Agro-Fiber Thermoplastic Composites

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1.INTRODUCTION

Several billion pounds of fillers and reinforcements are used annually in the plastics industry. The use of these additives in plastics is likely to grow with the introduction of improved compounding technology and new coupling agents that permit the use of high filler/reinforcement content (Katz and Milewski, 1987). As suggested by Katz and Milewski, fillings up to 75 parts per hundred (pph) could be common in the future: this could have a tremendous impact in lowering the usage of petroleum based plastics. It would be particularly beneficial, both in terms of the environment and also in socio-economic terms, if a significant amount of the fillers were obtained from a renewable agricultural source. Ideally, of course, an agro-/bio-based renewable polymer reinforced with agro-based fibers would make the most environmental sense.

1.1 Advantages of Using Agro-Fibers in Plastics

The primary advantages of using annual growth lignocellulosic fibers as fillers/reinforcements in plastics are listed below:

Property Advantages
Low densities
Non abrasive
High filling levels possible resulting in high stiffness properties
High specific properties
Easily recyclable
Unlike brittle fibers, the fibers will not fracture when processing over sharp curvatures.

Environmental and Socio-Economic Advantages
Biodegradable
Wide variety of fibers available throughout the world
Generates rural jobs
Non-food agricultural/farm based economy
Low energy consumption
Low cost
Low energy utilization

Material cost savings due to the incorporation of the relatively low cost agro-fibers and the higher filling levels possible, coupled with the advantage of being non-abrasive to the mixing and molding equipment, are benefits that are not likely to be ignored by the plastics industry for use in the automotive, building, appliance, and other applications.

Prior work on lignocellulosic fibers in thermoplastics has concentrated on wood-based flour or fibers, and significant advances have been made by a number of researchers (Woodhams et al.. 1984; Klason and Kubat, 1986a, b; Myers et al., 1992; Kokta et al., 1989; Yam et al., 1990; Bataille et al., 1989, Sanadi et al., 1994a). A recent study on the use of annual growth lignccellulosic fibers indicates that these fibers have the potential of being used as reinforcing fillers in thermoplastics (Sanadi

et al., 1994b). The use of annual growth agricultural crop fibers such as kenaf has resulted in significant property advantages as compared to typical wood-based fillers/fibers such as wood flour, wood fibers, and recycled newspaper. Composites containing compatibilized polypropylene (PP) and kenaf have mechanical properties comparable with those of commercial PP composites (Sanadi et al., 1994b).

1.2 Limitations

The primary drawback of the use of agro-fibers is the lower processing temperature permissible due to the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures are thus limited to about 200°C, although it is possible to use higher temperatures for short periods. This limits the type of thermoplastics that can be used with agro-fibers to commodity thermoplastics such as polyethylene (PE), PP, polyvinyl chloride (PVC), and polystyrene (PS). However, it is important to note that these lower-priced plastics constitute about 70% of the total thermoplastic consumed by the plastics industry, and subsequently the use of fillers/reinforcement presently used in these plastics far outweighs the use in other more expensive plastics.

The second drawback is the high moisture absorption of the natural fibers. Moisture absorption can result in swelling of the fibers, and concerns about the dimensional stability of the agro-fiber composites cannot be ignored. The absorption of moisture by the fibers is minimized in the composite due to encapsulation by the polymer. It is difficult to entirely eliminate the absorption of moisture without using expensive surface barriers on the composite surface. If necessary, the moisture absorption of the fibers can be dramatically reduced through the acetylation of some of the hydroxyl groups present in the fiber, but with some increase in the cost of the fiber (Rowell, Tillman, and Simonson, 1986) (see Chapter 11). Good fiber-matrix bonding can also decrease the rate and amount of water absorbed by the composite. Research on this area is presently underway at the University of Wisconsin and the USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin.

It is important to keep these limitations in perspective when developing end-use applications. We believe that by understanding the limitations and benefits of these composites, these renewable fibers are not likely to be ignored by the plastics/composites industry for use in the automotive, building, appliance, and other applications.

2. PROCESSING CONSIDERATIONS AND TECHNIQUES

Separation of the fibers from the original plant source is an important step to ensure the high quality of fibers. Details of the different processes used for processing to composites were given in Chapter 8. The limiting processing temperatures when using lignocellulosic materials with thermoplastics are important in determining processing techniques. High processing temperatures (>200°C) that reduce melt viscosity and facilitate good mixing cannot be used (except for short periods), and

other routes are needed to facilitate mixing of the fibers and matrix in agro-fiber thermoplastics.

An excellent review by Milewski (1992) on short fiber composite technology covers a variety of reasons that result in problems associated with composite properties falling short of their true reinforcing potential. The major factors that govern the properties of short fiber composites are fiber dispersion, fiber length distribution, fiber orientation, and fiber-matrix adhesion. Mixing the polar and hydrophilic fibers with non-polar and hydrophobic matrix can result in difficulties associated with the dispersion of fibers in the matrix. Clumping and agglomeration must be avoided to produce efficient composites. The efficiency of the composite also depends on the amount of stress transferred from the matrix to the fibers. This can be maximized by improving the interaction and adhesion between the two phases, and also by maximizing the length of the fibers retained in the final composite (Biggs et al., 1988). Using long filaments during the compounding stage can result in higher fiber length distribution. However, long fibers sometimes increase the amount of clumping resulting in areas concentrated with fibers and areas with excessive matrix; this ultimately reduces the composite efficiency. Uniform fiber dispersion cannot be compromised, and a careful selection of processing techniques, initial fiber lengths, process conditions, and processing aids are needed to obtain efficient composites. Several types of compounding equipment, both batch and continuous equipment, have been used for blending lignocellulosic fibers and plastics.

The ultimate fiber lengths present in the composite depend on the type of compounding and molding equipment used. Several factors contribute to the fiber attrition such as the shearing forces generated in the compounding equipment, residence time, temperature, and viscosity of blends. An excellent study on the effect of processing and mastication of several types of short fibers in thermoplastics was conducted by Czarnecki and White (1980). They concluded that the extent of breakage was most severe and rapid for glass fibers, less extensive for kevlar (aramid) fibers, and the least for cellulose fibers. The level of fiber attrition depends on the type of compounding and molding equipment used, level of loading, temperature, and viscosity of the blend (Czarnecki and White. 1980).

The properties of the agro-based thermoplastic composites are thus very process-dependent. Yam et al. (1990) at Michigan State University studied the effect of twin screw blending of wood fibers and high density polyethylene (HDPE) and concluded that the level of fiber attrition depended on the screw configuration and the processing temperature. Average fiber lengths decreased from about 1.26 mm prior to compounding to about 0.49 mm after extrusion. Modification of the screw configuration reduced fiber attrition to an average length of about 0.78 mm. Fiber weight percent up to 60% was reported to have been mixed. The tensile strength of the pure HDPE was higher than that of the wood fiber-HDPE, irrespective of the level of fiber filling. This was explained to be because of a lack of dispersion with fibers clumping in bundles and poor fiber-matrix bonding. Use of stearic acid in HDPE/wood fibers improved fiber dispersion and improved wetting between the fiber and matrix (Woodhams, 1984) and resulted in significant improvement in mechanical properties. Work by Raj and Kokta (1989) indicates the importance of using surface modifiers to improve fiber dispersion in cellulose fibers/PP composites. Use of a small amount

of stearic acid during the blending of cellulose fibers in polypropylene decreased both the size and number of fiber aggregates formed during blending in an internal mixer (Brabender roil mill).

Another technique that is gaining acceptance is the high intensity compounding using a turbine mixer (thermokinetic mixer). Woodhams et al. (1990) and Myers et al. (1992) found the technique effective in dispersing lignocelluiosic fibers in thermoplastics. Addition of dispersion aids/coupling agents further improved the efficiency of mixing. The high shearing action developed in the mixer decreased the lengths of fibers in the final composite. However, the improved fiber dispersion resulted in improved composite properties. A recent study evaluating fiber lengths of a jute-PP composite blended in a thermokinetic mixer, and then injection molded, was conducted by dissolving the PP in the composite in xylene and then using image analysis to measure the length of the fibers (Karmakar, 1994). The ultimate fibers lengths varied from about 0.10 mm to about 0.72 mm with an average of 0.34 ± 0.13 mm. Recent work using a thermokinetic mixer to blend kenaf in PP (Sanadi, Caulfield, unpublished results) has confirmed the usefulness of the compounding technique in effectively dispersing natural fibers in the thermoplastic matrix. An added advantage is that no pre-drying of the fibers is needed prior to the blending stage in the mixer.

3. SURFACE ENERGIES AND ADHESION

When a fiber composite fails by an interracial or adhesive type failure, it is presumed that part of the failure arises from the lack of sufficient chemical bonding between fiber and matrix. But it is also likely that part of the failure arises from the inability to achieve intimate intermolecular contact between components. Strength of composites will thereby improve if one can modify the nature of the component surfaces so that their surface energies are more compatible with one another.

3.1 Cellulose Fiber Surfaces

The cellulose molecule is inherently extremely hydrophilic. The hydroxyl groups that cover the surface of a pulp fiber provide hydrogen bonds that are the ultimate forces that hold paper together and provide the basis of its mechanical strength properties (Caulfield, 1980). The good wetting of cellulose fibers by water is essential to the paper-making process, but also responsible for the poor strength properties of paper when wet. Water readily wets a cellulose fiber, whereas a non-polar material may interact very poorly with a cellulose fiber surface.

The necessary intimacy of contact essential for good adhesion in composite fabrication is achieved by good wetting of one component by the other. This compatibility between the surface energies of the two components and the resultant good adhesion are reflected in the mechanical strength of the composite (Westerlind and Berg, 1988). In order to improve the adhesion between cellulose fibers and polymer matrix, one may either modify the surface of the cellulose fiber or modify the polymer matrix in order to achieve the necessary compatibility of surface energies.

3.2 Surface Energies and Nettability

One way of characterizing surface energies is through nettability measurement, or measurement of contact angles formed at the interface between the solid, air and a liquid of knowm surface tension (Miller, 1985). In recent years techniques for measurement of wettabilities and contact angles of fibers have become well established (Berg, 1986: Young, 1986). The typical method uses an electronic micro-balance to measure the forces. Techniques have been developed to deal with buoyancy effects and crimped fibers. In textile research the micro-balance method for contact angle measurement is now widely accepted for surface energy characterization. Additional difficulties arise when studying small natural fibers, but research has shown that meaningful measurements are possible even on wood pulp fibers (Young, 1976: Klungness, 1981).

Consider, for example, the simple depiction of two limiting cases. Case I is a fiber partially immersed in a fluid which tends to wet the fiber. The wetting angle is less than 90°. In Case H a fiber is partially immersed in a fluid that tends not to wet the fiber and the contact angle is greater than 90°. For Case I in which the liquid wets the fiber, the balance of the surface energies and surface tension is such that the net force on the fiber is one that draws the fiber further into the liquid. For Case II, the net force on the fiber is one that pushes the fiber from the liquid. The well established Wilhelmy equation relates the force, F, exerted on the fiber to the perimeter of the fiber, r, the surface, tension of the liquid, and the γ contact angle, q, between the solid (fiber) and liquid (Wilhelmy, 1863).

$$F = p\gamma\cos\theta - Agh\rho$$

The second term accounts for the effect of buoyancy; where r is the liquid density, γ is the gravitational constant, A is the cross-sectional area of the fiber, and h is the depth of immersion. In most cases the second term can be safely ignored.

Using Wilhelmy's equation to measure surface tensions along with Young's equation allows the surface energy, or more generally the thermodynamic energy of interaction or the work of adhesion, to be evahtated. This work of adhesion may be viewed as the sum of terms corresponding to the contributions from the different types of interactions (Fowkes, 1972).

$$W = W^d + W^p + W^h + W^i$$

The superscript d refers to dispersive forces, p to dipole-dipole interactions, h to hydrogen bonding and i to induced dipole interactions. Since dipole and induction force contributions are usually small, this equation is more often written:

$$W = W^{lw} + W^{ab}$$

where the dispersion forces are combined with the dipole and induced dipole contributions and designated Lifshitz-van der Waals (lw) forces (Fowkes, 1987). All the

other forces are described as acid/base interactions (ah). Lewis acid/base interactions cover any interaction that involves the sharing of an electron pair, most especially hydrogen bonding. In the case of cellulose, with a surface dominated by hydroxyl groups, the acid/base interactions can be described as predominantly hydrogen bonding.

Coupled surface energy and internal bond strength measurements indicate a strong correlation between the extent of hydroxyl-rich (acid/base) interface and good adhesive properties (Quillin, Caulfield, and Koutsky, 1992). To improve adhesion between cellulose and polypropylene (or other polyolefins), the general recommendation is to modify the hydrophobic polymer in a way that introduces chemical moieties on its surface that are capable of producing strong acid/base (hydrogen bonding) interactions with the groups on the surface of the cellulose.

3.3 Adhesion and the Interphase

The adhesion between the plastic matrix and polar lignocellulosic fibers is critical in determining the properties of the composite. Sever al different types of functionalized additives have been used to improve the dispersion and the interaction between cellulose-based fibers and polyolefins, polyvinyl chloride, polystyrene, etc. (Dalvag et al., 1985, Kokta, Raj. and Daneault, 1990).

The inherent polar and hydrophilic nature of the lignocellulosic fibers and the non-polar characteristics of the polyolefins result in difficulties in compounding and adhesion between the fibers and matrix. Proper selection of additives is necessary to improve the interaction and adhesion between the fiber and matrix phases. Maleic anydnde (MA) -grafted polypropylene (MAPP) has been reported to function efficiently for lignocellulosic-PP systems. Earlier results suggest that the amount of MA grafted and the molecular weight are both important parameters that determine the efficiency of the additive (Felix et al., 1993; Sanadi et al., 1993). The maleic anhydride present in the MAPP not only provides polar interactions, but can covalently link to the hydroxyl groups on the lignocellulosic fiber (Figure 12.1). Han, Saka, and Shiraishi (1991) reported that the MAPP was localized on the cellulosic surface in a PP marnx: this was inferred from TEM-EDXA studies of osmium tetroxide-labeled MAPP. The formation of covalent linkages between the MA and the -OH of cellulose has been indicated through IR and ESCA analysis by Gatenholm et al. (1992).

The interactions between non-polar thermoplastics such as PP and arty coupling agents such as MAPP are predominantly those of chain entanglement. Stresses applied to one chain can be transmitted to other entangled chains, and stress is distributed among many chains. These entanglements function like physical cross links that provide some mechanical integrity up to and above the glass transition temperature, T^g, but become ineffective at much higher temperatures (Neilsen, 1974). When polymer chains are very short, there is little chance of entanglement between chains and they can easily slide past one another (Neilsen, 1977). When the polymer chains are longer, entanglement between chains can occur and the viscosity of polymer becomes high. A minimum chain length or a critical molecular weight (MJ is necessary to develop these entanglements and a typical polymer has a chain length
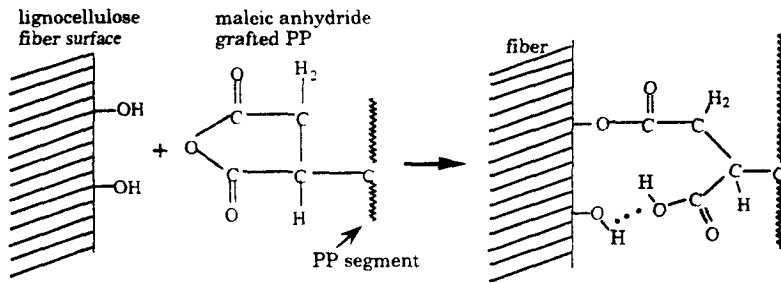
Figure 12.1 Reaction mechanism of maleated PP with the surface of the lignocellulosic fiber. Note potential of both covalent and H-bonding.

between entanglements equivalent to a M_e varying from 10,000 to about 40,000. The M_e varies depending on the structure of a polymer and, for example, linear polyethylene has a corresponding M_e for entanglements of about 4.000 (Neilsen, 1977), while for polystyrene it is about 38.000. Factors such as the presence of hydrogen bonding or the presence of side chains that affect the glass transition temperature of the polymer also will affect the M_e of the polymer melt. It is also important to note that the presence of the fiber surface is likely to restrict the mobility of the polymer molecules, and the minimum entanglement lengths will vary according the fiber surface characteristics.

Two major factors need to be considered while selecting additives to develop enough mechanical integrity of the interphase region so that there is sufficient stress transfer properties between the non-polar matrix and the polar fiber. Firstly, the functional additive present near the fiber surface should be strongly interacting with the fiber surface through covalent bonding and/or acid-base interactions (Figure 12. 1). This means that sufficient functional groups should be present in the functional additive so that interactions can occur with the -OH groups on the fiber surface (Figure 12.2). Secondly, the polymer chains of the functional additive should be long enough to permit entanglements with the PP in the interphase (Figure 12.3).

In the case of MAPP interaction with the fiber surface there is a possibility of two or more MA groups, from the same MAPP molecule, interacting with different -OH groups on the fiber surface to form a tightly-bound MAPP molecule (Figures 12.2 and 12.3). Segmented loops are then formed between sites of MA and -OH interactions. It must be pointed out that although loop formation can and may occur, there will also be cases where, a tail section of the MAPP 'sticks out' into the interface region. This section, we believe, has a greater possibility of interaction with the PP molecules because of greater entanglement possibilities as compared to any MAPP that has formed loops. It must be noted that a minimum segmented length is necessary for good interaction, whether through a tail or loop section of the MAPP. An ideal situation would be to create a molecule with a "head-tail" configuration, where one or more MA groups are grafted onto one end of the MAPP molecule, while the other end has no grafted MA molecules. This would maximize the length of entanglement with the PP molecules and also permit the MA groups to interact with the -OH groups on the fiber surface.
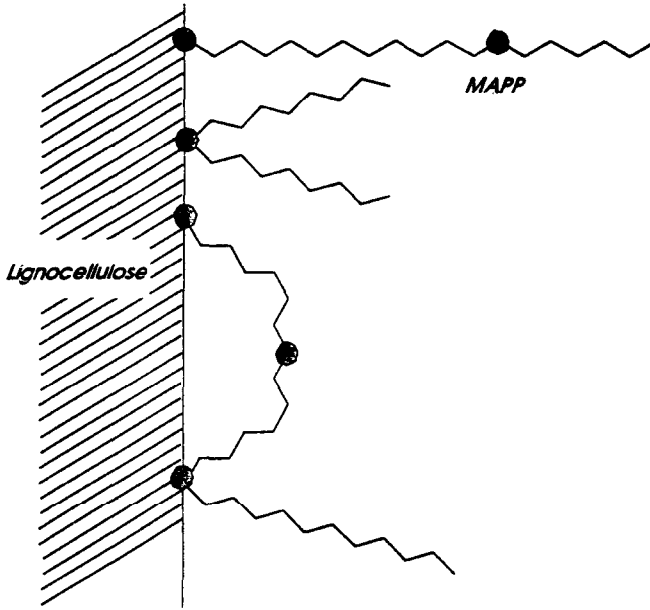
Figure 12.2 Different type of MAPP-fiber interactions. The dot represent maleic anhydride.

Using G-3002, a maleic anhydride-grafted PP, has resulted in efficient composites, and this is probably due to the higher molecular weight coupled with a high MA content (Sanadi et al., 1994a). The G-3002 from Eastman Chemical Co. is reported to have a number average molecular weight (M_n) of 20,000, a weight average molecular weight (M_w) of 40,000 and an acid number of 60. An acid number of 60 is about equivalent to a 6% by weight of maleic anhydride in the G-3002 (Eastman Chemical Company, 1992). However, there is some free anhydride present in the G-3002 and this complicates the understanding of the characteristics and function of the MAPP on the properties of the fiber-matrix interphase. The free MA may preferentially bond to available-OH sites on the fiber and reduce the interaction between the MAPP and the fiber. Furthermore, free MA bonded to the fiber surface can change the surface energetic of the fiber surface. Use of MAPP's with very higher molecular weights but low MA contents does not perform as well as the G-3002 (Sanadi et al., 1994b).

Theoretically, extremely long chains of MAPP with a lot of grafted MA would bean ideal additive in lignocellulosic-PP composites, creating both covalent bonding to the fiber surface and extensive molecular entanglement to improve properties of the interphase. However, extremely long chains may reduce the possibility of migration of the MAPP to the fiber surface because of the short processing times. If the MW of the MAPP is too high, the MAPP may entangle with the PP molecules so that the polar groups on the MAPP have difficulty "finding" the -OH groups on the fiber surface (Figure 12.3).
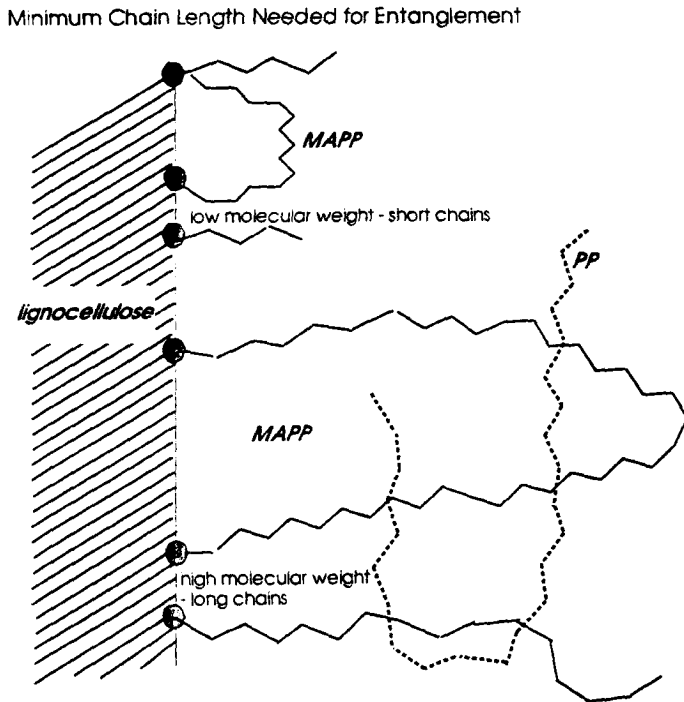
Minimum Chain Length Needed for Entanglement

Figure 12.3 Schematic of possible PP molecules' entanglement with the longer chains of MAPP. Shorter chains of MAPP have less opportunity to entangle with the PP molecules.

Furthermore, the crystallization of the PP with MAPP depends on the amount of graft on the MAPP (Duvall et al., 1993, 1994). Lower anhydride (0.2% by weight) coupled with high molecular weight ($M_n = $ 42,500 and $M_w = $ 135,000) resulted in co-crystallization of a PP/MApp blend and higher fracture strains as compared to a higher anhydride (2.7% by weight) coupled with low molecular weight (Mn = 16,100 and $M_w = $ 52,100) that crystallized as a second phase (Duvall et al., 1993). It is again important to remember that the presence of the fiber surface and the potential of covalent attachment of the MAPP to the hydroxyl groups on the cellulose fiber surface will influence the morphological interaction between the MAPP and PP. Thermodynamic segregation of the MAPP to the fiber surface will result in the major part of the interaction between the MAPP and PP to occur in the interphase region.

Transcrystallinity around the fiber surface complicates the understanding since crystallite can act like cross links by tying many molecules together. The influence of the molecular weight on the interphase morphology and transcrystallinity are also important considerations. Crystallite have a much higher maduli as compared to the amorphous region and can increase the modulus contribution of the plastic matrix to composite modulus.

Previous studies are somewhat conflicting in the effects of surface characteristics on transcrystalline formation. Quill in, Caulfield, and Koutsky (1993) found that

improvement in surface energetics between the cellulosic fibers and the PP resulted in the prevention of transcrystalline zones. Transcrystallinity was abundant when there was no surface modification of the polar fiber and the non-polar matrix. On the other hand, Gatenholm et. al. (1992) found that the higher the molecular weight of the MAPP, the greater were the number of nuclei formed at the fiber surface. It should be pointed out that both the above experiments were *model* single fiber (cellulose) tests with controlled cooling cycles. Vollenberg and Heikens' (1989a) studies on small particle size glass or alumina filled PP *composites* suggested that the use of sizing or coupling agent on the glass or alumina eliminated the formation of high modulus material near the fiber surface. This hypothesis was suggested for the annealed composite based on eliminating other possiblities. Sold state nuclear magnetic resonance experiments (Vollenberg and Heikens, 1989b) support this explanation.

4. PROPERTIES OF COMPOSITES

Cellulosic fillers/fibers have been incorporated in a wide variety of thermoplastics such as PP, PE, PS, PVC, and polyamides (Klason and Kubat, 1986 a, b). In general dispersing agents and/or coupling agents, are necessary for property enhancement when fibers are incorprated in thermoplastics. Grafting chemical secies onto the fiber surface has also been reported to improve the interaction between the fibers and matrix. Although grafting can improve the properties of the composite to a significant extent, this process incseases the material cost the of system. The use of dispersing agents and/or coupling agents is a cheaper route to improve properties and makes more practical sense for high volume, low cost composite systems.

In general, cellulosic fillers or fibers have a higher Young's modulus as compared to commodity thermoplastics. thereby contributing to the higher stiffness of the composites. The increase in the Young's modulus with the addition of cellulosics depends on many factors such as the amount of fibers used, the orientation of the fibers, the interaction and adhesion between the matrix, the ratio of the fiber-to-matrix Young's modulus, etc. The Young's modulus of the composite can be crudely estimated through the simple rule of mixtures and other simple models if the Young's modulus of the filler-fiber is known (Hull. 1981). The use of dispersing or coupling agents can change the molecular morphology of the polymer chains both at the fiber-polymer interphase and also in the bulk matrix phase. Crystallites have much higher moduli as compared to the amorphous regions and can increase the modulus contribution of the polymer matrix to the composite modulus. A good understanding of the effect of dispersing agents and coupling agents on transcrystallinity at the fiber-matrix interphase and the corresponding effect on the composite Young's modulus is nonexistent. Therefore the influence and contribution of the molecular morphology on estimating the composite modulus through simple models are lacking.

In order to use any models to estimate composites properties, it is necessary to know the property of the fibers. In general, natural fibers such as kenaf and jute are in the form of strands that consist of discrete individual fibers, generally 2 mm to 6 mm long, which are themselves composites of predominantly cellulose, lignin,

and hemicelluloses. Strand and individual fiber properties can vary widely depending on the source. age, separating techniques, moisture content, speed of testing, history of the fiber. etc. The properties of the individual fibers are very difficult to measure. Earlier work on a natural bast strand, sunn hemp *(Crotalaria juncea)* suggested that the strand properties ranged widely. The tensile strengths of the strands of sunn hemp varied from about 325-450 MPa, while the tensile modulus ranged from 27-48 MPa (Sanadi et al., 1985). In a natural fiber-thermoplastic composite, the lignocellulosic phase is present in a wide range of diameters and lengths, some in the form of short strands and others in forms that seem closer to the individual fiber. The high shearing energy of blending the strands and the polymer in a mixer results in fiber attrition but can also axially separate the strands into discrete individual fibers.

Cellulosic fillers/fibers can be classified under three categories, depending on their performance when incorporated in a plastic matrix. Wood flour and other low cost agricultural-based flour can be considered as particulate fillers that enhance the tensile and flexural moduli of the composite with little effect on the composite strength. Wood fibers and recycled newspaper fibers have higher aspect ratios and contribute to an increase in the moduli of the composite, and can also improve the strength of the composite when suitable additives are used to improve stress transfer between the matrix and the fibers. The improvement in modulus is not significantly different than the cellulosic particulate fillers. The most efficient cellulosic additives are some natural fibers such as kenaf, jute, flax, etc. The specific Young's modulus and specific flexural modulus, the ratio of the composite modulus to the composite specific gravity of composites with natural fibers such as kenaf are significantly higher than those possible with wood fibers. The specific moduli (the ratio of the composite modulus to the composite specific gravity) of high fiber volume fraction bast fibers-PP composites are high and in the same range as glass fibers-PP composites. The most efficient natural fibers are those that have a high cellulose content coupled with a low microfibril angle resulting in high mechanical properties.

Although several plastics have been used with cellulosic fibers, the major part of the work at the University of Wisconsin-Madison and the Forest Products Laboratory has been on polypropylene (PP). The following case study concentrates on this versatile plastic in combination with kenaf as a promising example of an agro-based fiber/plastic composite.

4.1 Experimental Methods

Kenaf strands harvested from mature plants were obtained from AgFibers Inc., Bakersfield, CA, and cut into lengths of about 1 cm. The fibers were not dried to remove any of the moisture present, and the moisture content of the fibers varied from 6% to about 9% by weight. In all our experiments the weight and volume percent reported is the amount of dry fiber present in the blend. The homopolymer was Fortilene-1602 (Solvay Polymers, 1991) with a melt flow index of 12 g/10 min. as measured by ASTM D-1238. A maleic anhydride grafted polypropylene (MAPP), Epolene G-3002, from Eastman Chemical Products, TN, was used as a coupling agent to improve the compatibility and adhesion between the fibers and matrix. The G-3002 had a number average molecular weight of 20,000 and a weight average

molecular weight of 40,000 and an acid number of 60. An acid number of 60 is about equivalent to a 6% by weight of maleic anhydride in the G-3002 (Eastman Chemical Company, 1992).

The strands were not pulped prior to compounding as the former procedure can consume a significant amount of energy. The short kenaf fibers. MAPP and PP (the latter two in pellet form) were compounded in a high intensity kinetic mixer (Synergistic Industries Ltd., Canada) where the only source of heat is generated through the kinetic energy of rotating blades. The blending was accomplished at 4.600 rpm and then automatically discharged at 190°C. A total weight (fibers. PP and MAPP) of 150 g was used for each batch and about 1.5 kg of blended material was prepared for each set of experiments. Fiber weight varied from 20-60% and coupling agent weight varied from 0 to 3%. The total residence time of the blending operation depended on the proportions of fiber and PP present and averaged about 2 min.

The mixed blends were then granulated and dried at 105°C for 4 h. Test specimens were injection-molded at 190°C sing a Cincinnati Milacron Molder and injection pressures varied from 2.75 MPa to 8.3 MPa depending on the constituents of the blend. Specimen dimensions were according to the respective ASTM standards. The specimens were stored under controlled conditions (20% relative humidity and 32°C) for three days before testing. Tensile tests were conducted according to ASTM 638-90, lzod impact strength tests according to ASTM D 256-90, and flexural testing using the ASTM 790-90 standard. The cross-head speed during the tension and flexural testing was 5 mm/min. Although all the experiments were designed around the weight percent of kenaf in the composites, fiber volumes fractions can be estimated from composite density measurements and the weights of dry kenaf fibers and matrix in the composite. The density of the kenaf present in the composite was estimated to be 1.4 g/cc. A flow chart of the experimental methods is shown in Figure 12.4.

4.2 Mechanical Properties

4.2.1 *Effect of MAPP on Composite Properties*

A small amount of the MAPP (0.5% by weight) improved the flexural and tensile strength, tensile energy absorption, failure strain, and un-notched Izod impact strength of the kenaf/PP composits. The anhydride groups present in the MAPP can covalently bond to the hydroxyl groups of the fiber surface. Any MA that has been converted to the acid form can interact with the fiber surface through acid-base interactions. The improved interaction and adhesion between the fibers and the matrix leads to better matrix to fiber stress transfer. There was little difference in the properties obtained between the 2 and 3% (by weight) MAPP systems. The drop in tensile modulus with the addition of the MAPP was probably due to polymer morphology.

Transcrystallization and changes in the apparent modulus of the bulk matrix can result in changes in the contribution of the matrix to the composite modulus and will be discussed later. There was little change in the notched impact strength with the addition of the MAPP, while the improvement in un-notched impact strength is
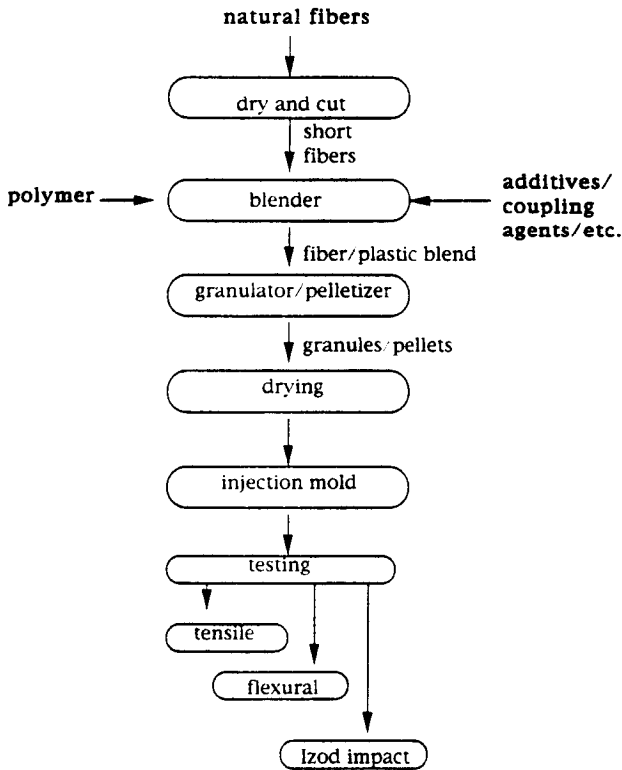
natural fibers

```
              ↓
    ╭─────────────────────╮
    │     dry and cut     │
    ╰─────────────────────╯
              │ short
              ↓ fibers
```
```
                                              additives/
  polymer ──▶  ╭─────────────────╮  ◀──────── coupling
              │     blender      │            agents/etc.
               ╰─────────────────╯
              ↓ fiber/plastic blend
    ╭─────────────────────────╮
    │   granulator/pelletizer │
    ╰─────────────────────────╯
              ↓ granules/pellets
    ╭─────────────────────╮
    │      drying         │
    ╰─────────────────────╯
              │
              ↓
    ╭─────────────────────╮
    │   injection mold    │
    ╰─────────────────────╯
              │
              ↓
    ╭─────────────────────╮
    │      testing        │
    ╰─────────────────────╯
     ↓              │
  ╭─────────╮       │
  │ tensile │       │
  ╰─────────╯       ↓
     ╭──────────────╮
     │   flexural   │
     ╰──────────────╯
                    │
                    ↓
          ╭──────────────╮
          │  Izod impact │
          ╰──────────────╯
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Figure 12.4 Flow chart of experimental processes for the blending and testing of composites.

significant. In the notched test, the predominant mechanism of energy absorption is through crack propagation as the notch is already present in the sample. Addition of the coupling agent had little effect in the amount of energy absorbed during crack propagation. On the other hand, in the un-notched test, energy absorption was through a combination of crack initiation and propagation. Cracks are initiated at places of high stress concentrations such as the fiber ends, defects, or at the interface region where the adhesion between the two phases is very poor. The use of the additives increases the energy needed to initiate cracks in the system, thereby resulting in improved un-notched impact strength values with the addition of the MAPP.

Use of the MAPP increased the failure strain and the tensile energy absorption. Thermodynamic segregation of the MAPP towards the interphase can result in covalent bonding to the -OH groups on the fiber surface. Entanglement between the PP and MAPP molecules results in improved interphase properties and the strain to failure of the composite. There is a plateau after which further addition of coupling agent results in no further increase in ultimate failure strain. The number average MW of the G-3002 is about 20,000 and the amount of entanglements between the PP molecules and MAPP is limited, and molecules flow past one another at a critical strain. Any further increase in the amount of G-3002 does not increase the failure

strain past the critical amount. However, a minimum amount of entanglements is necessary through the addition of about 1.5% by weight for the critical strain to be reached.

4.2.2 Strength and Modulus

There is little difference in the tensile strength of uncoupled composites compared with the unfilled PP. irrespective of the amount of fiber present. This suggests that there is little stress transfer from the matrix to the fibers due to incompatibilities between the different surface properties of the polar fibers and non-polar PP. The tensile strengths of the coupled systems increase with the amount of fiber present and strengths of up to 74 MPa were achieved with the higher fiber loading of 60% by weight. or about 49% by volume. As in the case with tensile strength, the flexural strength of the uncoupled composites was approximately equal for all fiber loading levels, although there was a small improvement as compared to the unfilled PP. The high shear mixing using the thermokinetic mixer causes a great deal of fiber attrition. Preliminary measurements of the length of fibers present in the composite after injection molding showed that few fibers are longer than 0.4 mm. The strengths obtained in our composites were thus limited by the short fiber lengths. Higher strengths are likely if alternate processing techniques are developed that reduce the amount of fiber attrition while at the same time achieving good fiber dispersion.

The tensile modulus of the kenaf composites showed significant improvements with the addition of the fibers. The uncoupled composites exhibited some very interesting behavior. with moduli higher than the coupled systems at identical fiber loading. The possibility of a high stiffness transcrystalline zone forming around the fiber in the unmodified systems could lead to the high moduli observed. Although the possibility of different fiber orientations contributing to the higher modulus cannot be ruled out, preliminary studies on fiber orientation suggest that the difference in moduli cannot be explained exclusively by the difference in fiber orientations. Several studies suggest that the morphology of the polymer chains are affected by the presence of filler particles.

The specific tensile and flexural moduli of the 50% by weight kenaf coupled composites were about equivalent to or higher than typical reported values of 40% by weight coupled glass-PP injection molded composites. Table 12.1 shows typical commercial PP composites compared with kenaf-PP composites. Data on mineral filled systems from various sources, Modern *Plastics Encyclopedia* (1993) and *Machine Design: Materials Guide Issue* (1994), are included for comparison. The specific flexural moduli of the kenaf composites with fiber contents greater than 40% were extremely high and even stiffer than a 40% mica-PP composite.

4.2.3 Failure Strain and Tensile Energy of Absorption

The failure strain decreases with the addition of the fibers. Addition of a rigid filler/fiber restricts the mobility of the polymer molecules to flow freely past one another and thus causes premature failure. Addition of MAPP followed a similar trend to that of the uncoupled system, although the drop in failure strain with

increasing fiber amounts was not as severe. Figure 12.5 (Sanadi et al., 1994c) shows typical stress strain curves of pure PP. uncoupled 5% by weight of kenaf-PP. and coupled systems with increasing amounts of kenaf in the composite. The decrease in the failure strain with increasing amounts of kenaf for the coupled systems is apparent. The non-linearity of the curves is mainly due to plastic deformation of the matrix. The distribution of the fiber lengths present in the composite can also influence the shape of the curve since the load taken up by the fibers decreases as the strain increases and detailed explanations are available elsewhere (Hull, 1981). The tensile energy absorption, the integrated area under the stress-strain curve up to failure, behaves in roughly the same manner as the tensile failure strain. The difference between the coupled and uncoupled composites increases with the amount of fibers present, although the drop in energy absorbed for the coupled composites levels off after the addition of about 35 volume % of fiber.
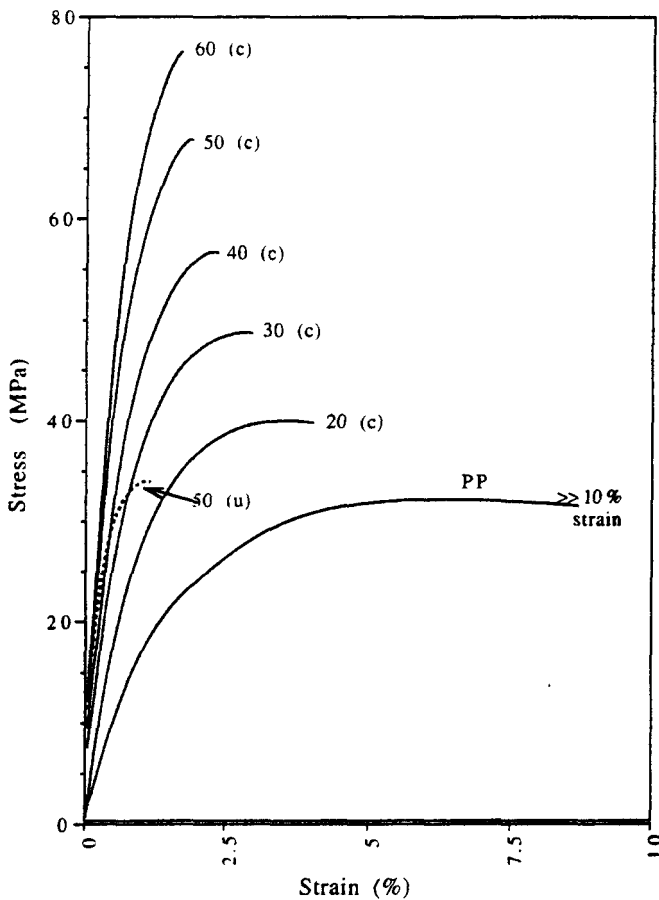

Figure 12.5 Tensile stress–strain curves of kenaf–PP. The numbers near the end of curves indicate kenaf weight % and (c) indicates coupled and (u) uncoupled composites. All coupled systems contained 2% by weight of MAPP. PP failure strain was >10%.

4.2.4 Impact Properties

The impact strength of the composite depends on the amount of fiber and the type of testing. i.e., whether the samples were notched or un-notched. In case of notched samples, the impact strength increases with the amount of fibers added until a plateau is reached at about 45% fiber weight, irrespective of whether MAPP was used or not. The fibers bridge cracks and increases the resistance of the propagation of the crack. Contribution from fiber pullout is limited since the aspect ratio of the fibers in the system are well below the estimated critical aspect ratio of about 0.4 mm (Sanadi et al., 1993). In the case of the unnotched impact values of the uncoupled composites, the presence of the fibers decreases the energy absorbed by the specimens. Addition of the fibers creates regions of stress concentrations that require less energy to initiate a crack. Improving the fiber-matrix adhesion through the use of MAPP increases the resistance to crack initiation at the fiber-matrix interface, and the fall in impact strength with the addition of fibers is not as dramatic. The impact strength can be increased by providing flexible interphase regions in the composite or by using impact modifiers and some work has been done in this area at the UW and FPL (Wieloch, Caulfield, and Sanadi, 1994). The use of an impact copolymer of PP (Amoco Impact Copolymer) improves the notched and un-notched impact resistance (Table 12.1), albeit with some reduction in modulus and strength of the composite.

4.3 Physical Properties

Water absorption and specific gravity of lignocellulosic fiber composites are important characteristics that determine end use applications of these materials. Water absorption could lead to a decrease in some of the properties and should be considered when selecting applications. It is difficult to entirely eliminate the absorption of moisture in the composites without using expensive surface barriers on the composite surface. Water absorption in lignocellulosic based composites can lead to a build-up of moisture in the fiber cell wall and also in the fiber-matrix interphase region. Moisture build-up in the cell wall could result in fiber swelling and affect the dimensional stability. If necessary, the moisture absorbed in the fiber cell wall can be reduced through the acetylation of some of the hydroxyl groups present (Rowell, Tillman, and Simonson, 1986) in the fiber, but with some increase in the cost (see Chapter 11). Good wetting of the fiber by the matrix and adequate fiber-matrix bonding can decrease the rate and amount of water absorbed in the interphasial region of the composite. A typical 50% by weight of kenaf-homopolymer PP blend absorbed about 1.05% by weight of water in a 24 h water soak test. This is considerably higher than any mineral filled systems. It is therefore very important to select applications where this high water absorption is not a critical factor such as in electrical housing components.

The specific gravity of lignocellulosic based composites is much lower than the mineral filled thermoplastic systems. The apparent density of the lignocelluiosic fibers in PP is about 1.4 g/cc as compared to mineral fillers/fibers (about 2.5 g/cc). The specific gravity of a 50% (by weight) kenaf-PP composite is about 1.07, while

Table 12.1 Comparison of PP Composites

Filler/Reinforcement in PP	ASTM Standard	None	Kenaf	Kenaf-PP impact copolymer	Recycled newspaper fiber	Talc	CaCO$_3$	Glass	Mica
% filler by weight		0	50	50	40	40	40	40	40
% filler by volume (estimated)		0	39	39	30	18	18	19	18
Tensile Modulus, GPa	D638	1.7	8.3	7.5	4.4	4	3.5	9	7.6
Specific Tensile Modulus, GPa		1.9	7.8	7.0	4.5	3.1	2.8	7.3	6.0
Tensile Strength, MPa	D638	33	65	53	53	35	25	110	39
Specific Tensile Strength, MPa		37	61	50	54	28	20	89	31
Elongation at Break, %	D638	>10	2.2	2.5	3			2.5	2.3
Flexural Strength, MPa	D790	41	98		80	63	48	131	62
Specific Flexural Strength, MPa		46	92		82	50	38	107	49
Flexural Modulus, GPa	D790	1.4	7.3		3.9	4.3	3.1	6.2	6.9
Specific Flexural Modulus, GPa		1.6	6.8		4.0	3.4	2.5	5.0	5.5
Notched Izod Impact, J/m	D256A	24	32	74	21	32	32	107	27
Specific Gravity		0.9	1.07	1.07	0.98	1.27	1.25	1.23	1.26
Water Absorption %, 24 h	D570	0.02	1.05	1.3	0.95	0.02	0.02	0.06	0.03
Mold (linear) Shrinkage, cm/cm		0.028	0.003	0.004		0.01	0.01	0.004	0.03

Data on mineral filled PP from various sources. (Modern Plastics Encyclopedia, 1993; and Material Design: 1994 Materials Selector Issue).
Data for PP was using a homopolymer, unless otherwise mentioned.

that of a 40% (by weight) glass–PP composite is 1.23. The specific mechanical properties of kenaf–PP composites compare favorably to other filled commodity plastics. Since materials are bought in terms of weight and pieces or articles are, in general, sold by the number, more pieces can be made with lignocellulosic fibers as compared to the same weight of mineral fibers. This could result in significant material cost savings in the high volume and low cost commodity plastic market.

4.4 Effect of Fiber Type

Jute, kenaf, flax, sisal, sunn hemp, henequin, and coir are some of the many fibers being evaluated for their use in thermoplastics (Jacobson and Walz, 1994). Selection of the natural fibers to be used in plastics would depend on the availability of the fibers in the region and the properties of the composite needed for the selected application. For example, if high tensile and flexural strengths are needed, fibers such as flax or jute can be used. For applications where high impact toughness is necessary, fibers such as henequin can be utilized. Kenaf-PP composites have the advantage of being easier to compound and mold at high fiber loading and can result in very stiff composites at low material cost through the use of lower amounts of the plastics. The properties of coir–PP are slightly lower than even the newspaper fibers and the reinforcing efficiency of this fiber is low. The fiber may be useful as a filler in highly filled plastics. The low mechanical properties are probably due to the relatively low cellulose and high lignin content of the coir fibers. It is important to note that coir fibers are a byproduct of the coconut industry and not a plant/tree grown only for its fiber.

4.5 Recycling/Reprocessing

Agro-based fibers are less brittle and softer than glass fibers and are likely to result in composites that are easier to recycle than mineral based fibers. Although no post-consumer based recycling studies have been done on agro-based fibers, a short study on the effect of reprocessing has been conducted at the Forest Products Laboratory and the University of Wisconsin-Madison (Walz et al., 1994). Experimental details are as follows:

Short kenaf filaments were compounded with polypropylene (Fortilene-1602, Solvay Polymers) and MAPP using the thermokinetic mixer explained earlier in the text. The blend ratio was 50% kenaf to 49% PP to 1% MAPP, based on dry weight of material. The mixer was operated at 5200 rpm. A total of 2.25 Kg (15 batches of 150 g each) of material was blended for the experiment.

All the compounded material was then granulated, dried at 105°C for 4 hours and then molded at 190°C using the injection molder. Specimens were randomly selected to evaluate the tensile, flexural, and impact properties and five samples were used for each test: this first set of data was the control or virgin data denoted by "0" in Figures 12.6, 12.7, and 12.8. All the remaining non-tested specimens were once again granulated and injection molded. Once again, five specimens were randomly selected for mechanical property evaluation: this set was labeled as the 1st recycle data point. This procedure of injection molding and granulation was repeated for a

total of nine recycle data points. Figures 12.6. 12.7, and 12.8 show that the repeated grinding and molding results in a deterioration of composite properties. The loss in properties is a combination of repeated fiber attrition and oxidative degradation of the polypropylene through chain scission.
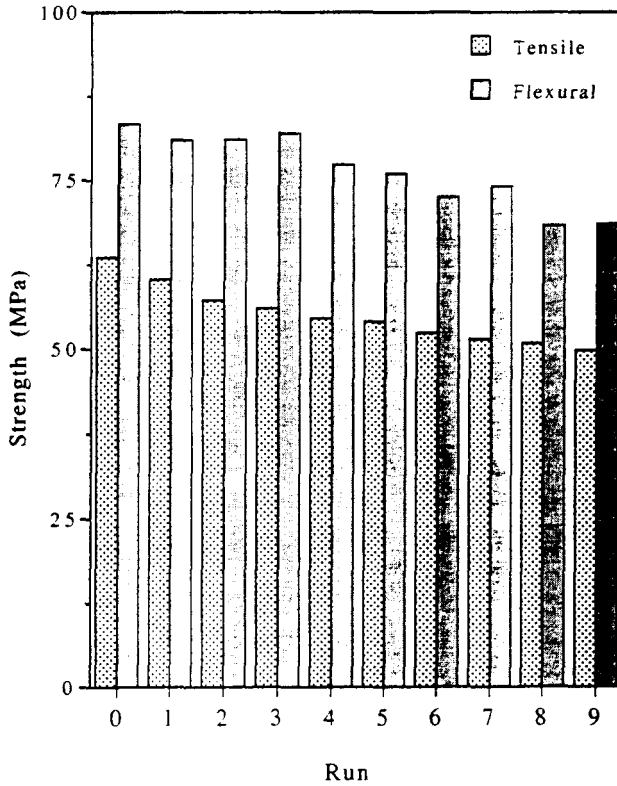

Figure 12.6 Effect of reprocessing 50% by weight kenaf–MAPP coupled–PP on composite tensile strength. The numbers in the abscissa indicate the number of times the composites were reprocessed.

5. CONCLUDING REMARKS ON ECONOMIC ASPECTS AND POTENTIAL MARKETS

The costs of natural fibers are, in general, less than those of the plastic matrix in trio-based composites, and high fiber loading can result in significant material cost savings. The cost of compounding is unlikely to be much more than for conventional mineral-inorganic based composite presently used by the plastics industry. Due to the lower specific gravity of the cellulosic based additives (approximately 1.4 as compared to about 2.5 for mineral based systems), there would be a definite weight advantage for these composites which may have implications in the automotive and other transportation applications. Furthermore, using the same
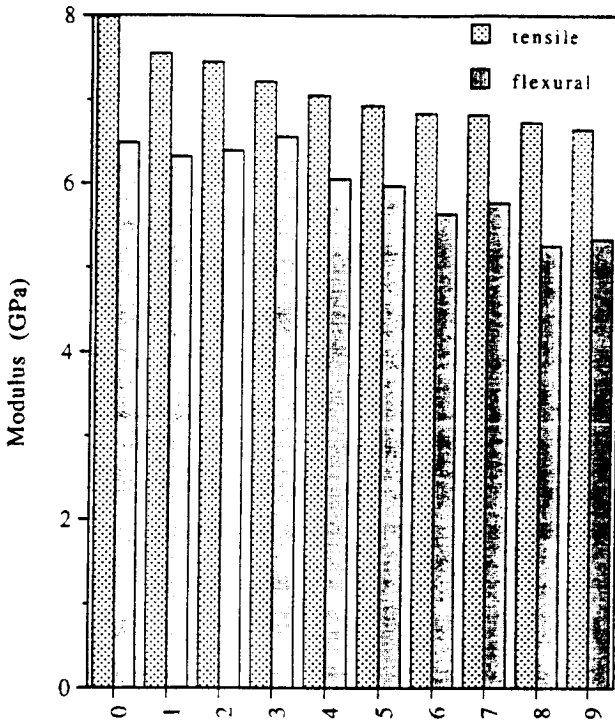
Figure 12.7 Effect of reprocessing 50% by weight kenaf–MAPP coupled–PP on composite tensile modulus. The numbers in the abscissa indicate the number of times the composites were reprocessed.

weight of plastic/natural fiber as, for example, plastic/glass fiber, about 20% more pieces are possible with the cellulosic based system. Cellulosic fibers are soft and non-abrasive and high filling levels are possible; 60% by weight of fiber has been successfully incorporated in PP-based composites. Reduced equipment abrasion and the subsequent reduction of re-tooling costs through the use of agricultural based fibers are definitely factors that will be considered by the plastics industry when evaluating these natural fibers. It is important to point out that we do not anticipate nor intend the total replacement of conventional based fillers/fibers with agricultural based fillers/fibers. We do, however, believe that these natural materials will develop their own niche in the plastics filler/fiber market in the future.

The volume of thermoplastics used in the housing, automotive, packaging and other low-cost, high volume applications is enormous. Recent interest in reducing the environmental impact of materials is leading to the development of newer materials or composites that can reduce the stress to the environment. In light of petroleum shortages and pressures for decreasing the dependence on petroleum products, there is an increasing interest in maximizing the use of renewable materials. The use of agricultural materials as a source of raw materials to the industry not
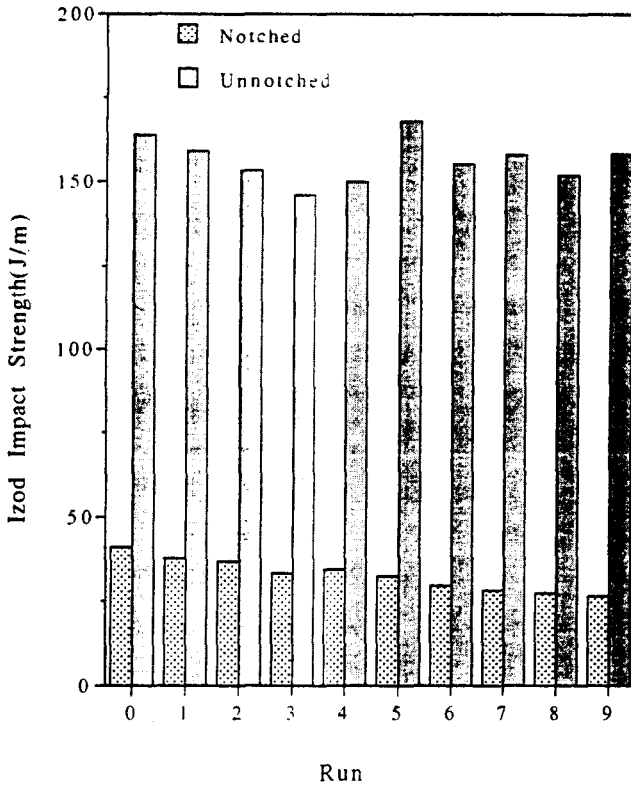
Figure 12.8 Effect of reprocessing 50% by weight kenaf–MAPP coupled–PP on composite Izod impact strength. The numbers in the abscissa indicate the number of times the composites were reprocessed.

only provides a renewable source, but could also generate a non-food source of economic development for farming and rural areas. Appropriate research and development funding in the area of agricultural based fillers/fibers filled plastics could lead to new value-added, non-food uses of agricultural materials. We believe that the amount of these fibers used in the automotive, furniture, housing, packaging, toy, and other industries could easily be in the range of hundreds of millions of pounds annually.

ACKNOWLEDGMENTS

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