

Biofiber-Reinforced Polypropylene Composites

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Biofibers, natural lignocellulosics, have an outstanding potential as a reinforcement in thermoplastics. This study deals with the preparation of lignocellulosic 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 modified lignocellulosic component, in-situ. 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 lignocellulosic fiber/filler and modified polymer 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. These composite blends were then injection molded for mechanical characterization. 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 enhanced polar interactions at phase boundaries.

INTRODUCTION

Government regulations and a growing environmental awareness throughout the world have triggered a paradigm shift towards designing materials compatible with the environment. The use of biofibers, derived from annually renewable resources, as reinforcing fibers in both thermoplastic and thermoset matrix composites provides positive environmental benefits with respect to ultimate disposability and raw material utilization (1).

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 PP composites have properties similar to traditional glass fiber reinforced PP composites (2). Lignocellulosic-plastic composites have been reviewed by Kowell, Youngquist, and Narayan (3).

The main bottlenecks in the broad use of these fibers in thermoplastics have been the poor compati-

bility between the fibers and the matrix, and the inherent high moisture sorption, which brings about dimensional changes in the lignocellulosic based fibers. A review by Maldas and Kokta (4) covers the complexities involved with the compatibilization of these materials and the different techniques used to understand the interfacial interaction. The efficiency of a fiber reinforced composite depends 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 good stiffness to impact strength balance in order to expand the applicability of these natural fiber-reinforced composites.

Kenaf, an annual hibiscus fiber plant, has been found to be an important source of fiber for composites and other industrial applications. The kenaf bast fiber has high potential as a reinforcing fiber in thermoplastic composites because of its superior toughness and high aspect ratio in comparison with other fibers. A single fiber of kenaf can have a tensile strength and modulus as high as 11.9 GPa and 60.0 GPa respectively (5). These properties can vary depending on the source, age and separating techniques

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of the fiber. *Figures 1 and 2* show SEM pictures of kenaf and glass fibers.

The kenaf bast fiber is a composite made up of a crystalline, thermoset polymer matrix (lignin and the hemicelluloses). Chemical modification of the fiber has been studied by Rowell *et al.* (6) to make it more hydrophobic, which improves its compatibility with non-polar thermoplastics. Sanadi *et al.* (7) studied the potential of kenaf as a reinforcing fiber in the PP matrix and compared the mechanical properties with other commonly used composite systems. Schneider and Karmaker (8) examined the effects of fiber type, percent composition, polymer type, and coupling agent on mechanical property values of composites from jute and kenaf reinforced PP.

This study examines ways of achieving good interfacial adhesion between a lignocellulosic fiber like kenaf and PP by ways of (i) functionalization of matrix and (ii) fiber modification. It is purported to overcome the problems associated with simple mechanical blending by reactively compatibilizing the blend components.

The mechanical properties of injection molded samples of various PP-kenaf composites are reported in this paper; and an attempt is made to study the influence of various factors on these properties. A comparison is made between the mechanical properties of kenaf and sisal reinforced composites based on the results from this and our previous work (2).

EXPERIMENTAL METHODS

Materials

In this work, PROFAX 6501, an isotactic polypropylene homopolymer manufactured by Montell Polyolefins, was used. The melt flow index of the polymer was experimentally determined to be 8 g/10 min. The kenaf fibers were obtained from Department of Agriculture, Mississippi State University, and were

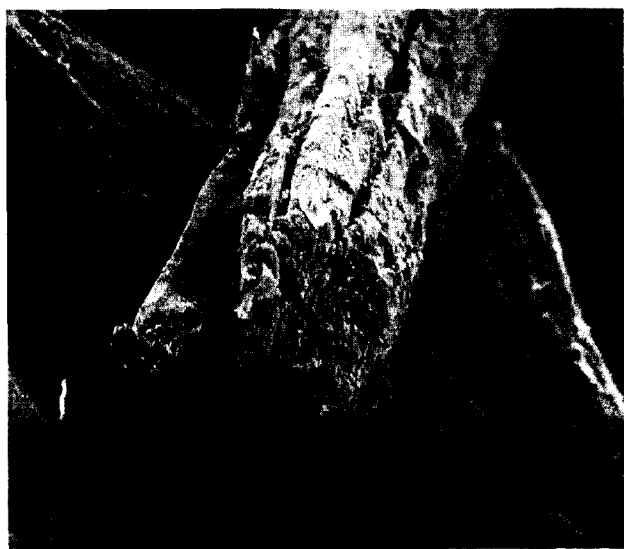


Fig. 1. SEM image of kenaf bast fiber.

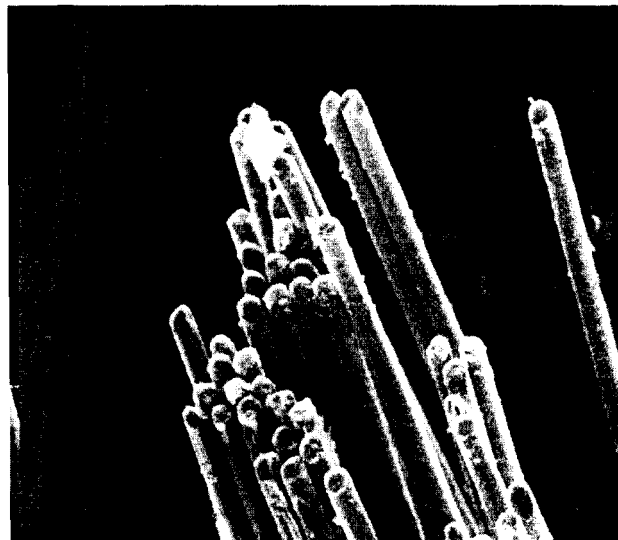


Fig. 2. SEM image of glass fiber bundles.

chopped into lengths of approximately 1/16 inch (1.58 mm). The coupling agent, maleic anhydride grafted polypropylene (MAPP), was prepared in the laboratory. Dow Corning's 26032, primarily containing amino-ethyl amino-propyl trimethoxy silane, was used for modification of kenaf fibers.

Processing

Functionalization of Polypropylene

Maleic anhydride modification of PP powder was performed in a 30 mm corotating intermeshing twin screw extruder (ZSK30, Werner and Pfleiderer) with a length of 960 mm (32 D). The screw configuration was designed with a melting zone of about 8 D followed by 13 D for mixing. The rest of the machine consisted of conveying elements of various pitches.

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 at 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, followed by a water bath, and finally to a pelletizer.

Preparation of composite blends

Prior to feeding, the kenaf fibers were dried in an oven at 80°C for 48 hours. Two gravimetric feeders were used to feed the polymer and the dried fibers separately through a common feed port. The feed rates were controlled so that composites of various fiber weight fractions could be prepared. In the composites containing the compatibilizer, maleated polypropylene (MAPP) was mixed in a fixed ratio with PP and fed into the feeder. The polymer and fiber mixture was

compounded at a maximum temperature of 175°C and a screw speed of 150 rpm in the twin screw extruder. The extrudate was air-dried and pelletized. All the pelletized formulations were injection molded in a 40 ton Arburg plunger type injection molder as ASTM Type I (D-638) specimens. Mold temperature, screw speed, and injection speed were varied so as to produce samples with good surface appearance as to minimize reduction of the aspect ratio of the kenaf fibers.

Modification of Fiber

Kenaf fibers were surface-grafted with siloxane chains using a 2 wt% silane solution in water. Amino-ethyl amino-propyl trimethoxy silane (Dow Corning 26032) was used as the fiber surface modifying agent. These silanized fibers were then extruded as before with PP and injection molded into test samples. The reactions steps involved are shown in **Fig. 3**. The hydrolysis step is important since that controls the ex-

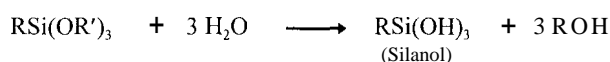
tent of silanol formation, which in turn affects the extent of condensation/oligomerization. Long siloxane chains are expected to be better for maintaining a ductile interface, but excessive chain lengths can also increase probability for cross-linking reactions, thereby forming a brittle interface.

Mechanical Tests

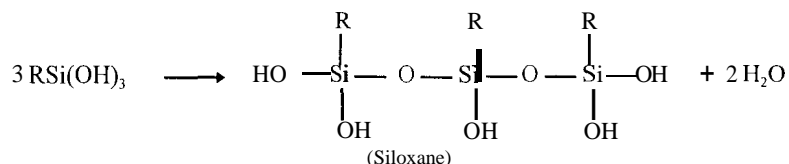
The specimens were stored in a desiccator for three days before testing. At least five specimens were tested for each composite blend and property. Tensile tests were conducted following ASTM D638-90, flexural tests using ASTM D790, and Izod impact conducted using ASTM D 256-90 standard. A scanning electron microscope (SEM-JEOL6400) was used to observe the tensile fracture surface of the samples.

The mechanical properties (e.g. modulus at 0.1% strain, tensile strength at yield point and the corresponding elongation and energy) of all the samples were measured with a UTS of United Calibration Cor-

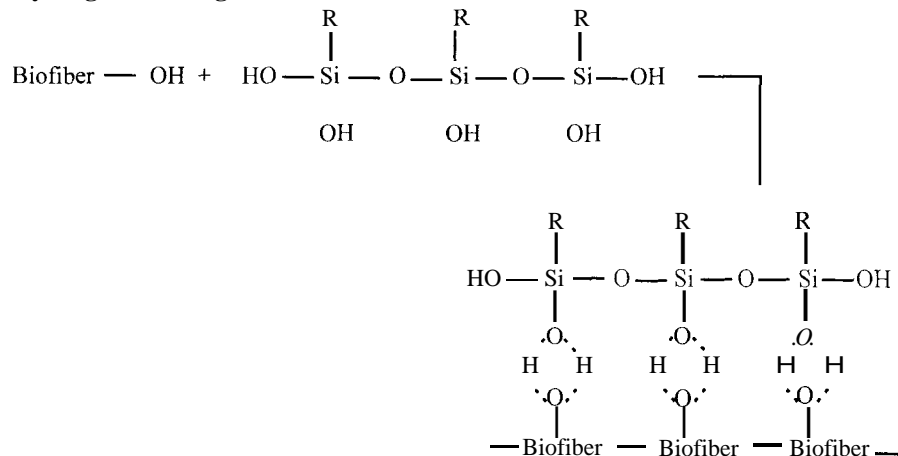
Hydrolysis



Condensation



Hydrogen Bonding



Surface Grafting

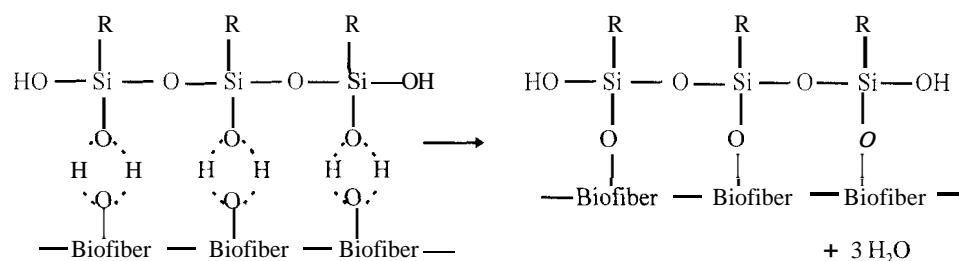


Fig. 3. Reaction steps in the silane grafting of biofibers.

poration (Model SFM 20) following ASTM D-638. The strain rate was 0.25 in/min. Toughness was evaluated as the area under the stress-strain curve till the point of break.

The notched Izod impact strength was tested following ASTM D-256 with an Impact Tester (Model TMI, No. 43-01) of Testing Machines Inc. Melt Flow Index was measured using Ray-Ran Melt Flow Indexer. The melt temperature was 225°C and the cylinder load was 2.16 kg.

RESULTS AND DISCUSSION

Fractography

SEM observations of the fracture surface of notched Izod specimens indicate that there is considerable difference in the fiber-matrix interaction between the compatibilized and uncompatibilized composites. *Figure 4* shows the fracture surface of an uncompatibilized composite with some fiber pull-out and fairly clean fiber surface. 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 *Fig. 5* where the fiber has pulled out from the matrix but a fair amount of polymer residue remains on the fiber.

Mechanical Properties

The stress-strain curves of the uncompatibilized and compatibilized composites are shown in *Fig. 6*. The addition of 20% kenaf fiber to the polymer matrix caused a significant increase in the initial tensile modulus or stiffness of the composite. The compatibilized PP-kenaf composites exhibit greater tensile strength than the uncompatibilized composites or just PP. The increase in elongation at break is attributable to the addition of MAPP to the PP-kenaf composite. This is accompanied by an increase in the toughness or ductility of the composite.



Fig. 4. SEM micrograph of the tensile fracture surface of PP-kenaf (20%) with MAPP.



Fig. 5. SEM micrograph of the tensile fracture surface of PP-kenaf (20%) without MAPP.

The mechanical properties of a series of formulations based on unmodified and maleated PP containing various weight fractions of kenaf fibers are shown in *Table 1*. The addition of kenaf fibers increases the tensile and flexural strength (see *Figs. 7* and *8*) in both unmodified and maleated PP, but with reduced elongation at yield and toughness (*Fig. 10*). The uncompatibilized PP-kenaf composites exhibited a reduction in tensile strength as compared to the virgin polymer, PP. The notched impact strength (*Fig. 9*) of these composites is superior to PP but it decreases with increase in fiber content.

The effects are more pronounced for the composite containing MAPP as compatibilizer. This may be attributed primarily to the enhanced interfacial adhesion resulting from the presence of a matrix with increased polarity that may react or interact favorably with the hydroxyl group on the fiber surface. *Figure 11* shows the proposed mechanism behind such bond formation. It is believed that the peroxide catalyst initiates radical formation on the PP backbone by H abstraction and chain scission. The radical then reacts with MA to form MAPP (9). In a subsequent step the MAPP reacts with the hydroxyl functionality on the cellulosic component of the biofiber to form a linear graft copolymer, which functions as a compatibilizer.

The increase in MAPP from 2% to 5% (*Figs. 7-10*) in the composites resulted in some modest property improvements compared to improvements on addition of MAPP to unmodified PP. This is attributed to the excess peroxide and free radicals not removed after the maleation reaction. Excess peroxide would initiate further chain scission of the PP during subsequent processing, i.e., injection molding, and decrease the molecular weight of the matrix polymer. The loss in properties associated with this molecular weight decrease would offset the maximum enhancement in composite properties that could be achievable by the

Fig. 6. Tensile stress us strain curves for PP-kenaf composites.

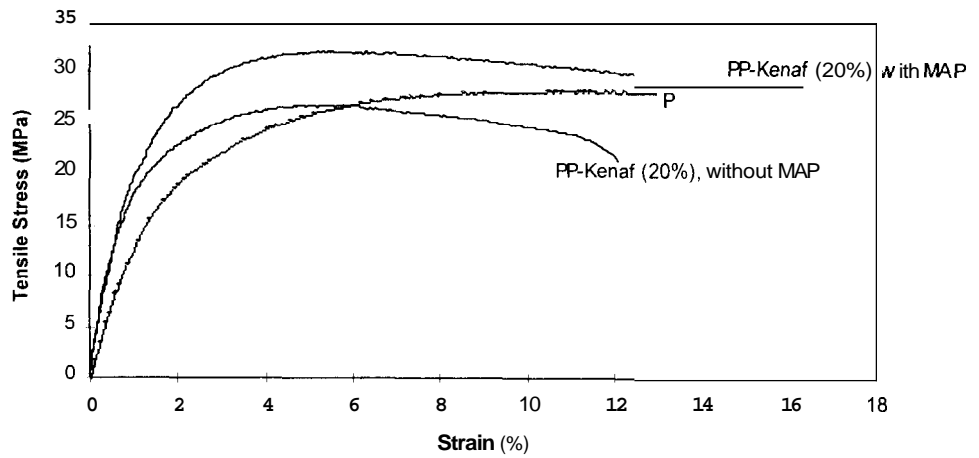
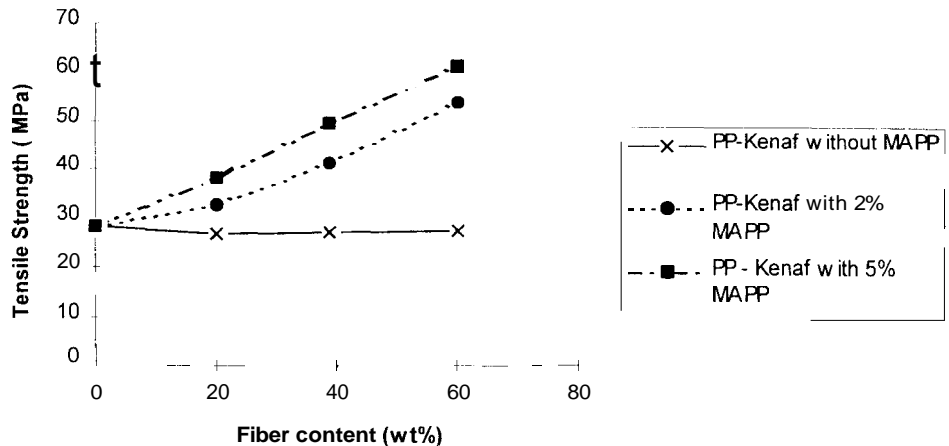


Table 1. Results of Mechanical Tests on Various PP-Kenaf Composite Blends.

Material	Kenaf Fiber (wt %)	Tensile ^a			Flexural ^b		Notched Izod ^c impact strength (J/m)	Toughness ^d (GPa)
		Strength (MPa)	Modulus (GPa)	Elongation at yield (%)	Strength (MPa)	Modulus (GPa)		
PP only	0	28.4	1.2	9.5	34.8	1.3	42.1	Very high
PP without MAPP	20	26.9	2.7	5.2	43.1	2.3	43.8	114.8
	40	27.1	2.8	3.0	44.9	2.7	39.9	110.0
	60	27.4	3.0	2.6	47.2	3.2	33.4	108.3
PP with 2% MAPP ^e	20	32.7	2.9	5.6	46.3	3.0	47.6	141.4
	40	41.3	3.4	4.8	54.6	3.9	41.4	136.8
	60	53.8	4.1	3.3	63.2	4.4	38.7	127.0
PP with 5% MAPP ^e	20	38.1	3.2	6.1	52.1	3.8	50.1	145.8
	40	49.4	4.3	5.0	59.8	4.1	43.9	139.3
	60	61.2	5.1	4.2	67.3	4.6	39.2	132.7
Silylated Kenaf	20	42.5	3.3	6.4	57.7	4.0	54.6	149.2

^a Tensile Test (ASTM D638). Loadcell: 1000 lbs, Test Speed 0.25 in/min, Gauge: 2 in, Width: 1/2 in, Thickness: 1/8 in.
^b 3 point Flex. Test (ASTM D790). Loadcell: 1000 lbs, Test Speed 0.1 in/min, Span: 2 in, Width: 1/2 in, Thickness: 1/8 in.
^c Impact Test (ASTM D256). Hammer: 5 lb Izod. Length: 2.4 in, Width 1/2 in, Thickness: 1/8 in.
^d Determined by evaluating the area under the stress-strain curve till the point of break.
^e Weight percent of PP.

Fig. 7. Tensile strength at yield data of the PP-kenaf composites.



catalyzed alloying of the functionalized matrix with the biofibers.

There is a significant mechanical property improvement (Table I) after surface modification of kenaf fibers with a silane. Specifically, the increase in notched impact strength is remarkable. This indicates that long siloxane chains form a ductile interface along with good fiber-matrix interfacial adhesion.

Sisal Reinforced PP Composites

The mechanical property differences between the sisal reinforced (2) and kenaf reinforced composites are shown in Figs. 12 and 13. In both the fiber systems there is an overall property improvement from unmodified to silylated composites. The tensile strengths of the kenaf reinforced composites are superior to the

Fig. 8. Flexural strength at yield data of the PP-Kenaf composites.

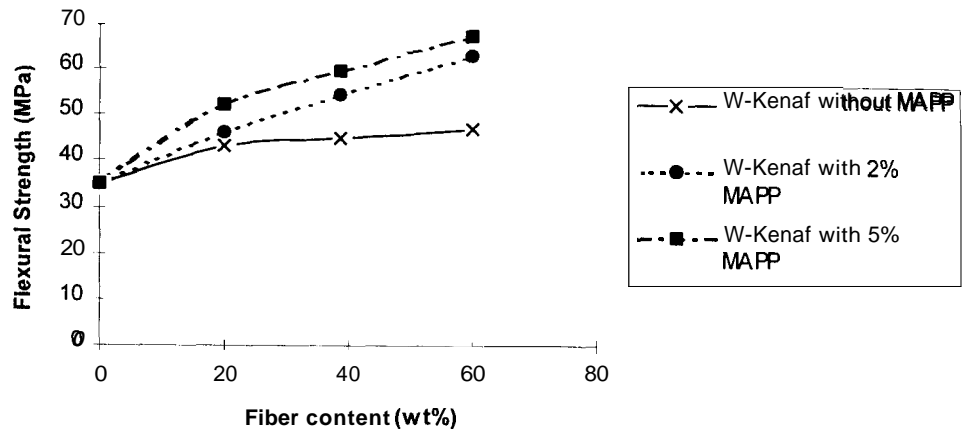


Fig. 9. Notched Izod impact strength of the PP-kenaf composites.

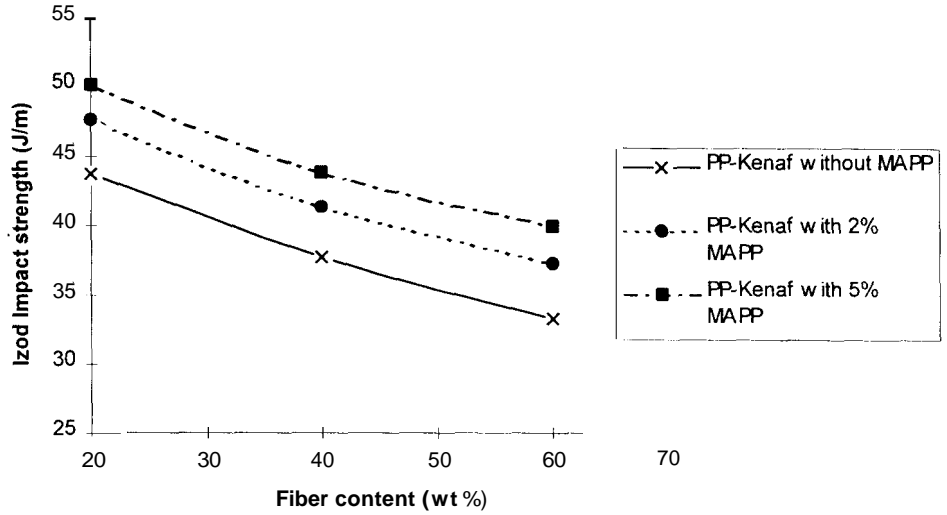
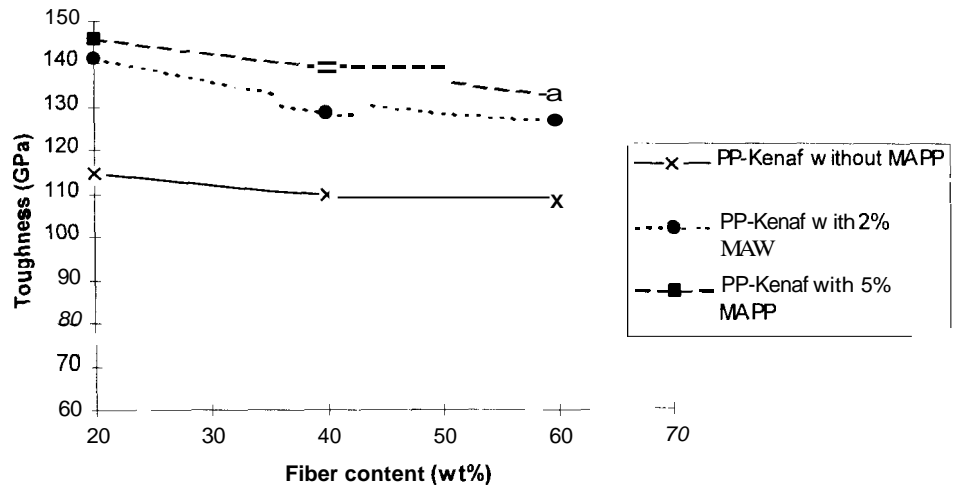


Fig. 10. Toughness of the PP-kenaf composites.



sisal reinforced, but the impact strengths are poorer. This could be explained by the differences in origin: Sisal (*Agave sisilana*) is of leaf origin and Kenaf (*Hibiscus cannabinus*) is of stem origin. Typically, sisal bundle has a tensile strength of 6.14 GPa and modulus of 12.7 GPa whereas the tensile strength and modulus of kenaf fibers are as much as 11.91 GPa and 60.0 GPa,

respectively (5) Kenaf is inherently superior to sisal in terms of tensile strength but poorer in impact.

Applications

Owing to the lower specific gravity of the biofibers compared to the synthetic fibers, the strength per unit

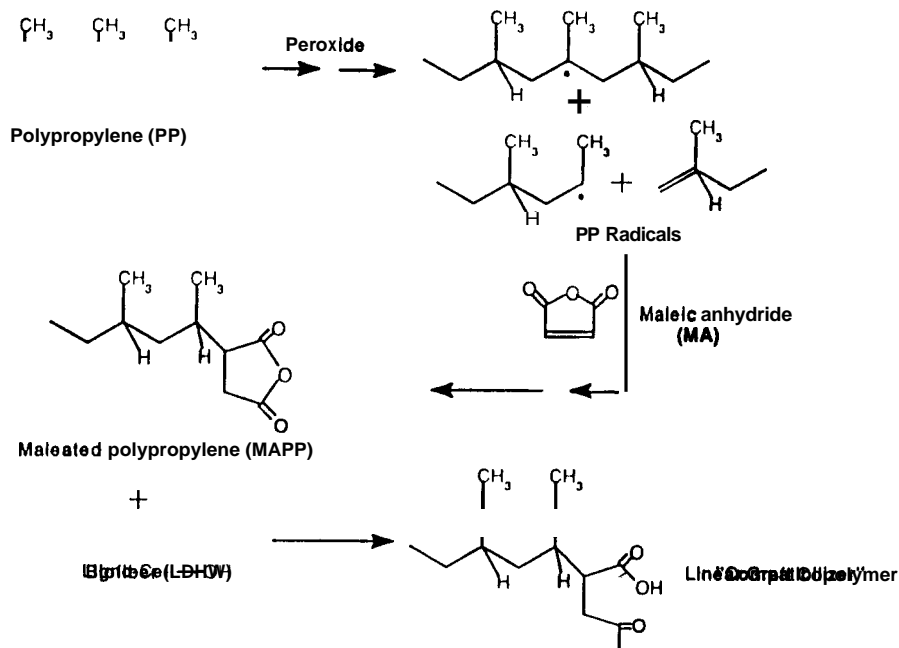


Fig. 11. Proposed reaction mechanism for compatibilization.

Fig. 12. Comparison of the tensile strengths of Kenaf and Sisal reinforced PP composites.

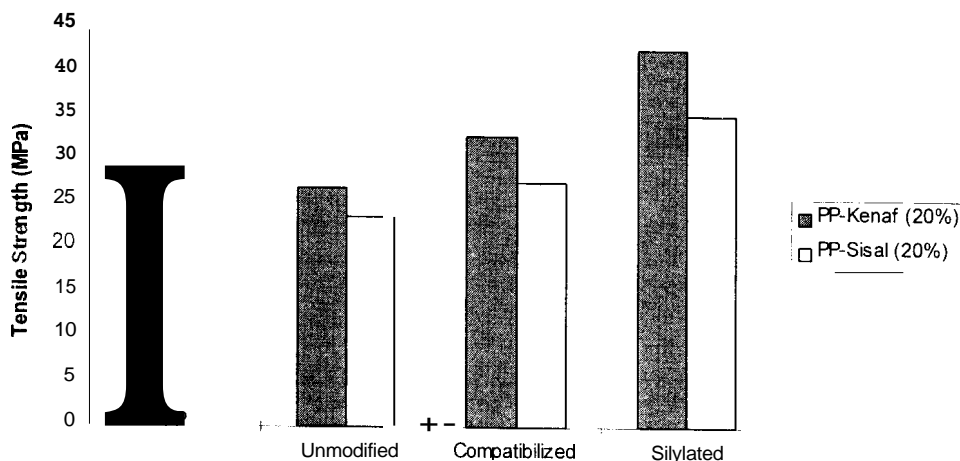
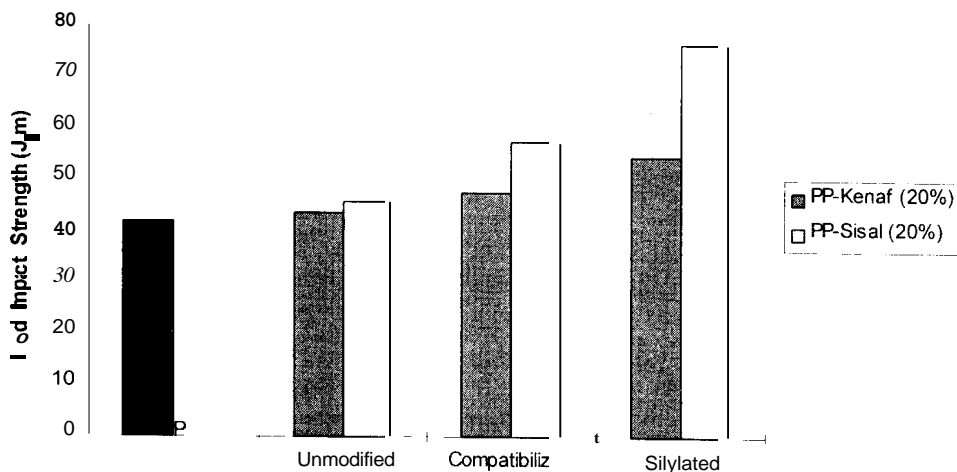


Fig. 13. Comparison of the notched izod impact strengths of Kenaf and Sisal reinforced PP composites.



weight (specific strength) of the biofiber 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 replace glass-fiber composites in applications where the strength can be traded off for less weight, lower cost, ease of recyclability or energy recovery.

CONCLUSIONS

The results presented in this work indicate that it is possible to enhance the properties of biofiber reinforced composites through functionalization of the polymer matrix with MA and fiber surface modification. Composites based on the modified matrix have, in general, superior mechanical properties to those containing the unmodified matrix, primarily as a result of improved adhesion and enhanced polar interactions at the fiber/matrix interface.

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NOMENCLATURE

- MA = Maleic Anhydride
 MAFP = Maleated Polypropylene
 PP = Polypropylene

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