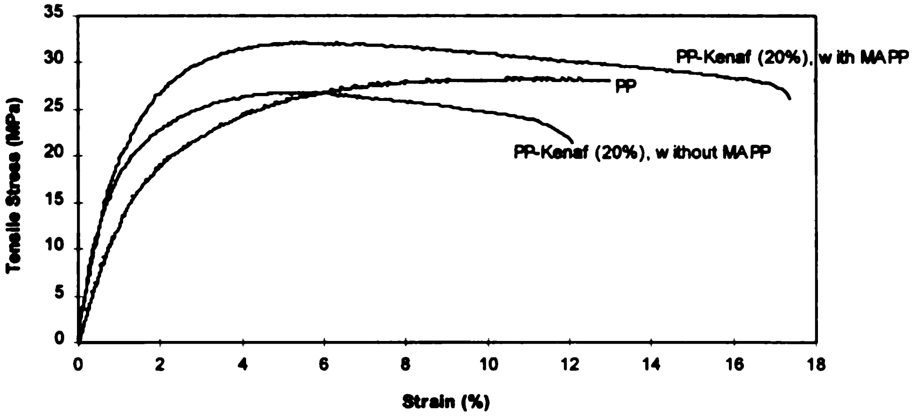


Figure 6.1 Tensile Stress vs Strain curves of kenaf - PP composites.

Table 6.1 Tensile test results for kenaf-PP composites.

Composite Material	Kenaf Fiber		Tensile Strength	Initial Tensile Modulus	Elongation to yield	Elongation to break
	(wt %)	(vol %)	(MPa)	(GPa)	(%)	(%)
Neat PP	0	0	28.4	1.2	9.5	300
PP without MAPP	20	36	26.9	2.7	5.2	11.8
	40	60	26.1	3.4	3.0	9.6
	60	77	25.8	3.9	2.6	8.0
PP with 2% MAPP	20	0	41.0	2.9	5.6	17.2
	40	36	39.0	3.7	4.8	15.9
	60	77	37.5	4.1	3.3	13.4
PP with 5% MAPP	20	0	46.0	3.0	6.1	18.4
	40	36	45.1	3.9	5.0	17.0
	60	77	44.8	4.0	4.2	14.8

The result of tensile strength is shown in Figure 6.3, indicating that the tensile strength of the composite increases with the addition of MAPP. However, a tremendous increase for its tensile strength was noted up to 2% addition, on the whole composite.

Surprisingly, such a small addition of MAPP could improve tensile strength by about 50% compared without MAPP. An addition of MAPP in a quantity up to 5% resulted in a slight improvement of the strength. From literature [34], it is known that further addition of MAPP would decrease the strength of the matrix portion of the composites.

The increase in fiber fraction causes a slight decrease in tensile strength in both compatibilized and uncompatibilized composites. The higher tensile strength of the MAPP-composite system over the uncompatibilized system is due to improved interphase properties. This is due to a combination of some formation of covalent linkages (due to reconversion to the anhydride form) and enhanced acid-base interactions between the fibers and MAPP (see Chapter 7). The elongation to break (Figure 6.4) increases on addition of MAPP but decreases with increase in fiber fraction.

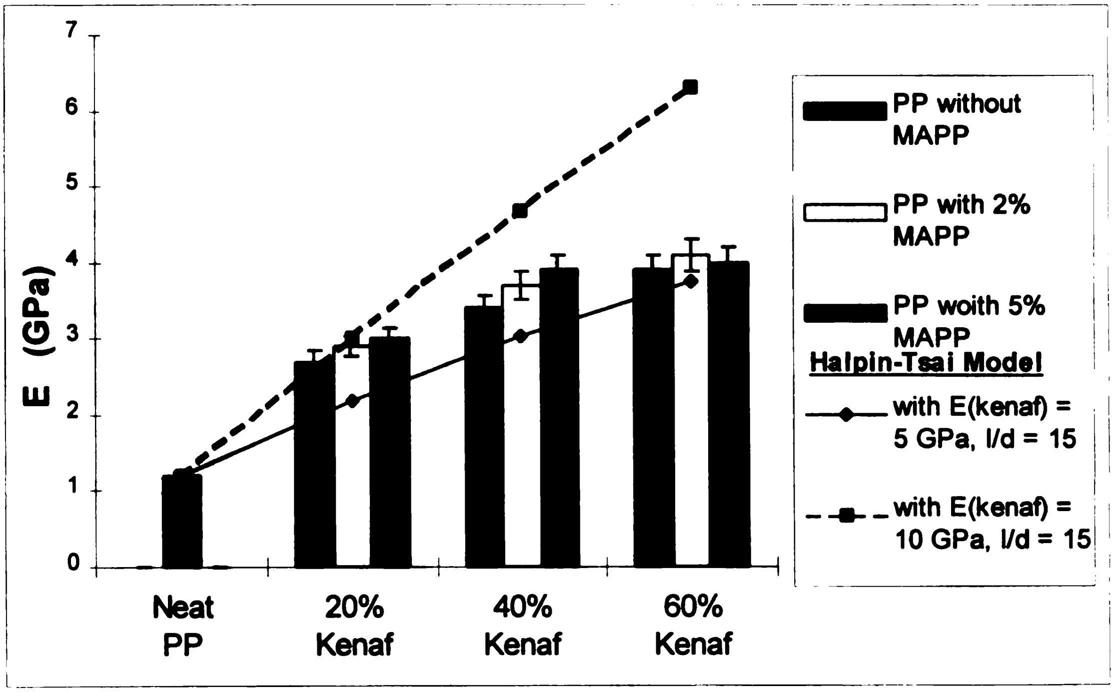


Figure 6.2 Tensile Modulus for kenaf-PP composites.

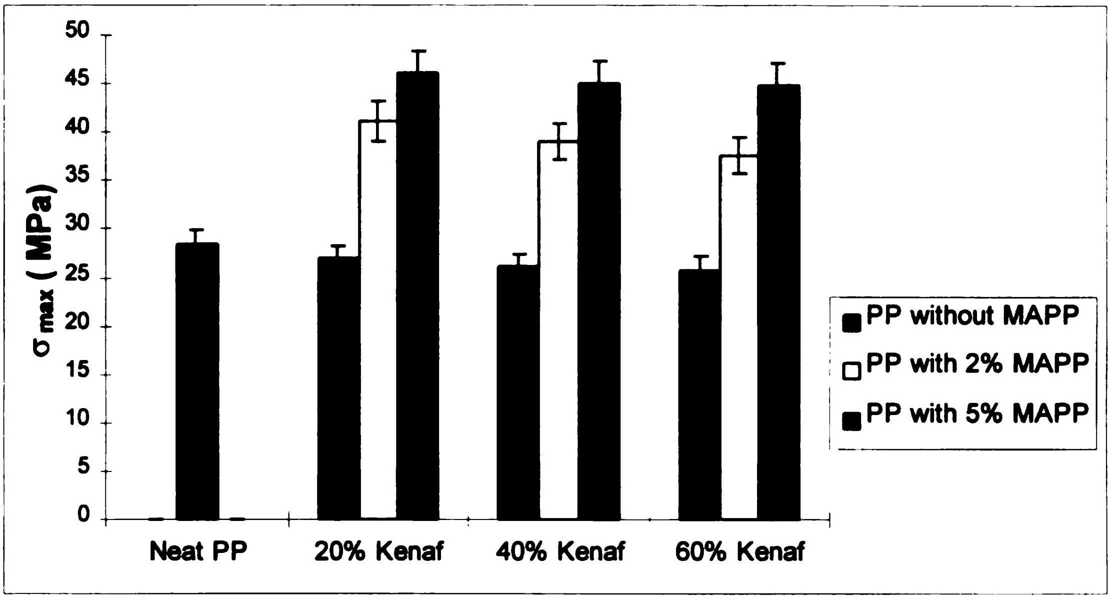


Figure 6.3 Tensile Strength for kenaf-PP composites.

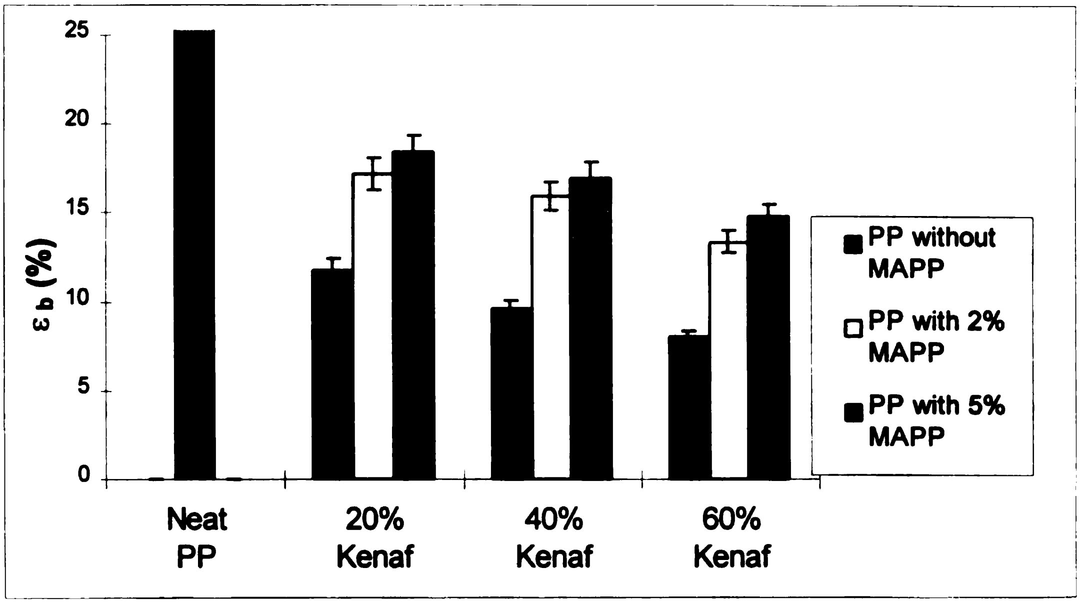


Figure 6.4 Elongation to break for kenaf-PP composites

6.3.2 Halpin-Tsai Prediction of Modulus

The Halpin-Tsai equations can be used to predict the elastic modulus of an anisotropic specimen of short fiber reinforced thermoplastics [53]. The following empirical relations are used:

$$E_{random} = \frac{3}{8}E_L + \frac{5}{8}E_T \tag{6.2}$$

$$\frac{E_L}{E_m} = \frac{1+(2l/d)\eta_L V_f}{1-\eta_L V_f} \tag{6.3}$$

$$\frac{E_T}{E_m} = \frac{1+2\eta_T V_f}{1-\eta_T V_f} \tag{6.4}$$

$$\text{where} \qquad \eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/d)} \tag{6.5}$$

$$\text{and} \qquad \eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \tag{6.6}$$

In the above equations E_{random} = overall elastic modulus, E_L= longitudinal modulus, E_T = transverse modulus, E_f = fiber modulus, E_m = matrix modulus, V_f = fiber volume fraction, and (l/d) = aspect ratio.

The comparison of Halpin-Tsai predictions with experimental results is shown in Figure 6.3. The fiber volume fraction (V_f) were calculated from the corresponding weight percentages using the specific gravity of kenaf fibers as 0.45 (experimental average). The results indicate that elastic modulus of kenaf fiber is between 5-10 GPa. Although the Halpin-Tsai model gives a good estimate of modulus it does not incorporate the effect of coupling agent on interfacial adhesion.

6.3.3 Flexural Properties

Table 6.2 compiles the 3-point flexural test results for various kenaf reinforced polypropylene composite systems. Since a flexural test subjects a specimen to a complex mixture of tension, compression and shear, the flexural properties are greatly dependent on the processing mode, fiber length and fiber orientation. The behavior of flexural strength and modulus is similar to tensile strength and tensile modulus respectively. Unlike tensile modulus, flexural modulus (Figure 6.5) improves tremendously by addition of MAPP. This indicates that the flexural properties give a better reflection of the improvement in interfacial adhesion between kenaf fibers and PP.

Table 6.2 Flexural test results for kenaf-PP composites.

Composite Material	Kenaf Fiber	Flexural Strength	Initial Flexural Modulus
	(wt %)	(MPa)	(GPa)
Neat PP	0	34.8	1.3
PP without MAPP	20	43.1	2.3
	40	44.9	2.7
	60	47.2	3.2
PP with 2% MAPP	20	46.3	3.0
	40	54.6	3.9
	60	63.2	4.4
PP with 5% MAPP	20	52.1	3.8
	40	59.8	4.1
	60	67.3	4.6

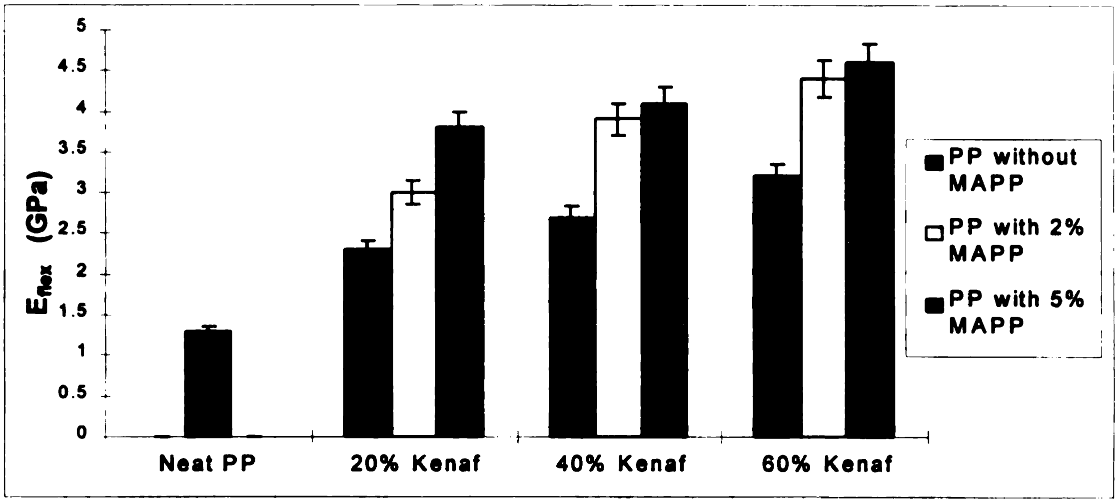


Figure 6.5 Flexural Modulus for kenaf-PP composites.

6.3.4 Impact Strengths and Toughness

Table 6.3 compiles the impact test results for various kenaf reinforced polypropylene composite systems. The notched Izod impact strength (Figure 6.6) decreases with increasing fiber content due to incorporation of more brittle fibers. In this case, the impact strength is only a measure of crack propagation energy since the initiation has already occurred because of the notch.

Impact strength does not have a simple relationship with adhesion between the fiber and polymer. It can be greatly affected by such factors as the perfection of packing and alignment of the fibers and imperfections such as voids. The increase in impact strength on addition of MAPP is probably due to improved adhesion.

Toughness, which was measured as the area under the stress-strain curve, also shows a similar behavior as the impact strength (Figure 6.7). Like impact, toughness is also a measure of the fracture energy of a composite. But it is not justifiable to compare the two because the rate and conditions under which the two tests are conducted is entirely different.

Table 6.3 Impact Strengths and Toughness for kenaf-PP composites.

Composite Material	Kenaf Fiber	Notched Izod Impact Strength	Toughness (area under stress-strain curve)
	(wt %)	(J/m)	(GPa)
Neat PP	0	42.1	Very high
PP without MAPP	20	41.3	114.8
	40	38.0	110.0
	60	33.4	108.3
PP with 2% MAPP	20	47.6	141.4
	40	41.4	136.8
	60	38.7	127.0
PP with 5% MAPP	20	50.1	145.8
	40	43.9	139.3
	60	39.2	132.7

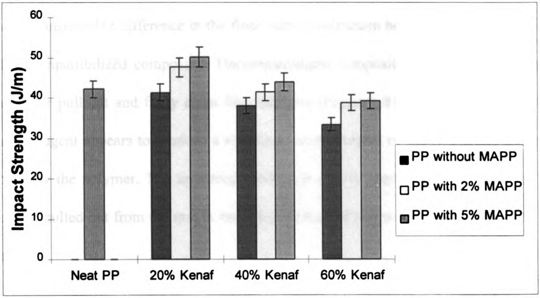


Figure 6.6 Notched Izod Impact Strength for kenaf-PP composites.

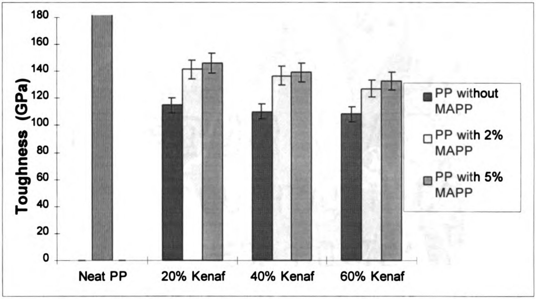


Figure 6.7 Toughness (area under stress- strain curve) for kenaf-PP composites.

6.3.5 SEM Analysis

SEM observations of the fracture surface of notched Izod specimens indicate that there is considerable difference in the fiber-matrix interaction between the compatiblized and uncompatilbilized composites. Uncompatibilized composite fracture surfaces show some fiber pull-out and fairly clean fiber surfaces (Figure 6.8). Addition of the MAPP coupling agent appears to produce a significant improvement of the wettability of kenaf surface by the polymer. The improved bonding is clearly seen in Figure 6.9 where the fiber has pulled out from the matrix but a fair amount of polymer residue remains on the fiber.

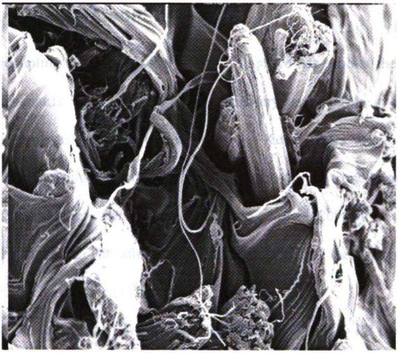


Figure 6.8 SEM of the fracture surface (notched Izod test) of kenaf (20%) - PP without MAPP.

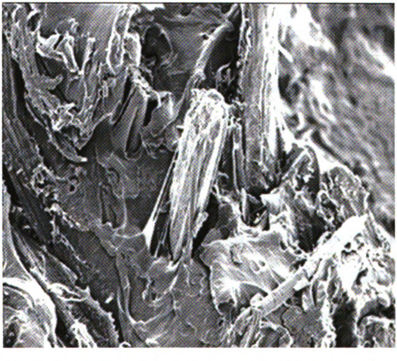


Figure 6.9 SEM of the fracture surface (notched Izod test) of kenaf (20%) - PP with 2% MAPP.

6.4 Effect of Silane Coupling Agent

Silane coupling agents are widely used to improve adhesion at the glass fiber or particulate filler-matrix interface. The silane chemistry and its role in improving the interfacial adhesion was discussed in section 3.3.1. Kenaf fibers were surface grafted with siloxane chains using a 2 wt% amino-ethyl amino-propyl trimethoxy silane (Dow Corning Z6032)solution in water. Composites were made with 20% by wt. silanized fiber loading in polypropylene. The injection molded specimens of these composites where then mechanically characterized (Table 6.4).

Table 6.4 Mechanical properties for silylated kenaf (20%) - PP composites.

Composite Material	PP - Kenaf without MAPP	PP - Kenaf with 2% MAPP	PP - silanized Kenaf with 2% MAPP
Tensile Strength, MPa	26.9	41.0	42.5
Tensile Modulus, GPa	2.7	2.9	3.3
Elongation to break, %	11.8	17.2	18.4
Elongation to yield, %	5.2	5.6	6.4
Flexural Strength, MPa	43.1	46.3	57.7
Flexural Modulus, GPa	2.3	3.0	4.0
Izod Impact Strength, J/m	41.3	47.6	54.6
Toughness, GPa	114.8	141.4	149.2

The results show that silane treatment of fiber improves the properties similar to the addition of MAPP. There is a remarkable increase in Izod impact strength and failure strain. The siloxane chains are believed to increase the ductility of fiber-matrix interface. Thus by incorporation of silane coupling agent stiffness could be increased without reducing the impact strength. But excess addition of silane to the fiber could cause the interface to become brittle.

Chapter 7

Maleation of Polypropylene

The role of maleated polypropylene (MAPP) in improving the mechanical properties of kenaf - PP composites was discussed in Chapter 6. Selection of MAPP with an optimal degree of grafting of maleic anhydride (MA) onto polypropylene (PP) is very crucial. The aim of this study was to understand the effect of MA and initiator concentration on the degree of grafting.

Reactive extrusion processing is an efficient approach for modification of polymers which involve grafting reactions and good control over rheology. Therefore the maleation of PP was carried out in a twin-screw extruder under controlled shear rates and temperature, with residence time of about 1.5 min.

7.1 Use of Maleated Polypropylene as a Compatibilzer

It was learnt from the results in section 6.3 that MAPP tremendously improves the interfacial adhesion between kenaf and PP. It is believed that the improved properties in the MAPP systems are due to a combination of formation of covalent linkage (by esterification with OH groups on fiber) and enhanced acid-base interactions between the fibers and MAPP.

7.2 Experimental Approach

The approach followed in these experiments was to prepare MAPP blends with varying concentration of MA and initiator. The amount of grafted MA on PP was then determined by titration and confirmed by IR spectroscopy. The rheological behavior and melt flow index (MFI) were determined for the blends on rheometrics mechanical spectrometer (RMS) and melt-flow indexer respectively.

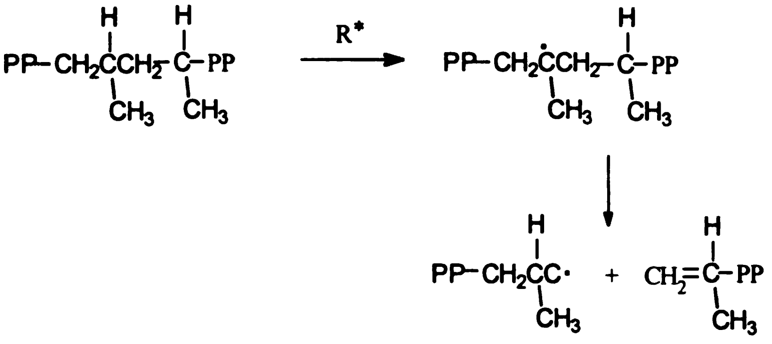
7.2.1 Functionalization of Polypropylene

The MA at 2 phr (parts per hundred resin) was added, after dissolving in a small amount of acetone, to the PP powder. The initiator, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane (Lupersol 101, Atochem) was also added at 0.1 phr to the mixture. The mixture was dry blended and fed into the hopper through a volumetric feeder at 5 kg/h. The extruder was run with a flat temperature profile at 180°C and a screw speed of 200 RPM. The modified polymer was extruded through a strand die, into a water bath, and finally to a pelletizer.

7.2.2 Reaction Mechanism

Although numerous studies have been made on maleation reactions no definitive mechanism is available. The following reaction mechanism has been proposed by Gaylord [54]:

The radicals generated by initiator decomposition attack the PP to generate PP$^\bullet$ macroradicals which disproportionate in the absence of MA and add MA when the latter is present.

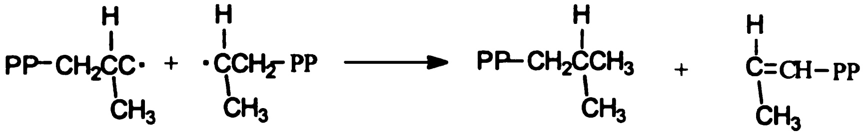


$$\mathrm{PP{-}CH_2C(H)(CH_3)CH_2{-}C(H)(CH_3){-}PP} \xrightarrow{R^*} \mathrm{PP{-}CH_2\dot{C}(CH_3)CH_2{-}C(H)(CH_3){-}PP}$$

(7.1)

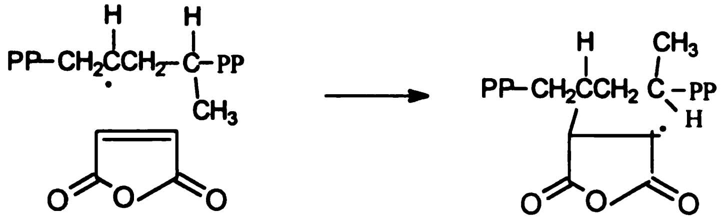
$$\downarrow \; \mathrm{PP{-}CH_2C(H)(CH_3)C\cdot + CH_2{=}C(H)(CH_3){-}PP}$$

(7.2)



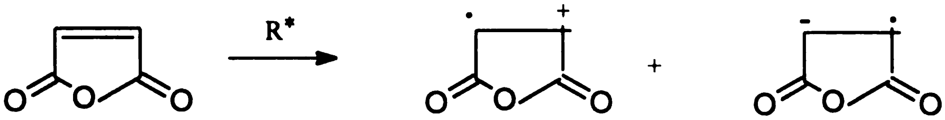
$$\mathrm{PP{-}CH_2C(H)(CH_3)C\cdot + \cdot C(H)(CH_3)CH_2{-}PP} \longrightarrow \mathrm{PP{-}CH_2C(H)(CH_3)CH_3 + C(H)(CH_3){=}CH{-}PP}$$

(7.3)



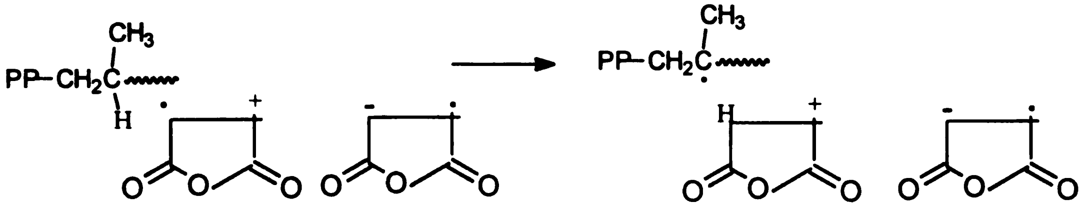
(7.4)

MA undergoes excitation as a result of the rapid decomposition of the initator.



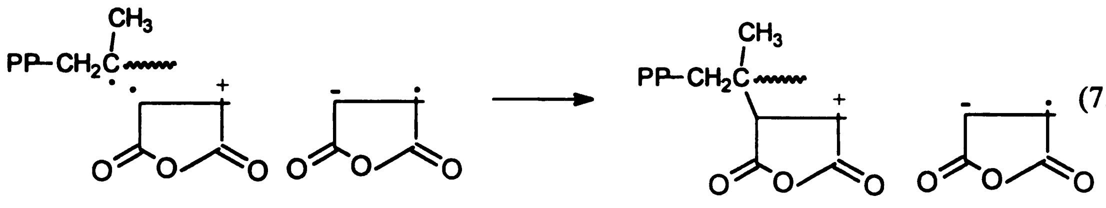
(7.5)

The MA excimer abstracts hydrogen from PP to generate a PP$^\bullet$ microradical.

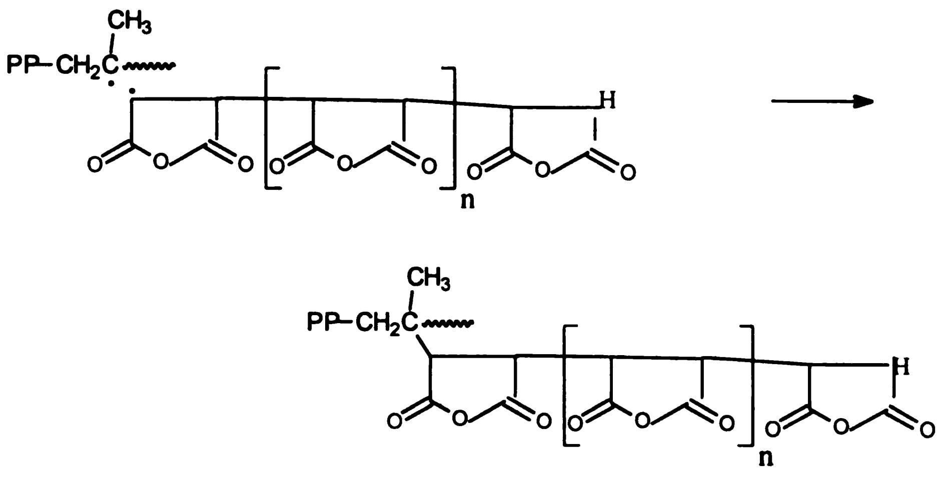


(7.6)

The PP• radical either undergoes degradative disproportionation, as shown in eqns. (7.2) and (7.3), adds MA as shown in eqn. (7.4), or couples with the MA excimer.


(7.7)

Graft copolymer is formed by the coupling of the PP• macroradical and the poly-MA• radical.


(7.8)

7.2.3 Determination of MA grafted by titration

Purification

The MAPP extrudate, which contains some unreacted MA, is dissolved by refluxing in xylene at 110-120°C for 45 min. The hot solution is then washed with excess acetone in order to precipitate out the polymer and extract unreacted MA in the solvent. About 1g of the precipitate is then used for titration.

Titration

Solutions of 0.05 N ethanolic KOH and 0.01 N ethanolic HCl were prepared. The KOH solution was standardized against a solution of potassium hydrogen phthalate, and HCl against KOH. A known amount (~ 1 g) of the MAPP sample is then dissolved in 50 ml xylene as mentioned earlier. To the hot solution was added 5 ml of ethanolic KOH and 3-4 drops of 1% thymol blue in dimethyl formamide as indicator. This was immediately followed by back-titration to yellow end point by the addition of ethanolic HCl (V_{HCl}) to the hot solution. A blank sample (50 ml xylene + 5ml KOH) was also titrated likewise. The difference between blank and sample is the % anhydride as follows:

$$\%\ \text{anhydride} = (V_{HCl\,(blank)} - V_{HCl\,(sample)}) * N_{HCl} * 98.06\ \text{g/mol} * 100 / W_{sample} \quad (7.1)$$

where V is volume in liters, W is weight in grams.

Table 7.1 Titration and IR results for maleated polypropylene blends.

MA wt % on PP	Initiator wt% on MA	% MA incorporated	Carbonyl Index	Melt Flow Index (g/10 min)
		Titration	FT-IR	ASTM 1238
Neat PP	0.0	0.0	0.0	5.8
PP - 1% MA	0.1	0.32	0.54	13.2
	0.2	0.21	0.28	24.7
	0.3	0.17	0.42	*
PP - 2% MA	0.1	1.17	1.76	18.3
	0.2	1.03	1.32	*
	0.3	0.94	1.61	*
PP - 3% MA	0.1	1.40	1.8	*
	0.2	1.22	1.92	*
	0.3	1.08	1.5	*

* Melt flow rate is too high to be measured.

The results (Table 7.1) show that the % MA incorporated decreases with increase in initiator concentration, and a fixed MA concentration to start with. This can explained by the fact that increased free radical presence favors dimerization of MA thus depleting it. Maximum change in MA incorporated occurs when the initial MA concentration is increased from 1% to 2%, further increase doesn't increase the MA grafting onto PP much.

7.2.4 Determination of MA grafted by IR spectroscopy

The MA content was determined by Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer System 2000 FT-IR). The purified MAPP sample films (50-100 μm thickness) were prepared using a Carver laboratory press at 180°C with 5-10 tons force between polyimide (Kapton) films. The spectrum was recorded in the region of 4000 - 400 cm^{-1}.

An empirical method of analyzing MA content in MAPP films was tried, using the ratios of the areas of the characteristic carbonyl absorption at 1790 cm^{-1} (in anhydride) and PP absorption bands at 900 cm^{-1}, the latter being used as the internal standard (Figure 7.2). A calibration curve of these ratios were constructed against the titration values of the same samples (Figure7.3). This preliminary result should encourage the use of this much simpler IR method for analyzing MA in MAPP.

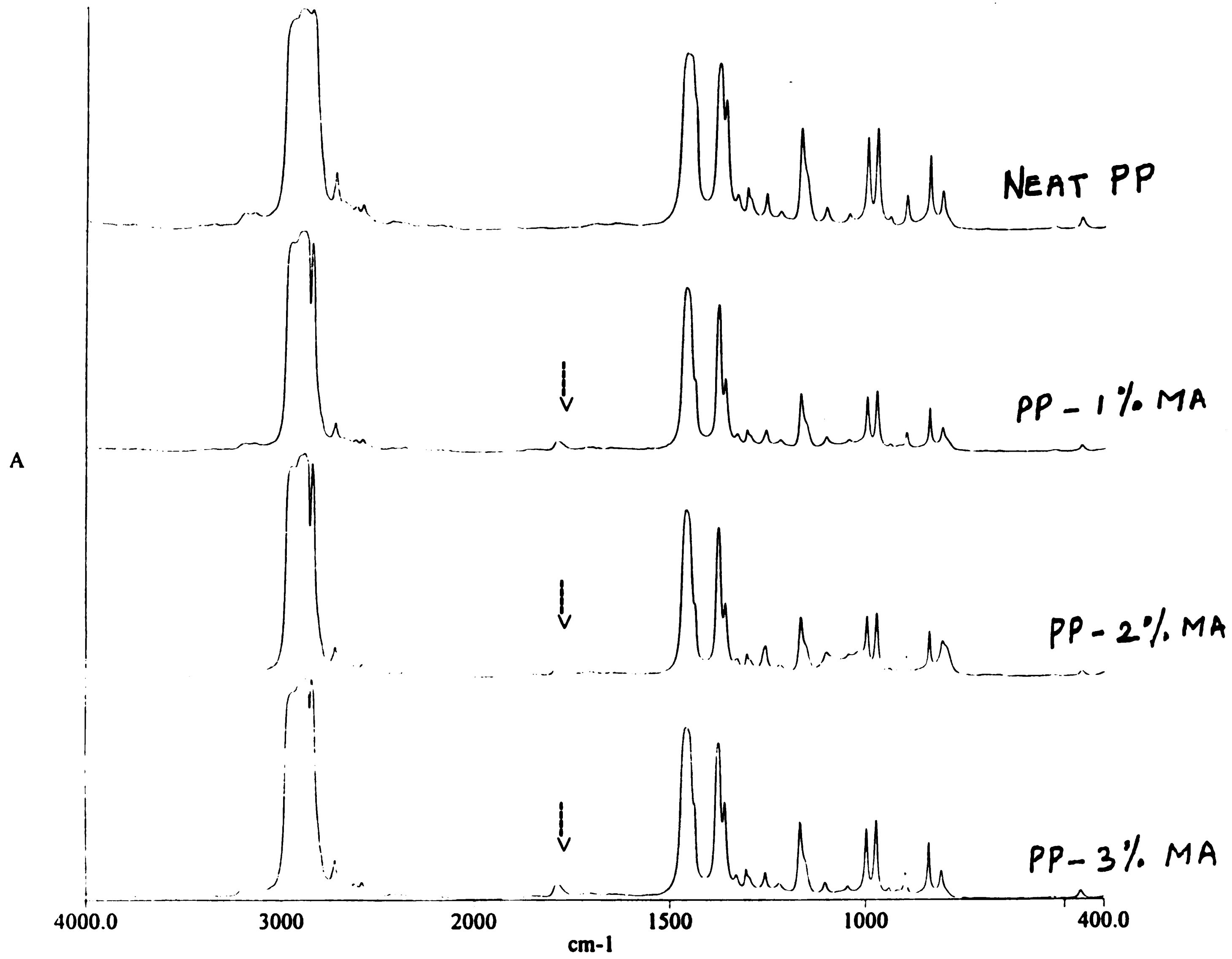


Figure 7.1 FTIR Spectra of MAPP with 0%, 1%, 2%, and 3% MA in PP.

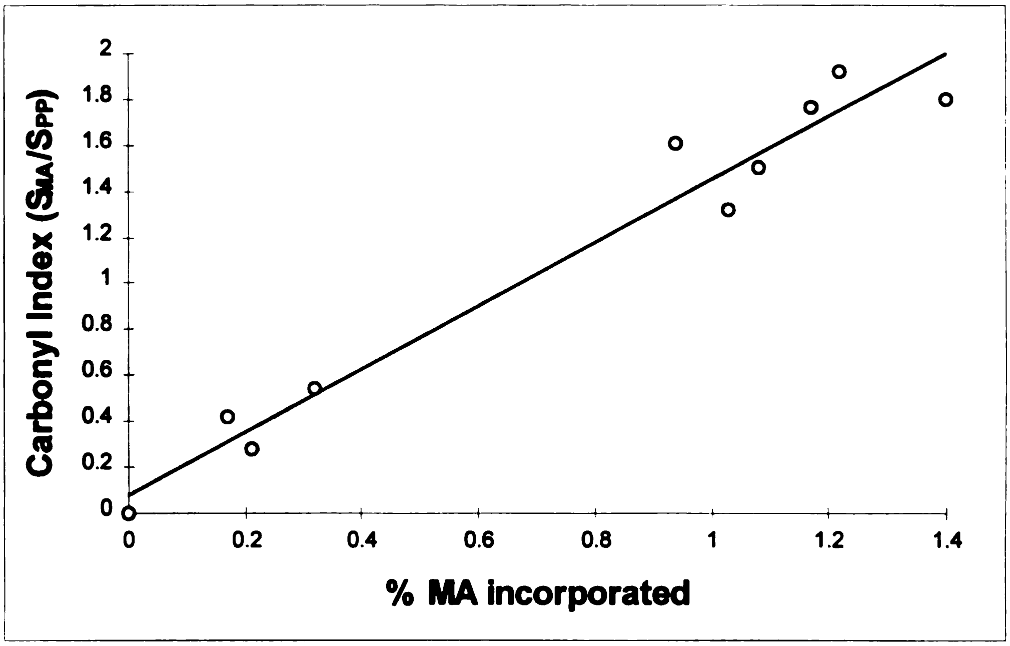


Figure 7.2 Calibration curve for determining the incorporated MA content from the FTIR spectrum.

7.3 Study of Rheological Behavior

The rheological behavior of the samples was determined in terms of viscoelastic properties by employing a Rheometrics Mechanical Spectrometer (RMS-800) with 25 mm diameter parallel plate at 180°C. The oscillatory shear experiments were done within the linear viscoelastic range of strain at frequencies from 0.1 to 100 rad/s. The dynamic mechanical properties like the storage modulus (G') and loss modulus (G``) were also measured.

The plot of complex viscosity (η*) vs frequency (ω) shows a dramatic decrease in viscosity for maleated blends at low ω though the shear thinning rate decreases relative to neat polypropylene (Figure 7.4). The plot of G`` vs G` known as the modified Cole-Cole plot (mCC) provides information on MWD, branching and morphology, etc.[55]. In general, data positioned to the right and below the equimodulii line, G' = G''(Figure 7.5), indicate that elastic mechanisms dominate the sample behavior, whereas data located to the left and above the equimodulii line show that the sample behavior is dominated by the viscous component, also, the broadening of MWD shifts the mCC plot to lower G' values and increases its slope.

The shear rates in an extrusion process are usually 500 sec^{-1} or more. Such high shear rates are not achievable on a RMS therefore a time-temperature superposition is used. An alternative technique would be to use a capillary rheometer.

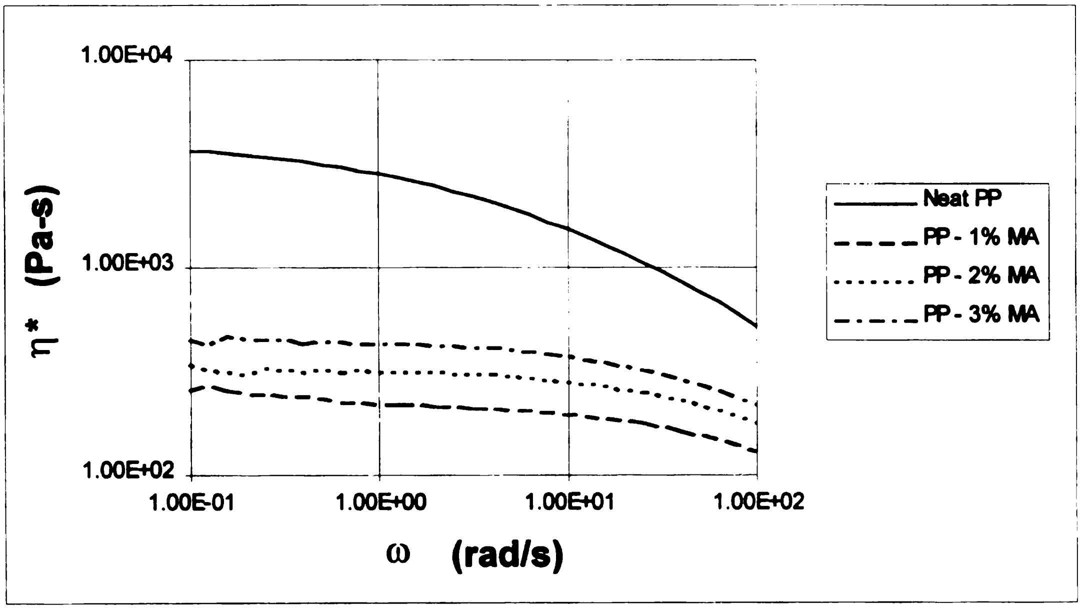


Figure 7.3 Complex viscosity vs. frequency of neat PP and MAPP with varying MA content.

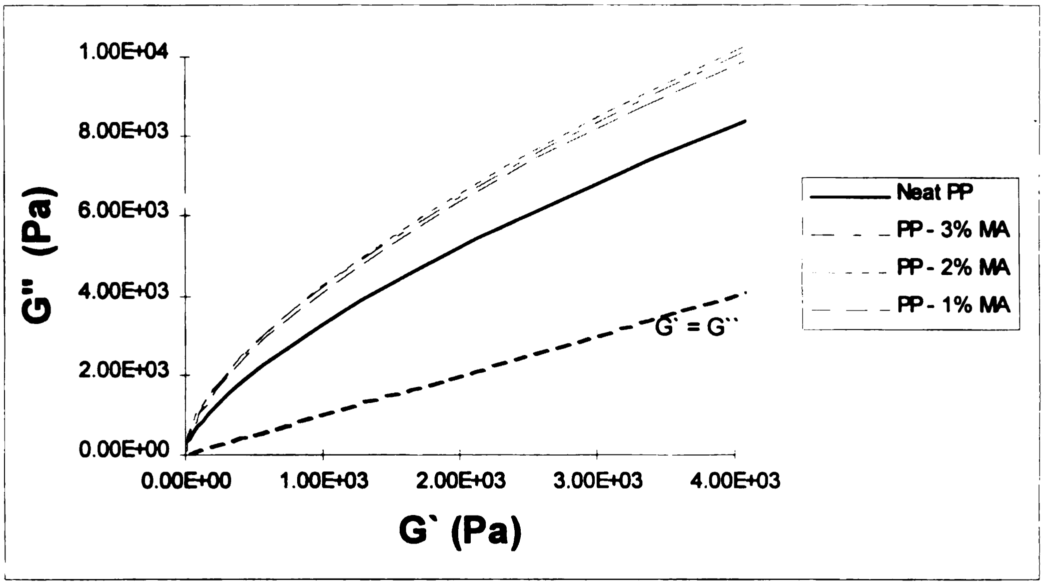


Figure 7.4 Modified Cole-Cole (mCC) plots of neat PP and MAPP with varying MA content.

7.4 Melt Flow Index

The melt flow index of the blends were determined in a Ray-Ran melt indexer at 230°C under a load of 2.16 kg (ASTM D1238). The increase in melt flow index (Table 7.1) of the maleated blends is due to increased chain scission. For some of the blends the increase in melt index was so high that it was not possible to accurately measure the melt index. Many studies [54,56-57] have being conducted with different additives that could inhibit chain scission without affecting the cross-linking capability of the maleated blends.

Chapter 8

Conclusions & Recommendations

8.1 Conclusions

Natural fibers possess a variety of appealing properties to be used in thermoplastic composites of moderate strength. Though most of the natural fiber thermoplastics are still in development stage, the interest in using them has been growing in recent times. In the end, the biodegradability and low-cost of natural fibers combined with the reprocessability of the thermoplastics might play the key role behind further progress in the field.

8.1.1 Development of Kenaf Reinforced Polypropylene Composites

Composites of kenaf and polypropylene were prepared by mixing in a twin screw extruder followed by injection molding. A systematic study of the different processing variables was done with a view to develop optimum processing conditions. The composite properties were improved by incorporation of maleated polypropylene (MAPP) as a coupling agent or by treatment of kenaf with a silane coupling agent. Since each of these variables affects the composite properties in its own way and also the variables are interdependent to a certain extent, the system presents a multivariable problem. Therefore, composites with different composition of fiber, resin and interfacial agents were prepared and characterized.

8.1.2 Improvement in Mechanical Properties

The inclusion of MAPP resulted in composites with good mechanical properties as compared to the uncoupled composites. Tensile and flexural strength and failure strain increased with the addition of MAPP at all levels, with the most significant increase occurring with the addition of 2% MAPP. Further addition of MAPP resulted in only slight improvement of the properties. The impact strength increases but the modulii are relatively unaffected.

The ability of MAPP to enhance mechanical properties supports the theory of it having the potential, to improve adhesion between the matrix and fibers. This was attributed to the anhydride functionality in the modified polymer which served to form bonds between the polar lignocellulosics and the non-polar thermoplastic component. A strong interfacial bond between the fiber and matrix allows the matrix to efficiently transfer stress to the fibers. Also a strong interfacial bond can prevent the propagation of microcracks along the fiber length.

The tensile modulus increased with the fiber content, while the yield and breaking stress remained relatively unaffected. The failure strain and the impact strength fell sharply when the fiber content was increased. The treatment of kenaf with a silane coupling agent increased the impact strength, toughness and the failure strain, other properties were relatively unaffected. Combination of silane treatment and addition of MAPP could be used to improve the stiffness of the composite without decreasing the impact strength.

The process conditions and the composition can be suitably modified to fabricate either composites that exhibit elastic modulii approaching glass-fiber reinforced materials or composites that duplicate the elongation characteristics of the neat PP, while showing improved tensile strengths.

8.1.3 Comparison with other Polypropylene Composites

Table 8.1 compares the tensile, flexural and impact properties of the neat PP and its composite systems containing 20% by wt. of sisal, kenaf, glass and talc. The comparison is meant as a general guideline and not as an exact comparison, which would be possible only if all the specimens were prepared and tested under identical conditions.

Addition of glass, sisal or kenaf fibers to neat PP with proper interfacial agents can improve the overall mechanical properties but to a different degree for each fiber system. Both the natural fiber composites, sisal and kenaf reinforced, have poorer flexural modulus and impact strengths (Figures 8.1 & 8.2) compared to the glass reinforced PP. But the difference is not so significant if one considers the specific strengths (per unit weight basis). It implies that for a given weight of composite the natural fiber reinforced would have almost an equal mechanical strength as the glass reinforced.

Talc just acts as filler when added to PP, it increases the modulii and flexural strength but decreases the impact strength and tensile strength. It produces a low cost composite with a good surface finish but poor mechanical properties.

Figures 8.1 and 8.2 show that kenaf reinforced PP has a higher flexural modulus compared to sisal reinforced but much poorer impact strength. The higher modulus is due to the higher stiffness of kenaf compared to sisal fibers. The poorer impact property of kenaf is possibly due to the irregular shape of kenaf fibers resulting in local stress concentrations in the matrix.

Table 8.1 Characteristics of some PP composites.

Property	Neat PP	PP - Sisal	PP - Kenaf	PP - Glass	PP- Talc
Fiber/Filler (wt %)	0	20	20	20	20
Density, gm/cm^3	0.9	1.0	0.95	1.15	1.05
Tensile Strength, MPa	28.4	35.6	41.0	55.0	24.1
Tensile Modulus, GPa	1.2	4.8	2.9	8.3	2.2
Elongation to break, %	300	9.2	5.6	3.5	4.0
Flexural Strength, MPa	34.8	56.4	46.3	75.8	44.1
Flexural Modulus, GPa	1.3	2.3	3.0	4.2	2.1
Izod Impact Strength, J/m	42.1	89.7	47.6	107.0	21.4
Specific Tensile Strength	31.6	35.6	43.2	47.8	22.9
Specific Tensile Modulus	1.3	4.8	3.0	7.2	2.1
Specific Flexural Strength	38.7	56.4	48.7	65.9	42.0
Specific Flexural Modulus	1.4	2.3	3.2	3.6	2.0

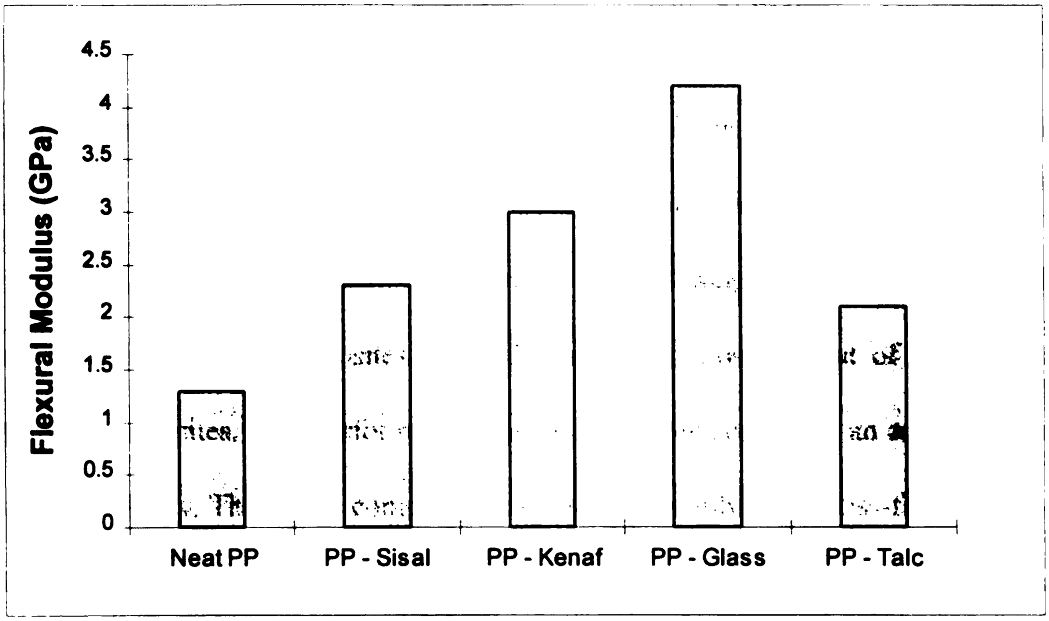


Figure 8.1 Flexural Modulus for some PP composites.

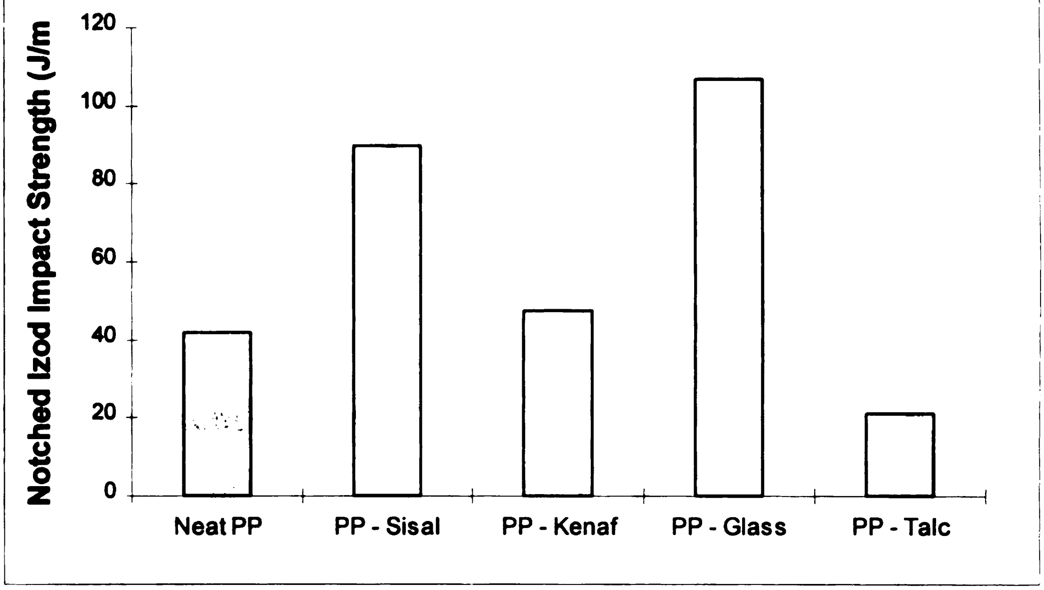


Figure 8.2 Notched Izod Impact Strength for some PP composites.

8.1.4 Applications

Kenaf - PP composites have distinct advantage of a substantially low density, an important factor in applications where light weight is imperative. Material cost savings resulting from the reduced use of PP can be significant. Judicious use of these fibers will make it possible for natural fibers to define their own niche in the plastics industry, and in manufacture of low-cost, high-volume composites for wide variety of applications.

As mentioned in Section 8.1.3, the strength per unit weight (specific strength) of the natural fiber reinforced composites is usually higher or close to that of synthetic fiber reinforced composites. This performance is afforded at low costs with an added advantage of biodegradability. Thus these composites can potentially substitute glass-fiber composites in applications where the strength can be traded off for less weight, lower cost, ease of recyclability or energy recovery.

Potential areas of application for such composites include traditional injection molded articles, consumer disposables, replacement for PVC laminates and profiles, automotive interior parts, etc. Commercial production of such composites would open a new avenue for the utilization of kenaf fiber and represent value addition to the agricultural crop.

8.2 Recommendations

Inspite of its high stiffness and strength potential, kenaf fiber did not produce as high a degree of reinforcement as would be expected for any synthetic fiber. It is believed that this could be due to several factors such as:

i) length reduction brought about by the intense shear forces in extruder and injection molder.

ii) poor interfacial adhesion between kenaf fiber and PP matrix.

iii) improper dispersion of the fibers in the matrix.

To overcome these problems a thorough understanding of the variables which influence this behavior is required. Optimum compounding and processing conditions need to be determined which would reduce the attrition of fibers. In addition, there is a scope for tailoring coupling agents which could function better than the ones used currently. Some technique or dispersion aids need to be developed to ensure proper dispersion of fibers to maintain homogeneity of the composite product.

Other major problems which hinder the commercialization of kenaf fiber composites is their poor stiffness - impact balance and poor water resistance. Research studies [15, 20-23, 25-26] are being conducted to understand and solve these problems.

Use of a biodegradable polymer such as a thermoplastic polylactide (corn based plastic) with natural fibers is recommended to make a composite which is fully biodegradable. This would be a completely new area requiring study of the compatibilization between polylactide and kenaf. Products developed from these composites could replace existing non-agricultural based plastics used in disposables and other consumer products.

Use of natural fibers in woven or non-woven mat form is recommended because it is believed that such continuous fiber composites would have better mechanical properties than the short-fiber reinforced.

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