

Cellulosic Reinforcement in Reactive Composite Systems

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SYNOPSIS

The two reactive systems using cellulosic fiber reinforcement emphasized in this article are twin screw extrusion maleation of polypropylene (PP) and structural reaction injection molding (SRIM). Both simultaneous and sequential compounding of sweet gum wood fiber (WF) with maleation were studied. Similar PP/WF mechanical properties are observed for simultaneous and sequential compounding. However, the melt viscosity of the simultaneous compounding and maleation decreases initially compared to neat polypropylene, whereas the sequential process does not have an initial decrease. After the initial response, the melt viscosity and shear thinning characteristics in both systems increase with WF content compared to their respective low WF behavior. The cellulosic reinforcement in the SRIM studies include: cheesecloth; and nonwoven mats formed separately from fiber bundles of sugar cane rind, kenaf, and sweet gum wood. In the SRIM system the modulus and tensile strength of the neat polyurea/urethane increases with cellulose content, independent of cellulosic source; the modulus doubles with only 4% cellulose, and the tensile strength doubles with only 7% cellulose. However, the elongation to break decreases from 300 to 30% with only 4% cellulose. Cellulose is as reactive with isocyanate in SRIM as are the commercial polyols. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of wood fiber (WF) as reinforcement in thermoplastic and thermosetting polymer systems is experiencing considerable interest due to the synergism of properties.¹⁻⁵ WF is an attractive reinforcement due to low density, low cost, high specific strength and modulus, renewable and biodegradable character, and reasonable processibility. The synthetic polymers contribute economical processing, stable properties to environmental conditions, and protection of the WF. The critical consideration in composites usage demanding mechanical properties is transfer of stress fields from one phase to the other.⁶ In this research compatibilization is enhanced by reacting the hydrophobic polypropylene (PP) with maleic anhydride causing succinic anhydride groups to be attached to backbone in the α hydrogen position. In the presence of water, the succinic anhydride is converted to succinic acid, thereby providing two carboxyl groups that alter the

character of the maleated polypropylene (MPP) to hydrophilic and enable reaction with the hydroxyl groups of cellulose.

In this study, PP is maleated and compounded with WF from sweet gum wood, both sequentially and simultaneous in a corotating twin screw extruder. The same base polypropylene is used for the entire study, in which first, the effect of maleation has upon the neat polymer is determined. Next, the MPP and wood fiber are compounded in the twin screw extruder and the effects on properties are noted. Finally the PP, maleic anhydride (MAH), initiator-dicumyl peroxide (DCP), and WF are compounded and reacted simultaneously in the same twin screw extruder with the same general purpose screw configuration.

RIM systems in general involve two components, commonly referred to as A and B, which are mixed by impingement in the mixhead and then fill the mold.⁸⁻¹⁰ In SRIM, the reinforcing medium is placed in the mold prior to filling. In the SRIM portion of this study, a commercial diisocyanate component and a commercial polyol component are used in the same ratio with and without cellulosic reinforce-

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Table I Effects of Maleation on Tensile Properties of Polypropylene

No.	MAH ^a (%)	SAH (%)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Neat PP			38.09 (0.31) ^b	51.12 (6.77)	529 (73)
1	1	0.33	36.93 (0.26)	20.03 (2.26)	479 (54)
2	3	1.06	36.68 (0.18)	28.20 (5.63)	450 (47)
3	5	1.26	35.39 (0.32)	59.70 (3.93)	492 (14)
4	7	1.29	35.43 (0.67)	62.20 (8.34)	503 (29)
5	9	1.27	34.53 (0.72)	55.63 (9.71)	508 (46)

^a 0.5% DCP used in this set of experiments.

^b Numbers inside parenthesis are standard deviation.

ment. Woven, and needle punched, and water laid nonwoven cellulosic mats are used from plant sources having 0 to nearly 20% lignin content including: cotton, kenaf, sugar cane rind, and sweet gum wood.

EXPERIMENTAL

PP from the Phillips 66 Co., grade HGX 030, density 0.909 g/cm³, melt flow index 3.0 g/10 min, 169°C melting peak by DSC was used in the MPP part of

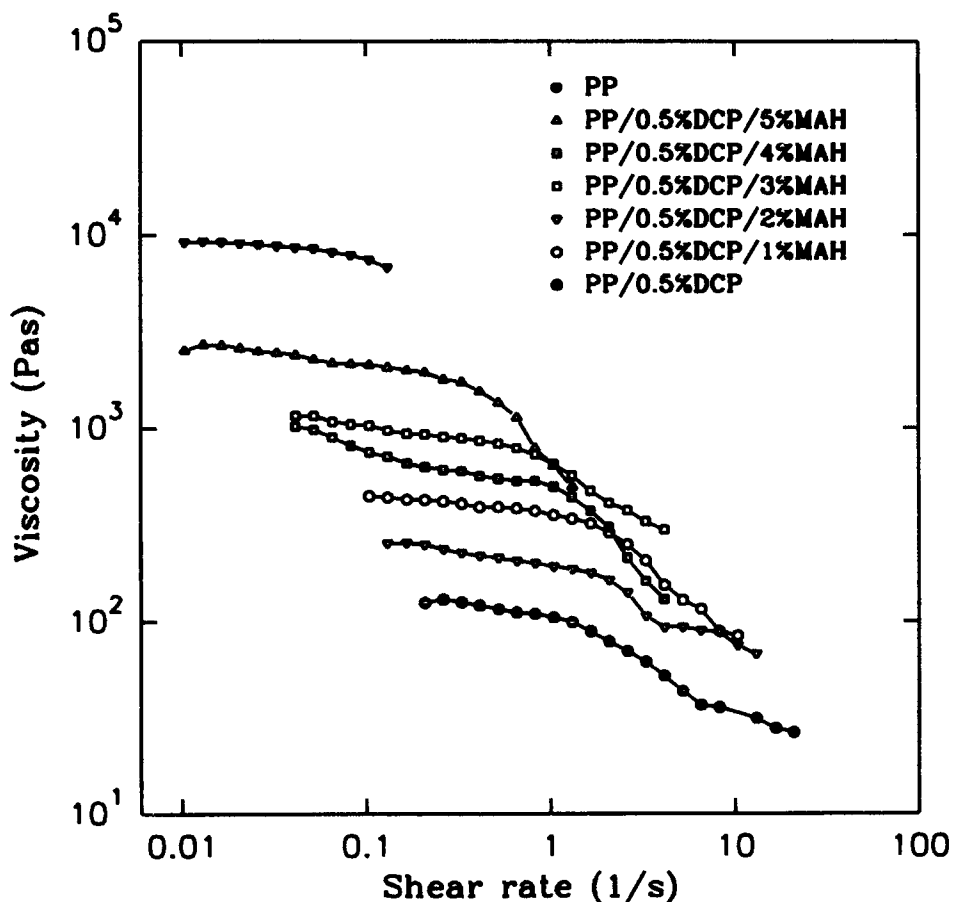


Figure 1 Effect of maleation on viscosity of polypropylene.

Table II Effects of Sequential Maleation and WF Compounding on Tensile Properties of Polypropylene/WF Composites

No.	WF (-20) (%)	WF (+20) (%)	MPP (%)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Neat PP				38.09 (0.31) ^a	51.12 (6.77)	529 (75)
6	10		5	40.66 (0.13)	25.90 (3.30)	590 (36)
7	20		5	43.70 (0.38)	17.23 (0.93)	745 (115)
8	30		5	46.83 (0.60)	11.22 (1.50)	780 (85)
9	50		5	51.47 (0.54)	9.76 (0.35)	925 (90)
10		10	5	38.28 (0.27)	25.03 (1.32)	653 (44)
11		20	5	43.94 (0.77)	14.25 (1.75)	632 (21)
12		30	5	47.34 (0.76)	10.18 (0.92)	866 (84)
13		40	5	52.53 (0.87)	8.90 (0.36)	1100 (64)
14		50	5	56.35 (0.89)	7.77 (0.98)	958 (106)
15		20	0	35.09 (0.41)	14.01 (1.48)	648 (47)
16		20	1	43.95 (0.74)	14.80 (0.88)	656 (61)
17		20	3	44.78 (0.47)	15.45 (0.56)	628 (19)
18		20	5	43.94 (0.77)	14.25 (1.75)	632 (21)
19		20	7	44.58 (0.53)	15.54 (0.66)	648 (16)
20		20	9	45.40 (0.36)	14.78 (0.60)	656 (11)

^a Numbers inside the parenthesis are standard deviation.

this study. WF was sweet gum wood supplied by Dr. Timothy Rials, U.S. Forest Service, Southern Forest Research Center, Pineville, LA; the amount used is in percent by weight. The commercial maleated PP from Adell Plastics in Baton Rouge, LA, was Adell 3000, Lot M30063R. Commercial grades of MAH and DCP were also used in the MPP studies. The equipment for this part of the study included: a Bertsch 25 mm corotating twin screw extruder, an Arburg Allrounder 170 CMD injection molder, an Instron 4301 tensile tester, and a Bohlin VOR rheometer with a cone and plate measuring head.

For the SRIM, Spectrim (R) from Dow Chemical Co. was used. The A components used were Spectrim 35-A and 50-A isocyanate and the B component used was Spectrim 50 B-W polyol. Representative composition for the 35-A isocyanate is: 50–55% diphenylmethane diisocyanate (MDI), MDI homopolymer 2–5%, and proprietary MDI/polyetherpolyol prepolymer 40–48%. The composition of 50-A is essentially the same for the nonproprietary components specified. A polyol is a mixture of compounds having two or more hydroxyl groups per molecule. The B component polyol composition was: diethyltoluene diamine (DETDA) 28%, and 72% of a proprietary polyether polyol and diamine blend incorporating a metal complex, fatty acid salt, catalyst, and surfactant. The cellulose sources included: commercial 100% cotton cheesecloth; and carded and needle punched kenaf mats prepared by Dr. Wei Ying Tao at the USDA SRRC facility in New Orleans. Also

included were nonwoven water laid mats of fiber bundles prepared using a research process developed at LSU.⁷ Water laid mats were prepared separately from sugar cane rind, kenaf, and sweet gum wood. The preparation for this process involved use of a pilot scale Tilby type separation system for splitting the sugar cane and kenaf stalks, routing out the pith, and leaving controlled length of rind segments. The sweet gum wood was disk refined at the U.S. Forest Service, Southern Forest Research Center, Pineville, LA, and supplied by Dr. Timothy Rials. The nonwoven water-laid mats of sugar cane rind, kenaf rind, and disk refined wood were separately prepared by partial, directional delignification conducted using either a purpose-built 200 liter reactor or a similar 20 liter reactor.⁷ Both employed a low concentration NaOH and specific mechanical action (either tumbling and/or agitation) and optional steam explosion at no more than 1.0 MPa (145 psi) steam pressure. The fiber bundles produced were suspended in water, then spread on a wire mesh, dewatered, and dried. In all cases the mats were cut to the mold shape and placed in the mold prior to injection of the RIM components. The levels of fiber loading reported in this work are in percent by weight.

The reaction injection molding (RIM) unit was a HI-TECH RIM unit, number 114, with a shot capacity of 300 g/s. The operating conditions used were: 38°C, flow rate ratio (B/A) 0.98, and total flow rate of 150 g/s. The Instron 4301 tensile tester was used in this part of the study also. All of the

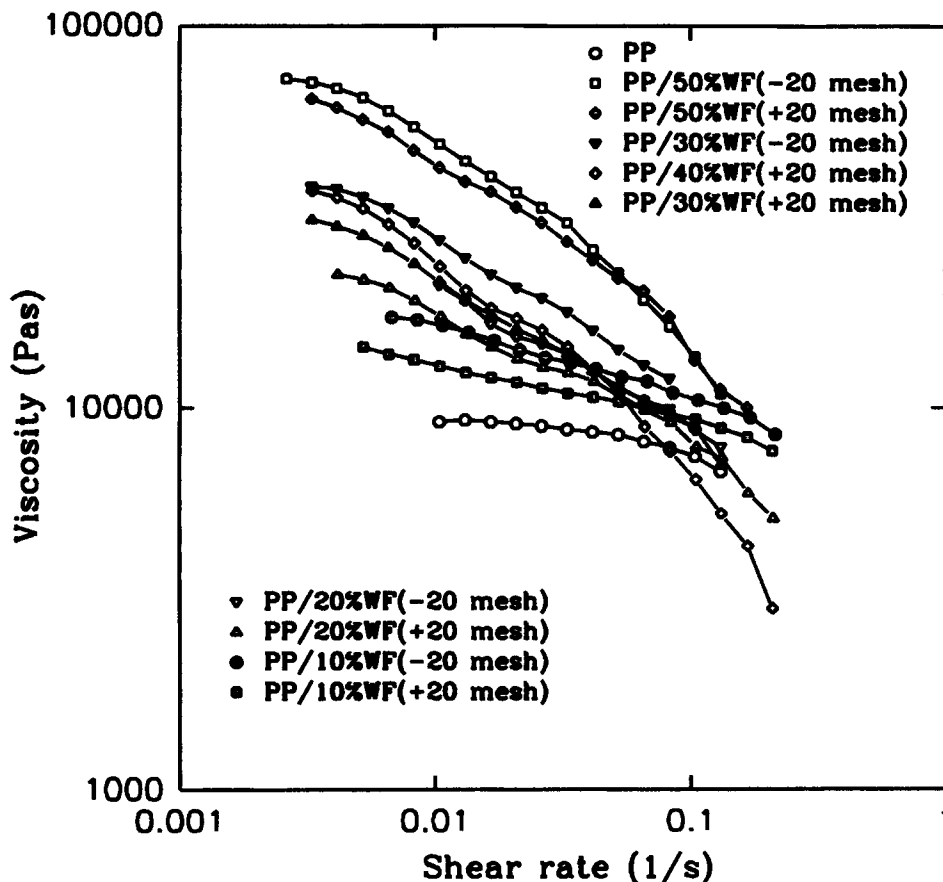


Figure 2 Effects of fiber content and size on the viscosities (PP/MPP/WF composites).

equipment used is at LSU and operated by the researchers.

RESULTS AND DISCUSSION

Polypropylene Maleation

As is shown in Table I, the amount of grafted succinic anhydride (SAH) formed with 0.5% DCP initiator increases with the amount of MAH used from 0.33% SAH for 1% MAH up to 1.26% SAH for 5% MAH; and then remains at nearly 1.3% independent of increasing amounts of MAH. The effects of maleation on tensile properties are also given in Table I. The tensile strength decreases from 38.09 MPa for neat PP to 34.53 MPa for 9% MAH. Both the modulus and elongation at break demonstrated a minimum at 1–3% MAH; the modulus starting at 529 MPa dropped to 450 MPa and then increased to 508 MPa; the elongation dropped from 51.12% to 20.03% and increased to about 60%. The shear viscosity of PP decreases significantly with DCP and then increases above the level for DCP with in-

creasing amount of MAH as shown in Figure 1. However, even with 5% MAH the viscosity is not as high as virgin PP. This is due to the synergic effects of maleation and degradation of PP. In the absence of MAH, PP was degraded by initiators dramatically. Melt viscosities of the degraded PP were lower by about two orders of magnitude than the values with neat PP. However, the presence of MAH during maleation results in both grafting reaction and degradation. There is a trend that melt viscosities of MPP increases with increasing amount of MAH. The viscosity regain is probably due to the grafting of SAH to the PP backbone and less degradation in the presence of MAH. It may also be noted from Figure 1 that the viscosity decreases with increasing shear rate, indicating the shear-thinning behavior of the material.

Sequential Maleation and WF Compounding

The commercial Adell MPP was used in sequential maleation and WF compounding in this study. The following mechanical properties are given in Table

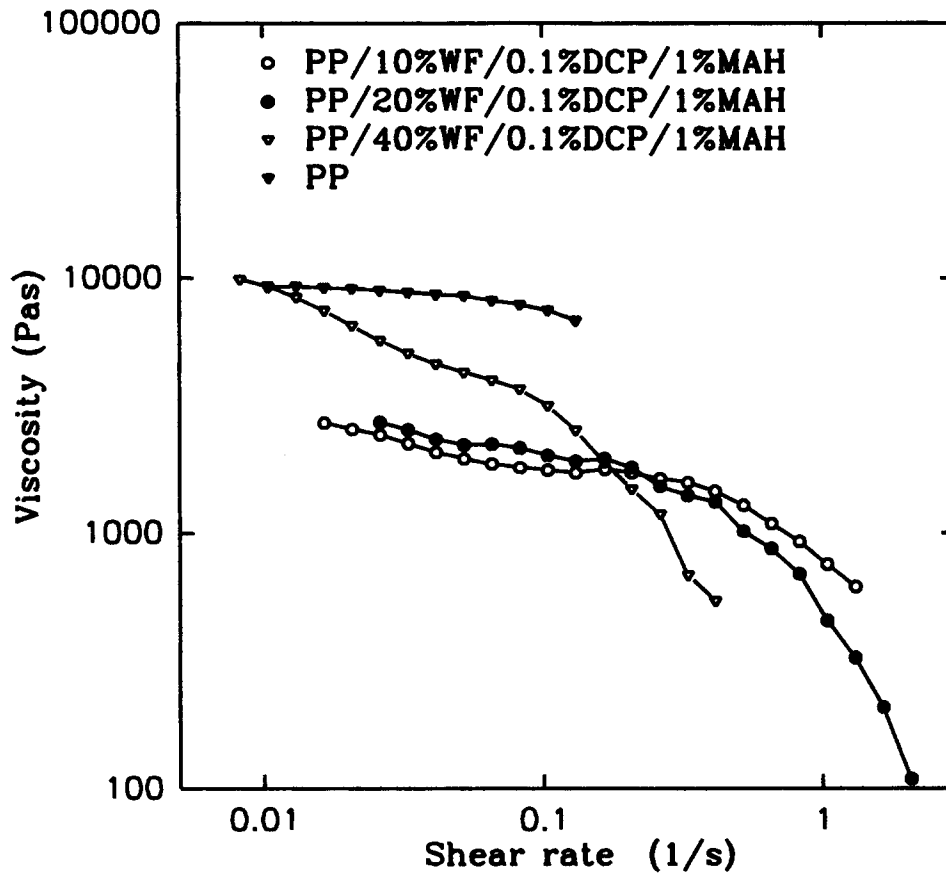


Figure 3 Effect of fiber loading level on viscosity (simultaneous composites).

II. Using a 20% WF (+20 mesh) loading for compounding with the base PP, the tensile strength exhibited a jump from 38.09 MPa for the 0% WF to 43.95 MPa with 1% MPP and then a slight increase to 45.40 MPa at 9% MPP.

The modulus and elongation to break were unaffected by the amount of MPP, the former main-

taining a value of about 650 MPa and the latter at about 14%. The tensile strength for a 5% MPP formulation increased in a nearly linear fashion from 38.09 MPa at 0% WF to 56.35 MPa for 50% +20 mesh WF, and to 51.47 MPa for a -20 mesh WF. The modulus had a similar linear response from 529 MPa at 0% WF to 958 MPa for 50% +20 mesh WF

Table III Effects of Simultaneous Maleation and WF Compounding on Tensile Properties of Polypropylene/WF Composites

No.	WF (+20) (%)	DCP (%)	MAH (%)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Neat PP				38.09 (0.31) ^a	51.12 (6.77)	529 (75)
21	20	0.5	1	40.42 (0.63)	13.41 (2.45)	676 (75)
22	20	0.5	2	40.91 (0.12)	12.04 (1.05)	669 (39)
23	20	0.5	3	39.66 (0.31)	12.16 (0.92)	610 (70)
24	20	0.5	4	38.71 (0.26)	13.85 (1.67)	596 (42)
25	10	0.1	1	40.26 (0.11)	19.27 (2.41)	652 (52)
26	20	0.1	1	41.60 (0.35)	14.86 (1.30)	601 (35)
27	40	0.1	1	45.73 (0.40)	6.54 (0.28)	766 (22)

^a Numbers in parentheses indicate standard deviation.

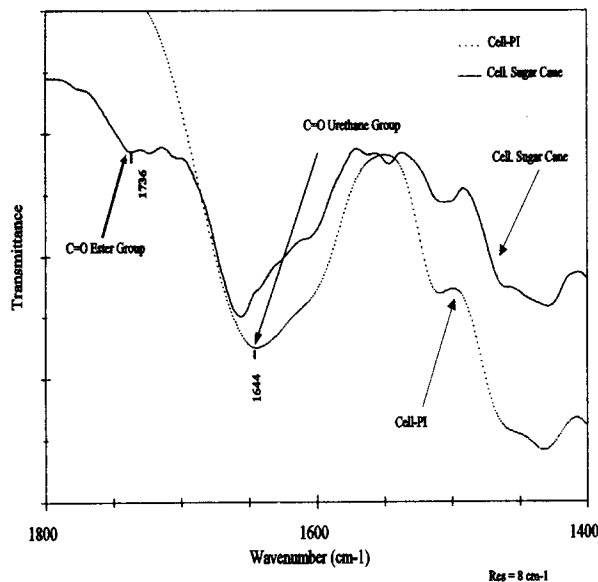


Figure 4 FTIR spectra for sugarcane cellulose and sugarcane cellulose phenyl isocyanate.

and to 925 MPa for 50% –20 mesh WF, but no significant difference was noted by the WF mesh size. Elongation to break exhibited a logarithmic decrease from 51.12% at 0% WF down to about 10% at 50% WF with no significant difference noted by WF mesh size. The rheological properties for sequential maleation and compounding exhibited an increasing viscosity [10^4 Pascal seconds (Pas) to nearly 10^5] and shear thinning behavior as the WF content increased from 0% to 50% as shown in Figure 2.

Simultaneous Maleation and WF Compounding

The most significant difference noted between sequential and simultaneous maleation and WF compounding was that in the former the viscosity increased with WF content; however, in the latter, the viscosity first dropped significantly then increased to the starting viscosity for 40% WF. As shown in Figure 3, the viscosity for simultaneous maleation and compounding dropped from an initial value of 10^4 Pas to 3×10^3 at 10% WF and then returned to the same low strain rate viscosity at 40% WF. The simultaneous maleation and WF compounding also indicated increased shear thinning behavior for higher WF contents as did the sequential maleation and compounding material.

As in the sequential system for a 20% WF (+20 mesh) loading, the simultaneous compounding and maleation exhibited an initial increase in tensile strength for the base PP resin from 38.09 MPa for the 0% MAH and 0% WF to 45.73 MPa with 1%

MAH and 40% WF and then was insensitive to increasing amounts of MAH. The modulus and elongation to break response also followed the behavior for sequential maleation and compounding by showing no effect within the significance of the test results. The simultaneous maleation and compounding also showed a slight increase in tensile strength and modulus with fiber loading, the former increasing from 40.26 MPa at 10% to 45.73 MPa at 40%, and the latter from 652 MPa to 766 MPa over the same WF content range. The elongation to break decreased from 19.27% down to 6.54% in this WF range for simultaneous maleation and compounding. These results are given in Table III.

Structural Reactive Injection Molding

As noted in the Experimental section of this article, in commercial systems, both the A and B components are mixtures of compounds. In forming a polyurea urethane system as used in this research the A component contains a high percentage of diisocyanate and the B component among other compounds contains a mixture of polyols (i.e., com-

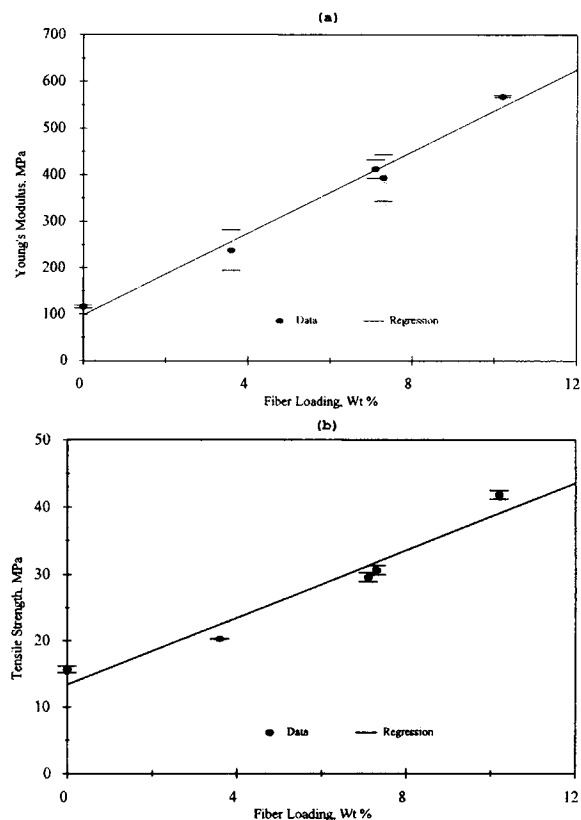


Figure 5 Effect of fiber content on the tensile properties.

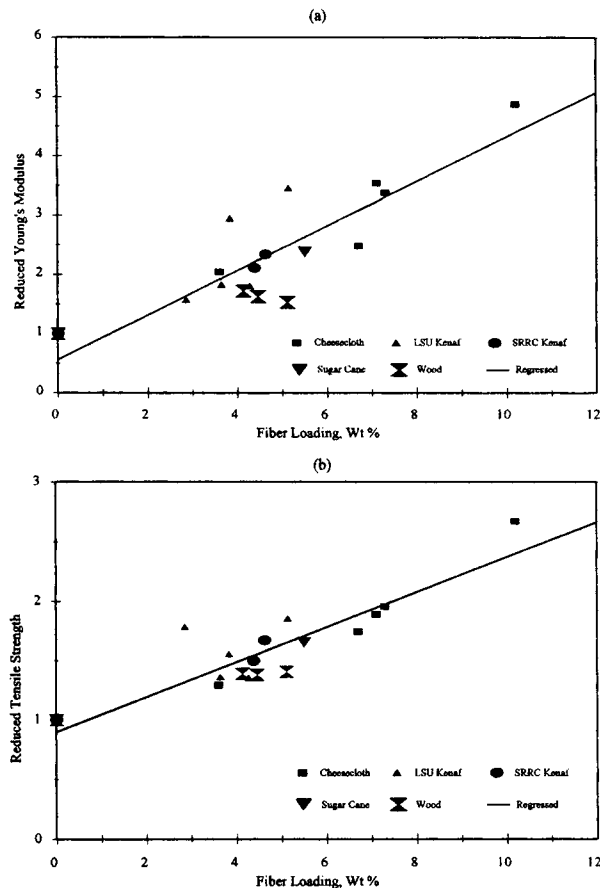


Figure 6 Effect of fiber properties and operating conditions on tensile properties.

pounds containing two or more hydroxyl groups that react with the isocyanate groups of component A, thereby forming carbamate bonds). As shown by the shift and increased intensity of the 1664 cm^{-1} peak in Figure 4, the sugar cane rind fibers used in this research are reactive with isocyanates, thereby not needing imposed reactive groups as developed by maleation of PP discussed earlier. This is probably due to the hydroxyl groups in cellulose being as reactive as the hydroxyl groups in the polyols. A linear increase in both tensile strength and modulus is shown in Figure 5, by increasing cellulose content in the form of cheesecloth. In fact, the modulus is more than doubled from 100 to 220 MPa with less than 4% cellulose and the tensile strength is doubled from 15 to 30 MPa with 7% cellulose. The strain at break decreases from nearly 300% to less than 10% with less than 4% cellulose and remains low.

Other cellulosic sources, component A formulations, mix ratios, and time intervals between formation and testing were used. Therefore, to compare results, the modulus and tensile strength values of

these other samples were divided by the corresponding values for 0% cellulose RIM prepared with the same component A formulation, mix ratios, and time intervals. The normalized modulus and tensile strength values for various cellulosic sources as compared in Figure 6 indicated that the source of cellulose is not a factor. Furthermore, lignin content is apparently not a significant factor. The cheesecloth is 100% cotton and free of lignin, whereas the sugar cane rind and wood fiber bundles as produced have about 10% lignin and the kenaf a lower but measurable amount.

CONCLUSIONS

Maleation of PP is effective in enhancing the mechanical properties of WF reinforced PP and can be achieved either by sequential or simultaneous compounding with WF. The major difference between sequential and simultaneous approaches is that the viscosity increases from 0% WF to higher levels in sequential systems, whereas in simultaneous systems the viscosity decreases significantly due to maleation effects then recovers due to the effects of increasing levels of WF. This decrease due to maleation is probably a result of molecular weight reduction typically reported for maleation reactions. Both sequential and simultaneous systems exhibit increasing shear thinning behavior with increasing WF content. Because the viscosity and shear thinning behavior must be matched to the fabrication system used, the difference in systems rheological behavior is neither good nor bad but must be considered in material choice and system used.

SRIM systems employing diisocyanates in component A and cellulosic reinforcement are particularly effective in enhancement of modulus and tensile strength at low cellulosic concentrations. Effective bonds are formed between the isocyanate groups and the hydroxyl groups of cellulose causing excellent stress transfer. The presence of lignin in the cellulosic reinforcement apparently does not affect the performance. Cheesecloth with no lignin was used, as were nonwoven mats formed from sugar cane, kenaf, and disk refined wood and all have equivalent properties. The sugar cane and wood mats had at least 10% lignin and the kenaf lesser amounts. Water-laid mats and carded and needle-punched mats behaved in the same fashion as did the woven cheesecloth. Apparently due to the carbamate bond formation with the cellulosic fibers, their macroscopic fabric form is not important because the stress transfer to the RIM phase is quite effective.

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