Effect of Natural Fibers on Thermal and Mechanical Properties of Natural Fiber Polypropylene Composites Studied by Dynamic Mechanical Analysis

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ABSTRACT: The present study deals with the effects of natural fibers on thermal and mechanical properties of natural fiber polypropylene composites using dynamic mechanical analysis. Composites of polypropylene and various natural fibers including kenaf fibers, wood flour, rice hulls, and newsprint fibers were prepared at 25 and 50% (by weight) fiber content levels. One and two percent maleic anhydride grafted polypropylene was also used as the compatibilizer for composites containing 25 and 50% fibers, respectively. Specimens for dynamic mechanical analysis tests were cut out of injection-molded samples and were tested over a temperature range of −60 to +120°C. Frequency of the oscillations was fixed at 1 Hz and the strain amplitude was 0.1%, which was well within the linear viscoelastic region. The heating rate was 2°C/min for all temperature scan tests. Storage modulus (E'), loss modulus (E''), and mechanical loss factor (tan δ) were collected during the test and were plotted versus temperature. An increase in storage and loss moduli and a decrease in the mechanical loss factor were observed for all composites indicating more elastic behavior of the composites as compared with the pure PP. Changes in phase transition temperatures were monitored and possible causes were discussed. Results indicated that glass transition was slightly shifted to lower temperatures in composites. α transition temperature was higher in the case of composites and its intensity was higher as well. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4341–4349, 2006

Key words: composites; polypropylene; natural fibers; transitions; DMA

INTRODUCTION

In recent years, the use of natural fibers as reinforcements and/or fillers in the manufacture of fiber-thermoplastic composites has been of great interest to many researchers. These fibers have many advantages such as low density, high specific strength and modulus, relative nonabrasiveness, ease of fiber surface modification, and wide availability. Natural fibers are also much cheaper than synthetic fibers and could replace synthetics in many applications where cost savings outweigh high composite performance requirements.[1] A comprehensive review of the properties of natural fiber thermoplastic composites can be found in the work of Bledzki and Gassan (1999).[2] The main disadvantages of natural fibers in composites are the lower allowable processing temperatures, incompatibility between the hydrophilic natural fibers and hydrophobic polymers, and potential moisture absorption of the fibers and in turn, the manufactured composite. To enhance the compatibility of the two phases in such composites, a compatibilizer or coupling agent is normally added to the mixture. Many researchers have reported improvements in the mechanical properties when a compatibilizer was used or the fibers were chemically modified prior to mixing.[3–10] Several mechanisms are involved determining the structure–property relationship in such composites. The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. The main chemical bonding theory alone is not sufficient. So, consideration of other concepts appears to be necessary, which include the morphology of the interphase, the acid–base reactions at the interface, surface energy, and the wetting phenomena.[11] Compounding process is one of the most important factors determining the mechanical properties of natural fiber plastic composites with twin-screw extrusion to be the most appropriate one.[12]

Composites of natural fibers and thermoplastics have found applications in many industries, particularly automotive industry.[13]

Conventional static tests are usually performed to characterize the mechanical properties of such composites. These tests generally include tensile, bending, and impact tests. Because fiber-reinforced thermoplas-

tic composite materials can undergo various types of dynamic stressing during service, studies on the dynamic mechanical properties of these materials are of great importance. Similar to other properties, dynamic mechanical properties depend on types of fiber, fiber length and orientation, fiber loading, fiber dispersion, and fiber-matrix adhesion.[14–18] Dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA) is a sensitive technique that characterizes the mechanical responses of materials by monitoring property changes with respect to the temperature and/or frequency of oscillation. The technique separates the dynamic response of materials into two distinct parts: an elastic part (E') and a viscous or damping component (E''). The elastic process describes the energy stored in the system, while the viscous component describes the energy dissipated during the process.[19] Both phases in a natural fiber-thermoplastic composite, exhibit time-dependent properties. Generally three different tests are performed to study the time-dependent properties of viscoelastic materials. These include creep, stress relaxation, and DMA. While the first two are usually considered to have the same basis and often only one of them is chosen to describe property changes over the time, the latter can give invaluable information on the viscoelastic properties of the materials over a relatively short time.[20] Therefore, a clear understanding of dynamic mechanical properties of natural fiber thermoplastic composites is necessary to determine the mechanical performance of the end product.

For semicrystalline polymers in the temperature range between the crystalline melting point and liquid nitrogen temperature ($-196°C$), at least three relaxation processes are often found. The high-temperature α process is often related to the crystalline fraction. The β process in these polymers is related to the amorphous phase and usually represents the glass transition. The low-temperature γ process is generally considered to originate in the amorphous phase, but may also have an important component associated with the crystalline phase.[21]

In semicrystalline polymers, the dominant thermal characteristic is the melting transition, which has the primary characteristics of a first-order thermodynamic transition. In highly crystalline polymers, an α or α_c relaxation involving the crystalline phase occurs below T_m and is the major relaxation in these materials. Thus a semicrystalline polymer must be considered as a multi-phase system. When the amount of crystallinity is low, the amorphous phase dominates. However, a simple two-phase model for semicrystalline polymers that delineates only the crystalline and amorphous phases is not adequate for explaining properties sensitive to morphology.[21] The study of these different transitions and the processes involved is of

great importance in terms of mechanical performance of the polymers and in turn the composites.

The objectives of this study are to develop basic information on the effects of various natural fiber types and contents on thermal, mechanical, and viscoelastic behavior of such composites through DMA.

MATERIALS AND METHODS

Materials

Polypropylene was used in this study as the polymer matrix. It was Basell Pro-fax® PD702 homopolymer with a melt flow index of 35 g/10 min (230°C, 2.16 kg) and a density of 0.902 g/cm^3. Wood flour, kenaf fibers, newsprint, and rice hulls were used as the discontinuous phase (filler and/or reinforcer) in the composites. Wood flour was 40-mesh maple flour and was supplied by American Wood Fibers, Schofield, WI. Kenaf fibers were supplied by Kengro, Charleston, MS. They contained ~97% bast fiber. Rice hulls were 20–80 mesh ground rice hulls and were supplied by Riceland Foods, Stuttgart, AR. Newsprint fibers were obtained by grinding old newspapers in the laboratory. MAPP (maleic anhydride polypropylene) was UNITE(R) MP and was supplied by Aristech Chemical, Pittsburgh, PA.

Methods

Composites preparation

Polymers, fibers, and the compatibilizer were initially weighed and bagged according to the various fiber contents indicated in Table I. The composition of each formulation is also shown.

Compounding process

The different ingredients were mixed in the proprietary mixing equipment of Teel Global Resources, Baraboo, WI. The compounded materials were then ground using a pilot scale grinder to prepare the granules.

Preparation of DMA specimens

The granules of the various composite formulations were injection-molded to produce standard ASTM impact specimens. Injection molding was performed using a 33 ton Cincinnati Milacron 32 mm reciprocating screw injection molder with an L/D ratio of 20 : 1. Prior to injection, all materials were dried for at least 4 h at 105°C to ensure that the moisture contents were below 0.5%. The injection molding parameters are presented in Table II.

Specimens for DMA testing were cut out of the impact specimens using a table saw. They were fur-

TABLE I
Composition of Evaluated Formulations (wt %)

Formulation	Code	Fiber content (%)	Resin content (%)	Compatibilizer type	Compatibilizer content (%)
1	PP	0	100	–	0
2	PP-WF-25	25	74	MAPP	1
3	PP-WF-50	50	48	MAPP	2
6	PP-KF-25	25	74	MAPP	1
7	PP-KF-50	50	48	MAPP	2
8	PP-RH-25	25	74	MAPP	1
9	PP-RH-50	50	48	MAPP	2
10	PP-NP-25	25	74	MAPP	1
11	PP-NP-50	50	48	MAPP	2

PP, polypropylene; WF, wood flour; KF, kenaf fiber; RH, rice hulls; NP, newsprint; MAPP, maleated polypropylene.

ther machined down to a nominal thickness of 2 mm using a knee-type Bridgeport vertical milling machine. A fly cutter with a carbide insert tool was used. The specimens were held in place using a vacuum chuck specifically manufactured for this project. Care was taken to obtain the specimens from the same area of the impact specimens. Each side of the specimen was machined to produce a balanced DMA specimen at the desired thickness. The final specimen dimensions were 52 mm by 8 mm by 2 mm.

Conditioning

After preparation, all specimens were conditioned in a humidity-controlled room at 23°C and 50% relative humidity for at least 40 h prior to performing dynamic mechanical tests.

Dynamic mechanical analysis

DMA was performed using a Rheometric Scientific DMTA V analyzer. A dual cantilever mode was selected and the composites were scanned over a temperature range of −60 to +120°C. Frequency of the oscillations was fixed at 1 Hz and the strain amplitude was 0.1%, which was well within the linear viscoelastic region. The heating rate was 2°C/min for all temperature scan tests. Storage modulus (E'), loss modulus (E''), and mechanical loss factor (tan δ) were collected during the test and were plotted versus temperature. The presented curves are the average of three specimens tested under the same testing conditions.

Statistical analysis

To evaluate the significance of differences observed among various composite formulations, data for five sets of temperatures namely −60, −20, +20, +60, and +100°C were tabulated and analyzed using Analysis of Variance (ANOVA) tests. Duncan's multiple range test (DMRT) was then used to determine which means were significantly different from each other. All comparisons have been made at 95% confidence level.

RESULTS AND DISCUSSION

Storage modulus spectra of PP/natural fiber composites at 25% fiber content are presented in Figure 1. While a considerable improvement in the storage

TABLE II
Injection Molding Conditions

Material	Mold temperature (°C)	Barrel temperature (°C) Zone 1	Zone 2	Zone 3	Nozzle temperature (°C)	Injection cycle (s) Packing	Holding	Cooling	Injection pressure (MPa) Packing	Holding	Injection speed (mm/s)
PP	37.8	187.8	187.8	187.8	187.8	4	4	8	2.76	2.76	12.7
PP-WF-25	37.8	187.8	187.8	187.8	187.8	10	4	8	3.45	3.45	25.4
PP-WF-50	37.8	187.8	187.8	187.8	187.8	10	4	8	8.41	8.41	22.9
PP-KF-25	37.8	187.8	187.8	187.8	187.8	10	4	8	3.45	3.45	25.4
PP-KF-50	37.8	187.8	187.8	187.8	187.8	10	4	8	7.79	7.79	25.4
PP-RH-25	37.8	187.8	187.8	187.8	187.8	10	4	8	3.45	3.45	25.4
PP-RH-50	37.8	187.8	187.8	187.8	187.8	10	4	8	7.58	7.58	20.3
PP-NP-25	37.8	187.8	187.8	187.8	187.8	10	4	8	4.48	4.48	25.4
PP-NP-50	37.8	187.8	187.8	187.8	187.8	10	4	8	9.97	9.97	50.8

modulus values is seen when fibers are added, a general falling trend can easily be observed for all formulations. A clear transition is seen at temperatures around 0°C. This is glass (β) transition, which is the major transition in the composites. Below glass transition temperature, the storage modulus values drop as the temperature increases. In the vicinity of glass transition temperature, a very considerable drop is observed, which indicates that the material is going through a glass/rubber transition. All composites showed improvements in storage modulus spectrum over the pure PP and among different fibers, kenaf fibers performed the best. All over the temperature range used in this study, rice hull-contained composites exhibited the lowest storage modulus. Newsprint and wood flour composites behaved in a very similar manner and they almost overlaid over the entire range of temperature. A slightly lower glass transition temperature was observed for the composites compared to the pure PP. It should be noted that it is difficult to pinpoint a single glass transition temperature for all formulations because the transition actually occurs over a range of temperature. This is typical in semicrystalline polymers and as it is seen, the general trend is quite the same in composites and pure plastic and no significant change in the location of the transition is observed. It is also important to keep in mind that glass transition determined from storage modulus spectrum generally differs from what is determined from loss modulus spectrum, because they actually show two different stages in transition. In the former, the onset of the transition is observed, while in the latter the peak point is considered.

Figure 2 shows the loss moduli spectra of PP/natural fiber composites at 25% fiber content. All composite formulations exhibited loss modulus values higher than that of pure PP. Two major transitions are easily seen. The first transition, which is seen around
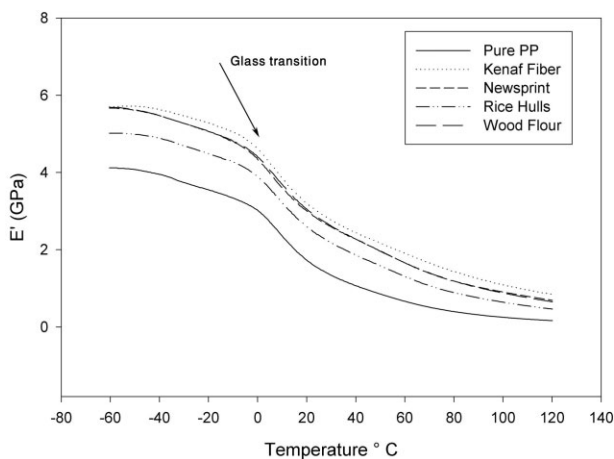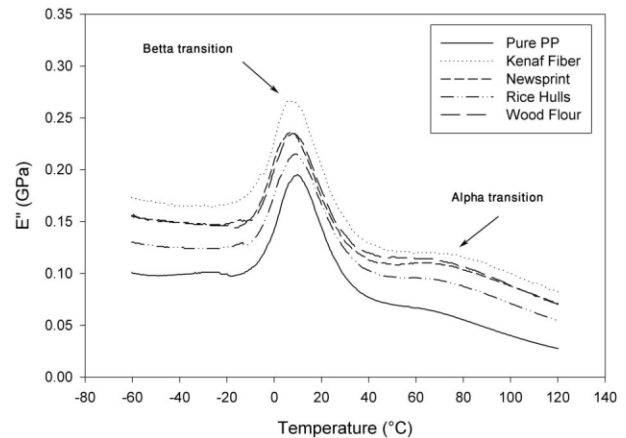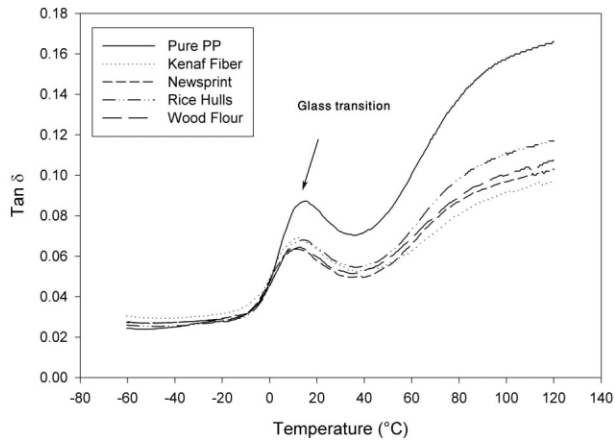

Figure 2 Loss moduli spectra of PP/natural fiber composites at 25% fiber content.

10°C, is the glass transition. As mentioned above, the glass transition temperature observed in loss modulus curve was about 10°C higher than what was determined from storage modulus curve. Again glass transition temperature was slightly shifted to lower temperatures in the case of composites as compared with the pure PP. As in the case of storage modulus, the same trend was observed for both pure PP and the composites, but the intensity of the transitions and their locations were different. Among different fibers, the same order as storage modulus was seen. The second transition is seen in the range of 60–80°C. This is the α transition. As it is seen, this transition was not very considerable in pure PP but became more distinct in the case of the composites. Also, it is interesting that the α transition temperature was shifted to higher temperatures when 25% fiber was present. Although no considerable change in the glass transition temperature was observed when fibers are added, the peak α transition temperatures seemed to have shifted to higher temperatures differently for different fibers. As it is seen, the peak temperature was the highest for kenaf fibers and the lowest for rice hulls. It seems that the effect of fibers on the secondary transitions such as α transition is much more than on the primary (glass) transition.

Figure 3 shows the mechanical loss factor spectra of PP/natural fiber composites at 25% fiber content. Below glass transition temperature, no significant difference between the different formulations was observed and tan δ values were very close even when compared with pure PP. It should be noted that this parameter is independent of the material's stiffness and hence is a very good parameter when the differences in viscoelastic response of the material are desired. At glass transition temperature, pure PP showed a significantly higher tan δ and stayed on the top all over the temperature range. As the materials went from the glass transition temperature toward the upper end of

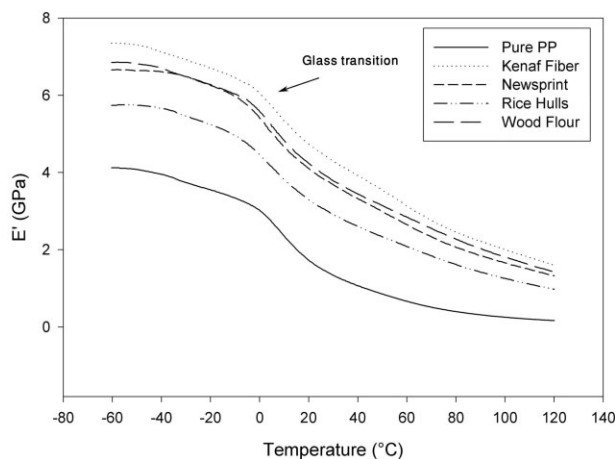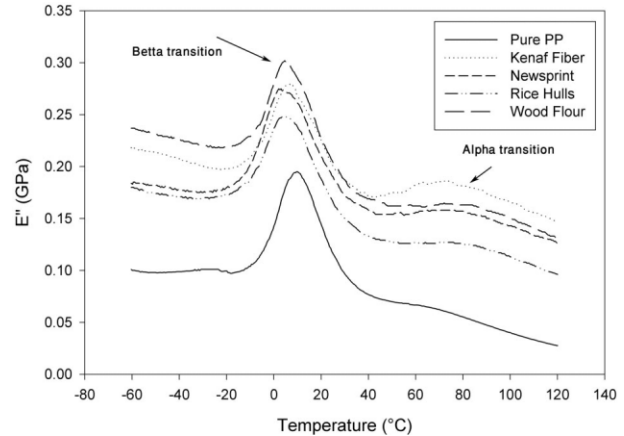**Figure 1** Storage moduli spectra of PP/natural fiber composites at 25% fiber content.

Figure 3 Mechanical loss factor spectra of PP/natural fiber composites at 25% fiber content.

Figure 5 Loss moduli spectra of PP/natural fiber composites at 50% fiber content.

the temperature range, the difference between pure PP and the composites became more pronounced. This was true for the differences between the different composites as well. As it is seen, at high temperatures, composites containing rice hulls had the highest tan δ values and the ones with kenaf fibers the lowest. Lower tan δ of the composite formulations clearly indicated that these formulations exhibited more elastic (spring-like) than viscous (dashpot-like) nature as compared with pure PP.

Storage modulus spectra of PP/natural fiber composites at 50% fiber content are presented in Figure 4 where the same trend as 25% fiber content was observed, and again kenaf fibers and rice hulls contributed to the storage modulus the most and the least, respectively. However, a slightly higher storage modulus was observed for composites having wood flour compared with the ones with newsprint. This difference was not detectable at 25% fiber content. Again

glass transition seemed to have slightly been shifted to lower temperatures when fibers were present.

Loss modulus spectra of PP/natural fiber composites at 50% fiber content are presented in Figure 5. The low temperature transition, which occurred at around 10°C is β (glass) transition. As it is seen, no considerable change in the glass transition temperature was observed. Also the amplitude of the transition was relatively the same in all formulations. However, a different behavior was seen as compared with composites containing 25% fiber. Below glass transition, the composite containing 50% wood flour exhibited the highest E″ values, which was followed by the kenaf fiber composite. After the transition was passed through, kenaf fiber-contained composites replaced the composites having wood flour. This is interesting because as Figure 4 shows, composites containing kenaf fibers had the highest storage modulus values all over the temperature range. This indicated that these two fibers behave differently in glassy and rubbery states. Also, composites containing kenaf fibers had a significantly lower α transition temperature as compared with the other fibers.

A visual comparison of Figures 2 and 5 indicates that loss moduli curves at 50% fiber content are more dispersed as compared with their 25% counterparts. This phenomenon could be both an indication of higher inconsistency of composites at higher fiber contents (indicated by generally higher standard deviations in Table III) and the presence of some additional viscous dissipation at higher fiber contents. The latter could be explained by the fact that the transitions (pertaining to the matrix and not the fibers) are affected by the presence of fibers in the system.

Tan δ curves of PP/natural fiber composites at 50% fiber content are presented in Figure 6. As in the case of 25% fiber content, no considerable difference was observed below glass transition temperature. After glass transition, which was slightly shifted to lower tempera-

Figure 4 Storage moduli spectra of PP/natural fiber composites at 50% fiber content.

TABLE III
Storage Modulus, Loss Modulus, and tan δ Values for Different Composite Formulations

| Temperature (°C)	Composite formulation	E′ (GPa)		E″ (GPa)		tan δ	
		Mean	SD	Mean	SD	Mean	SD
−60	PP-KF-25	5.530^{B,C}	0.167	0.164^{B,C}	0.011	0.030^{A,B}	0.001
	PP-KF-50	7.349^{F}	0.013	0.219^{D}	0.011	0.030^{B}	0.001
	PP-NP-25	5.668^{C}	0.074	0.155^{B}	0.001	0.027^{A,B}	0.001
	PP-NP-50	6.536^{D}	0.194	0.183^{C}	0.005	0.028^{A,B}	0.002
	PP-RH-25	5.019^{A}	0.031	0.130^{A}	0.003	0.026^{A}	0.001
	PP-RH-50	5.364^{B}	0.124	0.150^{A,B}	0.026	0.028^{A,B}	0.004
	PP-WF-25	5.687^{C}	0.177	0.155^{B}	0.008	0.027^{A,B}	0.002
	PP-WF-50	6.852^{E}	0.245	0.237^{D}	0.012	0.035^{C}	0.000
−20	PP-KF-25	5.118^{C}	0.160	0.156^{B}	0.011	0.030^{A,B}	0.001
	PP-KF-50	6.701^{E}	0.008	0.198^{D}	0.011	0.030^{A,B}	0.002
	PP-NP-25	5.060^{C}	0.028	0.148^{B}	0.002	0.029^{A,B}	0.000
	PP-NP-50	6.252^{D}	0.165	0.180^{C}	0.006	0.029^{A,B}	0.002
	PP-RH-25	4.486^{A}	0.021	0.125^{A}	0.004	0.028^{A}	0.001
	PP-RH-50	4.776^{B}	0.198	0.152^{B}	0.016	0.032^{B}	0.002
	PP-WF-25	5.065^{C}	0.191	0.146^{B}	0.008	0.029^{A,B}	0.003
	PP-WF-50	6.270^{D}	0.247	0.218^{E}	0.011	0.035^{C}	0.000
+20	PP-KF-25	3.126^{B}	0.071	0.189^{C}	0.015	0.060^{C,D}	0.003
	PP-KF-50	4.733^{D}	0.056	0.225^{D}	0.011	0.048^{A}	0.003
	PP-NP-25	3.002^{B}	0.026	0.173^{A,B,C}	0.006	0.058^{B,C,D}	0.002
	PP-NP-50	4.100^{C}	0.229	0.210^{D}	0.005	0.051^{A,B}	0.004
	PP-RH-25	2.595^{A}	0.043	0.166^{A,B}	0.005	0.064^{D}	0.003
	PP-RH-50	3.052^{B}	0.077	0.158^{A}	0.024	0.051^{A,B}	0.006
	PP-WF-25	3.046^{B}	0.244	0.180^{B,C}	0.000	0.060^{C,D}	0.005
	PP-WF-50	4.234^{C}	0.190	0.227^{D}	0.008	0.054^{A,B,C}	0.000
+60	PP-KF-25	1.835^{C}	0.074	0.117^{B,C}	0.003	0.064^{C}	0.001
	PP-KF-50	3.132^{F}	0.005	0.182^{E}	0.000	0.058^{A,B}	0.000
	PP-NP-25	1.658^{B}	0.013	0.110^{B}	0.001	0.066^{D}	0.001
	PP-NP-50	2.646^{D}	0.085	0.156^{D}	0.007	0.059^{B}	0.001
	PP-RH-25	1.306^{A}	0.002	0.096^{A}	0.001	0.074^{F}	0.001
	PP-RH-50	1.918^{C}	0.052	0.120^{C}	0.001	0.063^{C}	0.001
	PP-WF-25	1.659^{B}	0.067	0.114^{B,C}	0.007	0.069^{E}	0.001
	PP-WF-50	2.850^{E}	0.132	0.162^{D}	0.009	0.057^{A}	0.001
+100	PP-KF-25	1.047^{C}	0.045	0.096^{C}	0.004	0.092^{D}	0.000
	PP-KF-50	2.001^{G}	0.015	0.166^{G}	0.001	0.083^{A}	0.000
	PP-NP-25	0.906^{B}	0.010	0.088^{B}	0.000	0.097^{E}	0.001
	PP-NP-50	1.658^{E}	0.035	0.143^{E}	0.003	0.086^{B}	0.000
	PP-RH-25	0.640^{A}	0.017	0.071^{A}	0.002	0.111^{G}	0.000
	PP-RH-50	1.181^{D}	0.004	0.107^{D}	0.001	0.090^{C}	0.001
	PP-WF-25	0.881^{B}	0.020	0.088^{B}	0.002	0.100^{F}	0.000
	PP-WF-50	1.816^{F}	0.090	0.150^{F}	0.008	0.083^{A}	0.000

Values with common superscript alphabets are not significantly different at 95% confidence level.

tures in the case of composites, the difference between pure PP and the composites became very considerable and at about 100°C, tan δ value of pure PP was about twice as much as those of the composites.

Table III presents the means and standard deviations of storage modulus, loss modulus, and tan δ values for different composite formulations. DMRT tests indicated that significant differences existed among various composites. This has been shown in Table III using letters next to mean values. A common letter between two means indicates a nonsignificant difference between them. Thus, two means without a common letter are significantly different from each other. It is understood from Table III that the differences between various composite formulations increase as the temperature increases.

The general increase in storage and loss moduli and decrease in damping values due to the addition of natural fibers observed in the present study are consistent with the observations of many researchers. Amash and Zugenmaier[22] reported an increase in the stiffness and a decrease in the damping with increasing glass fiber content in isotactic polypropylene (PP) composites. Amash and Zugenmaier[23] reported simi-
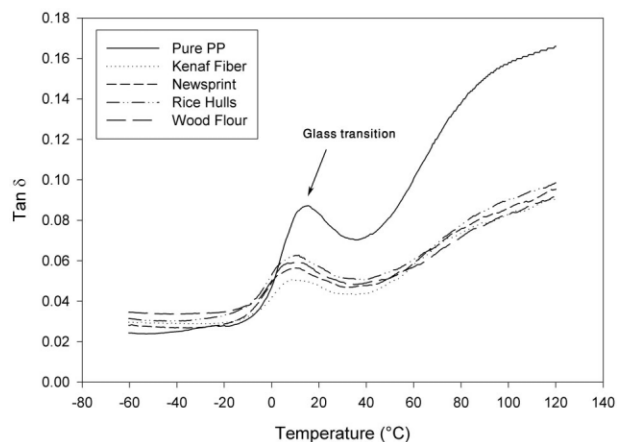
Figure 6 Mechanical loss factor spectra of PP/natural fiber composites at 50% fiber content.

lar behavior in polypropylene/cellulose and PP/xylan composites indicating significant increase in the stiffness and a remarkable decrease of the damping values. An increase in E' values with the increase of fiber content was reported by Rana et al.[24] in their study on short jute-fiber polypropylene composites using DMA. Neus Anglès et al.[25] reported the results of a comprehensive study on the steam-exploded residual softwood-filled polypropylene composites. A temperature scan was used in DMA, which showed little changes in storage modulus at low temperatures. However, the curves of pure polypropylene and other formulations containing fibers significantly deviated at higher temperatures. Thus, DMA temperature scans confirmed the significant improvement in the stiffness of the studied formulations.

β transition, related to the glass–rubbery transition, is due to the molecular motions associated with unrestricted amorphous PP.[21,26] Different observations have been made regarding the effect of fibers on the glass transition of polypropylene. Amash and Zugenmaier[23] reported that in polypropylene/cellulose and PP/xylan composites a significant decrease was detected for the intensity and magnitude of both α and β relaxations. However, only a slight decrease was observed for their shape and position. Amash and Zugenmaier[22] reported no change in the position of primary relaxations of isotactic polypropylene (PP) by the addition of short glass fiber (GF) and/or polyester fibers but a significant broadening of the α relaxation in the crystalline phase was observed.

Shifting of glass transition temperature to higher temperatures has also been reported. Rana et al.[10] reported that in short jute-fiber polypropylene composites, tan δ peak was shifted to a higher temperature as the amount of fiber loading increased. However, only a very slight change in transition was observed by varying the compatibilizer dose at the same level of

fiber content. Hristov and Vasileva (2003) studied changes in glass transition temperature of PP due to the addition of 10% wood flour and/or 10% MAPP.[27] A higher glass transition temperature was observed when the compatibilizer was added. They suggested that the modified PP wood fiber composite has more restricted macromolecules in the amorphous phase, likely to be near the fiber surface.[27]

On the other hand, Sanadi et al.[28] reported that β transition peak of pure polypropylene was at higher temperatures compared with the kenaf fiber-polypropylene composites. This was attributed to the plasticizing effect of MAPP used as the compatibilizer. α transition amplitude was found to increase almost linearly by the fiber content. Peak α transition was also significantly shifted to higher temperatures when fibers were present. Sanadi and Caulfield[29] also reported that the peak temperature of the β relaxation, associated with the glass–rubber transition of the amorphous molecules, of the coupled composites was higher than that of the uncoupled composites. It was suggested that restricted molecular mobility due to covalent interactions between the MAPP and the lignocellulosic surface might account for the shift to higher temperatures. The intensity of α transition, related to molecular mobility associated with the presence of crystals, was also found to be proportional to the fiber volume fraction. The same pattern of intensification of α transition has been reported by Botev et al.[30] for basalt fiber/PP composites. Simonsen et al.[17] also found no change in glass transition temperature of wood-fiber-reinforced styrene-maleic anhydride copolymers. However, a significant reduction in damping was observed. The authors concluded that there was no evidence of significant chemical bond formation between the anhydride and the wood fiber because if so, chemical bonding to the wood fiber would reduce the mobility of the polymer backbone and would eventually increase the T_g.

As presented above, there seemed to be a slight shift of β (glass) transition to lower temperatures when natural fibers were present. A lower glass transition temperature implies the presence of some processes, which have possibly led to the softening of the matrix and increasing the ability of the matrix chains to move more freely. Sanadi et al.[28] suggested that glass transition temperature was dependent on a variety of parameters and the direction of the shifting was determined by the dominant parameter. Nielsen and Landel[20] suggested that incorporation of fibers or fillers into polymer matrices restricted the mobility of polymer chains and therefore increased the glass transition temperature. As it is evident, this was not the case here and it can be concluded that some other factors must have been involved. MAPP is a low molecular weight polymer and is reported to have a plasticizing effect, which could possibly shift the glass transition to lower temperatures. However, this could

only be true if some free MAPP remained in the system. Tajvidi et al.[31] found no change in glass transition temperature due to the presence of MAPP in the system for wood flour-polypropylene composites. They concluded that only free MAPP was able to reduce glass transition temperature in such composites. Marcovich et al.[32] found no change in tan δ peaks for all composites and concluded that there was no free MAN in the system because if so, because of the plasticity effect of MAN a lower T_g would be observed. Sanadi et al.[28] found a higher glass transition temperature for lower fiber contents. However, they had used the same amount of compatibilizer at all fiber content levels, therefore the concentration of the compatibilizer was higher at lower fiber contents. Therefore, the higher peak β temperature could be attributed to the better adhesion at lower fiber contents. In this study, however, the compatibilizer was used in proportion to the fiber content and therefore its concentration was the same for both fiber contents. Thus it seemed that free compatibilizer could not be responsible for the lowering observed in glass transition temperature. On the other hand, use of compatibilizer means better adhesion between the fibers and polypropylene, which is expected to shift the glass transition to higher temperatures. The effectiveness of the compatibilizer on enhancing the interface is undeniable and has been reported by many researchers.[2] Therefore, it is certain that the compatibilizer has improved the adhesion but other factors have possibly masked its effect on increasing the glass transition temperature. In case of wood flour PVC composites, the glass transition temperature was reported independent of moisture content[33] but increasing with wood flour content.[34]

Crystallinity also increases the glass transition temperature. There is evidence that transcrystallinity occurs in natural fiber thermoplastic composites due to the nucleating properties of the cellulosic fibers. The presence of the coupling agents is also reported to increase transcrystallinity, which could enhance interfacial strength.[35] Interfacial shear strength also considerably increases when fibers are pretreated or a comatibilizer is used.[3]

Sanadi and Caulfield[29] reported that crystallinity remained unchanged at all fiber contents and even if this were the case, it would increase the glass transition temperature. They suggested that another factor played an important role. During blending, some of the surface material of the fibers themselves was sheared off the fiber and blended with the matrix. This sheared material could contain lignin, cellulose and oils and other surface extractives that are inherently present in the fiber. This could be clearly seen as the darkening of the polymer matrix after blending. In other words, the matrix material was a blend of PP and several constituents that were contributed by the fiber. The general decrease in glass transition temperature shows that in general, lowering factors are dominant. Therefore, it was quite possible that the sheared material was responsible for the decrease in glass transition temperature.

A high degree of interaction between wood and commercial polyurethane-alkyd lacquer was shown as a decrease by 10°C of the glass transition temperature (T_g) for the lacquer on wood compared to the pure lacquer. The reason for the decrease in T_g was reported to be probably because of the lacquer having a higher free volume when applied to the wood, most likely due to it being subject to tensile forces developed during the drying of the lacquer.[36]

On the other hand, as discussed earlier, the glass transition of composites containing 50% newsprint and rice hulls was clearly shifted to lower temperatures as compared with the 25% fiber content. A possible explanation for this can be that newsprint fibers contained some ink that could possibly act as a plasticizing agent and lower the glass transition. This was evident from the almost black color of these composites. Similar observations have been made by De Clerck (2004) for PET fibers where the decrease of T_g observed for the dyed fibers was reported to be due to the plasticizing effect of the dyes on the PET.[37]

In the case of rice hulls, the possible plasticizing effect of the compatibilizer could be considered responsible for because of its relatively lower cellulose content,[1] it is more likely to have some free compatibilizer in the system.

Table II shows that the processing conditions (pressure, speed, time) used for the unreinforced and reinforced samples were not the same in all cases. This is due to the fact that it is not possible to have the same injection parameters for both pure plastic and its composites because of their very different flow characteristics. However, temperature and cooling rate, which are crucial for crystal development, have been kept constant. Such variable processing conditions might have influenced the crystallinity and orientation of the chains in the PP matrix, leading to variations in the mechanical properties.

α transition in semicrystalline polymers is related to the relaxation of restricted PP amorphous chains in the crystalline phase (defects), also known as rigid amorphous molecules.[21,26,28,29] The higher intensity of the α transition in the composites in comparison with pure PP indicated that the number of these defects in composites were higher. Sanadi and Caulfield[29] suggested that the defects that cause the α transition for kenaf-polypropylene composites were predominantly near the fiber–matrix interface and existed in the transcrystalline zone. As mentioned earlier, the α transition intensities in this study increased with fiber content. Thus it could be inferred that the number of defects in the composites had increased. In other words, the

presence of the fibers induced more amorphous regions in crystalline zone. A shift to higher temperatures in α transition meant that the process in which this transition occurred was delayed by the fibers so that more energy was required for α transition to occur. Therefore, it can be concluded that the presence of more fibers restricted the mobility of the chains in the crystalline zone and hence, shifted the α transition to higher temperatures.

CONCLUSIONS

Composites of polypropylene and four different types of natural fibers including wood flour, rice hulls, kenaf fibers, and newsprint were prepared at 25 and 50% fiber contents and their dynamic mechanical properties were studied and compared with the pure plastic. The following conclusions could be drawn from the results of the present study:

- All composites had storage and loss modulus values higher than those of pure polypropylene, whereas their mechanical loss factor (damping) was lower. Therefore, natural fiber-filled polypropylenes behave more elastically than their pure counterpart. Composites containing kenaf fibers and rice hulls exhibited the highest and lowest storage modulus values, respectively, indicating better reinforcement efficiency. Among different composite formulations, the mechanical loss factor was highest for rice hulls and lowest for kenaf fiber composites all over the studied temperature range. Effect of fiber content was remarkable both on increasing the stiffness and on decreasing the damping in the composite systems.
- Glass transition was slightly shifted to lower temperatures in composites. Several factors govern the glass transition temperature in natural fiber polypropylene composites. A number of these factors tend to increase T_g, whereas others lower the transition temperature. It was concluded that lowering factors dominated in the studied systems with the effect of materials sheared off the fibers during mixing process being one of the possible causes. Another factor influencing the glass transition was considered to be the possible effect of variable processing conditions for preparing the test specimens. Further work is required to ensure such an effect.
- α transition temperature was higher in the case of composites and its intensity was higher as well. It was concluded that the number of so-called defects in the crystalline zone increased when fibers were added to the system.

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