Influence of Natural Fibers on the Phase Transitions in High-Density Polyethylene Composites Using Dynamic Mechanical Analysis

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Abstract

Dynamic mechanical analysis was employed to evaluate the performance of various natural fibers in high-density polyethylene composites. Kenaf, newsprint, rice hulls, and wood flour were sources of fiber. Composites were made at 25 percent and 50 percent by weight fiber contents. Maleic anhydride modified polyethylene was also added at 1:25 ratio to the fiber. Temperature scans in the range of −110° to +100°C were performed, and storage modulus, loss modulus, and mechanical loss factor (tan 6) were recorded over the selected temperature range. Different transitions were monitored, and the effects of natural fibers on location and intensity of such transitions were investigated. The **b** transition was hard to detect, whereas the a transition was shifted to higher temperatures when fibers were present. The results also indicated that **b** transition is not a major transition in such composites, whereas tan **d** curves of the composites tended to deviate from the pure plastic curve at temperatures above a transition temperature.

Introduction

In recent years, the use of natural fibers as reinforcement or filler 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 non-abrasiveness, ease of fiber surface modification, and wide availability. Natural fibers are much cheaper than synthetic fibers and could replace synthetics in many applications where cost outweighs high composite performance requirements (1). The main disadvantages of natural fibers in composites are the lower processing temperatures allowable, incompatibility between hydrophilic natural fibers and hydrophobic polymers, and potential moisture absorption of the fibers and the manufactured composite. To enhance the compatibility of the two phases in such composites, a compatibilizer or

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coupling agent is normally added to the mixture. Many researchers have reported improvements in mechanical properties when a compatibilizer was used or the fibers were chemically modified prior to mixing (2-9). Composites of natural fibers and thermoplastics are finding places in many industries, particularly the automotive industry (10).

Conventional static tests, including tensile, bending, and impact tests, are usually performed to characterize the mechanical properties of such composites. Because fiber-reinforced thermoplastic composite materials can undergo various types of dynamic stressing during service, studies on the dynamic mechanical properties of these materials are of great importance. Furthermore, because of the highly temperature-dependent mechanical properties of such composites, the application of a method that monitors property changes over a range of temperatures is critical. Similar to other properties, dynamic mechanical properties depend on types of fiber, fiber length and orientation, fiber loading, fiber dispersion, and fiber-matrix adhesion (1 1-14). 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 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, whereas the viscous component describes the energy dissipated during the process. In a natural fiber thermoplastic composite, both phases exhibit viscoelastic behavior. DMA provides rapid assessment on the viscoelastic properties of these materials.

Incorporation of natural fibers into polymers can cause significant changes in the dynamic response of the composites. Phase transitions are major phenomena in many amorphous polymers where mechanical properties may change on the order of decades when the material goes through a glass-rubber transition known as T_g. For semi-crystalline 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 a process is often related to the crystalline fraction. The **b** process in these polymers is related to the amorphous phase and usually repre-sents the glass transition. The low-temperature **g** process is generally considered to originate in the amorphous phase but may also have an important component associated with the crystalline phase (15). In these 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 a or a, relaxation involving the crystalline phase occurs below T_m and is the major relaxation in these materials.

Sirotkin et al. (16) summarize different theories on the mechanisms of relaxations in high-density polyethylene. Three major transitions are observed over the temperature range. The **g** transition is thought to be associated with short-range motions in the amorphous phase. The **b** transition is associated with inter-lamellar shear and is thought to be dependent on the lamellar fold surface morphology. The a transition is associated with shear within the crystalline lamellae; it is dependent only on the lamellar thickness and is unaffected by the lamellar fold surface morphology.

The glass transition in highly crystalline polymers is difficult to identify (15). This is true because in such cases T_g is a minor event, masked by crystallinity, and because crystalline polymers frequently have multiple transitions arising from relaxations associated with the amorphous phase, the crystalline phase, or both. The controversy concerning T_g of polyethylene centers around assigning it to one of the three temperature regions, $-33°C$, $-83°C$, and $-123°C$. Turi (15) suggests that evidence favoring the $-33°C$ temperature range has gained considerable credibility in recent years. On the other hand, it is suggested that **b** relaxation is associated with the relaxation of branch points. This seems to be true because in low-density polyethylene, which is a branched polymer, a clear **b** transition peak can be detected (17). Sirotkin et al. (16) report that for high-density polyethylene, the **b** relaxation is usually absent. This relaxation is therefore generally attributed to segmental motions in the non-crystalline phase.

The objectives of this study were to develop basic information on the influence of various natural fiber types and contents on the engineering and viscoelastic properties and phase transitions of such composites through DMA.

Table 1. ~ *Composition of evaluated formulations (% wt.).*

Formulation	Specimen code[a]	Fiber content	Resin content	Compatibilizer type	Compatibilizer content
		------------ (%) -----------			--- (%) ---
1	PE	0	100	--	0
2	PE-WF-25	25	74	MAPE	1
3	PE-WF-50	50	48		2
4	PE-WF-25-0	25	75	--	0
5	PE-WF-50-0	50	50	--	0
6	PE-KF-25	25	47	MAPE	1
7	PE-KF-50	50	48	WE	2
8	PE-RH-25	25	74	WE	1
9	PE-RH-50	50	48	MAPE	2
10	PE-NP-25	25	74	MAPE	1
11	PE-NP-50	50	48	MAPE	2

[a] PP = polypropylene; WF = wood flour; KF = kenaf fiber; RH = rice hulls; NP = newsprint; PE = polyethylene; MAPE = maleated polyethelene.

Materials and Methods

Materials

High-density polyethylene, Chevron HiD® 9035, with a melt flow index of 40 g/10 min. (190°C, 2.16 kg) and a density of 0.952 g/cm³, was used as the polymer matrix. Wood flour, kenaf fibers, newsprint, and rice hulls were used as the discontinuous phase (filler or reinforcement) in the composites. Wood flour (supplied by American Wood Fibers, Inc., Schofield, WI) was 40-mesh maple flour. Kenaf fibers (supplied by Kengro Corporation, Charleston, MI) contained approximately 97 percent bast fiber. Rice hulls (supplied by Riceland Foods, Stuttgart, AK) were 20-80 mesh ground rice hulls. Newsprint fibers were obtained by grinding old newspapers at Teel Global Resources. MAPE (maleic anhydride modified polyethylene) was Fusabond® C modified polyethylene, product MB-100D, and was supplied by DuPont Industrial Corporation.

Methods

Composites preparation

Polymer, fibers, and compatibilizer were initially weighed and bagged according to the various fiber contents indicated in **Table 1.** The composition of each formulation is also shown.

Compounding process

Polymer, fibers, and compatibilizer were mixed in the proprietary mixing equipment of Teel Global Resources Inc., 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. Mold temperature was 93°C, and barrel and nozzle temperature were set to 188°C. Prior to injection, all materials were dried for at least 4 hours at 105°C to ensure that moisture contents were below 0.5 percent. Specimens for DMA testing were cut from the impact specimens using a table saw. They were further machined 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 by 8 by 2 mm.

Conditioning

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

Temperature scan

A dual cantilever mode was selected, and the specimens were scanned over a temperature range of –110°C to +100°C. Frequency of oscillations was fixed at 1 Hz, and the strain amplitude was 0.1 percent, which was well within the linear viscoelastic region. The heating rate was 2°C/min. for all temperature scan tests. An 8-minute soak time was applied before the first measurement to let the specimens equilibrate. Storage modulus (E'), loss modulus (E''), and mechanical loss factor (tan **d**) were collected during the test and were plotted versus temperature.

Results and discussion

Storage moduli (E') spectra of high-density polyethylene (HDPE)-natural fiber composites at 25 percent fiber content are shown in **Figure 1.** A constantly falling trend in the values of storage modulus over the temperature range is observed, and no major transition is detectable. A significant increase in the E' values of composites is clearly seen with the addition of natural fiber. Among the different fibers, kenaf fibers contribute the most to increasing the storage modulus, followed by wood flour. Composites containing rice hulls have the lowest values over the temperature range investigated. The difference between rice hulls-HDPE composites and the other composites is considerable. At very low temperatures, composites containing kenaf fiber have slightly lower E' values than do composites containing wood flour **(Fig. 1).** However, this is reversed at high temperatures. A slight change in slope of the curves is seen (indicated by an arrow in **Fig. 1).** This is the transition, which is the only transition detectable over the temperature range investigated. Also, the a transition is shifted to higher temperatures when fibers are present. At high temperatures, the curves of pure HDPE and composites converge.

Loss moduli spectra of HDPE-natural fiber composites at 25 percent fiber content are presented in **Figure 2.** In the case of pure HDPE, a very slight loss modulus peak (indicated by the upward arrow) is observed around -30°C. This seems to be the transition. The **b** transition peak is masked when fibers are present. This indicates that the presence of fibers has altered the morphology of the system so that this transition is not detectable or is simply not observable because of the lower amount of polymer in the composite. Another peak is seen around 45°C for pure HDPE. This is a
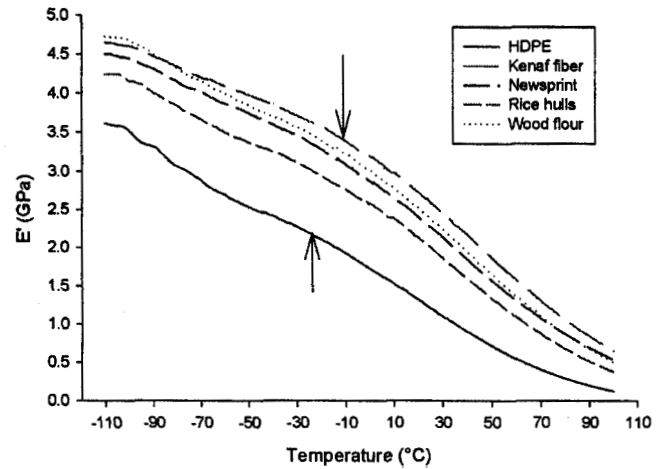
Figure 1. ~ *Storage moduli spectra of HDPE-natural fiber composites at 25% fiber content. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*
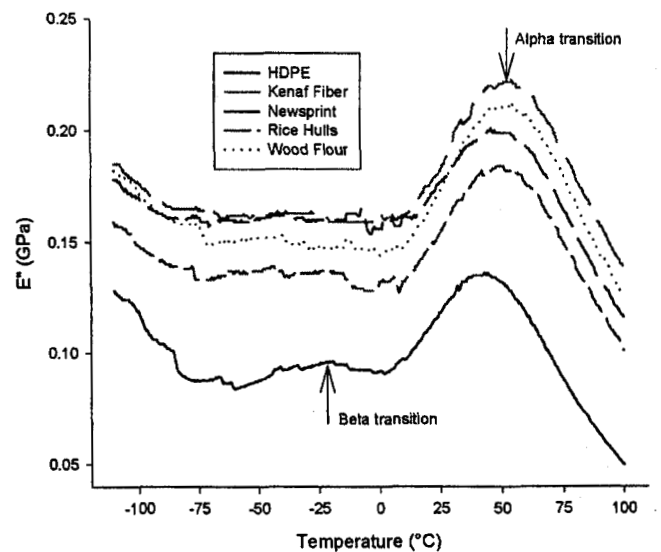

Figure 2. ~ *Loss moduli spectra of HDPE-natural fiber composites at 25% fiber content. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*

transition and is shifted about 20°C higher in the case of the composites. The shift is larger for kenaf fiber and woodflour composites. No considerable change in the intensity (height of the peak) of a transition is observed when 25 percent fibers are added.

Mechanical loss factor spectra of HDPE-natural fiber composites at 25 percent fiber content are shown is **Figure 3.** From –110°C to about 20°C, no significant change in tan 6 values is observed and all formulations have relatively the same values. It
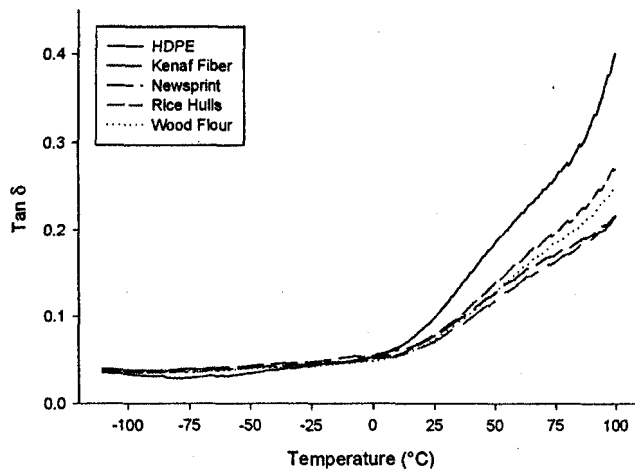
Figure 3. ~ *Mechanical loss factor spectra of HDPE-natural fiber composites at 25% fiber content, Frequency is 1 Hz, and maximum fiber strain is 0.1%.*

Figure 4. ~ *Storage moduli spectra of HDPE-natural fiber composites at 50% fiber content. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*

is also evident that the **b** transition, which was seen in loss modulus spectra, is not clearly seen here, indicating that this transition is not a major transition in pure HDPE or its composites. It is interesting that after the onset of a transition at about 20°C the curves start to deviate from each other and pure HDPE has the highest tan **d** value. Among composites, those containing kenaf fiber have the lowest values, whereas those containing rice hulls have the highest tan 6 values compared with the other fibers. The difference between various fibers becomes more pronounced at higher temperatures.

The general increase in storage and loss moduli and decrease in damping values due to the addition of natural fibers to polyethylene are in agreement with the observations of other researchers. Neilsen (18) concluded that in filled polyethylene systems, all rigid fillers increase the dynamic shear modulus. Damping also decreased by the addition of the fillers. Kuruvilla et al. (11) also reported that by the incorporation of short sisal fibers into low-density polyethylene (LDPE), the storage and loss moduli increased, whereas the mechanical loss factor (tan 6) decreased. The modulus values increased sharply by the addition of fibers and then leveled off when more fibers were added.

Storage moduli spectra of HDPE-natural fiber composites at 50 percent fiber content are shown in **Figure 4.** As in the case of composites containing 25 percent fiber, a constantly falling trend in the values of storage modulus over the temperature range is observed and no major transition is
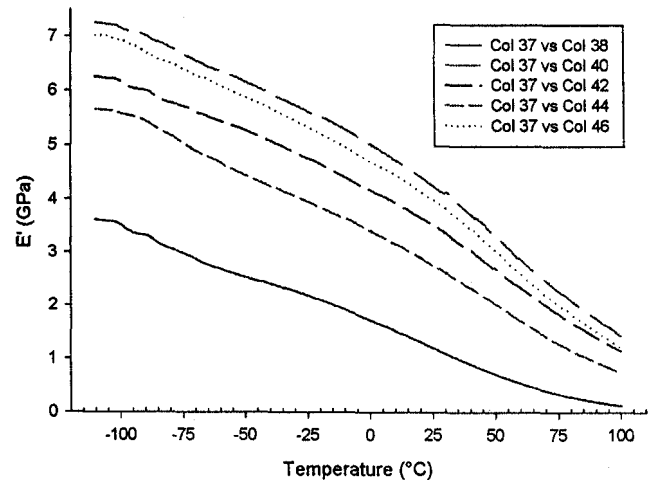
detectable. A significant increase in the E' values of composites is clearly seen compared with pure HDPE. Among different fibers, kenaf fibers increase the storage modulus the most, followed by wood flour. Composites containing rice hulls have the lowest values over the entire temperature range. While kenaf fiber and wood flour curves are close to each other over the entire temperature range, the difference between the newsprint curve and the kenaf fiber and wood flour curves decreases at higher temperatures. A slight change in slope of the curves **(Fig. 4)** indicates the a transition, which is the only transition detectable over the entire temperature range. It is also evident that the a transition is shifted to higher temperatures when fibers are present. As in the case of 25 percent fiber content, at the higher end of the temperature range, the curves of pure HDPE and composites converge.

Loss moduli spectra of HDPE-natural fiber composites at 50 percent fiber content are presented in **Figure 5.** As mentioned earlier, in the case of pure HDPE, a very slight **b** peak is observed at around -30°C. Again, the **b** transition peak is masked when 50 percent fibers are present. Another transition is seen at around 45°C for pure HDPE. This is the a transition, which is shifted about 20°C higher in the case of composites. This shift is highest for composites containing kenaf fiber and wood flour. It is evident that the a transition is a major transition in HDPE composites. The intensity of this transition is considerably higher in the composites investigated.
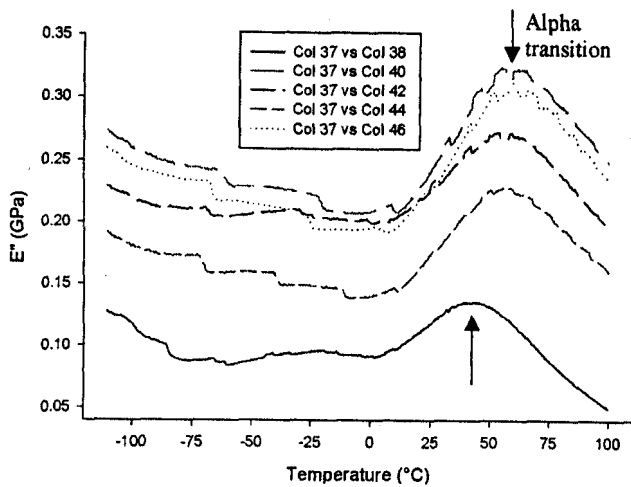
Figure 5. ~ *Loss moduli spectra of HDPE-natural fiber composites at 50% fiber content. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*
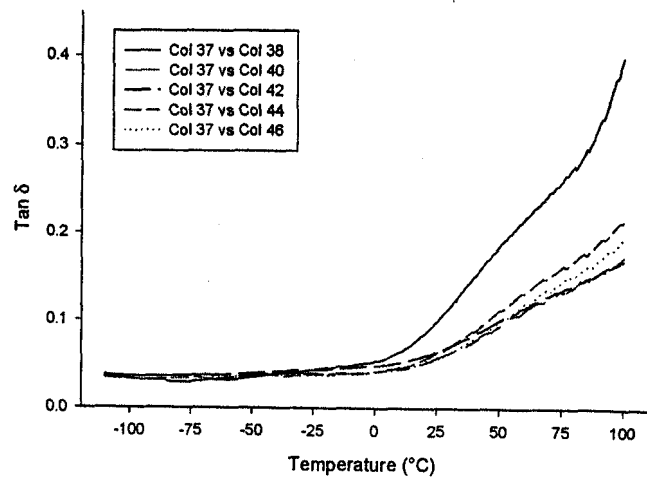

Figure 6. ~ *Mechanical loss factor spectra of HDPE-natural fiber composites at 50% fiber content. Frequency is 1 Hz, and maximum fiber strain level is 0.1%.*

Tan **d** spectra of HDPE-natural fiber composites at 50 percent fiber content are shown in Figure 6. Similar to 25 percent fiber content, from -110°C to about 20°C, no significant change in tan 6 values is observed and all formulations have similar values. The **b** transition, which was seen in the loss modulus spectrum, is not clearly seen here, indicating that this transition is not a major transition in pure HDPE or its composites. After the onset of the a transition at about 20°C, the curves start to deviate from each other and pure HDPE has the highest tan **d** value; at 100°C it is about five times the value at -100°C. Among composites, those containing kenaf fiber and wood flour have the lowest values, whereas composites containing rice hulls have the highest tan **d** values. The difference between various fibers becomes more pronounced at higher temperatures.

The effect of compatibilizer on the storage modulus of HDPE-woodflour composites is presented in **Figure 7.** In composites containing 25 percent wood flour, no significant difference between the coupled and uncoupled composites is observed, whereas in the case of 50 percent wood flour, a significant improvement due to the addition of the compatibilizer can be seen.

The effect of compatibilizer on the loss modulus of HDPE-woodflour composites is shown in **Figure 8.** Generally, coupled composites have higher loss modulus. It is evident that the a transition peak is significantly shifted to higher temperatures by the addition of more fibers; no significant shifting in the transitions peaks can be observed
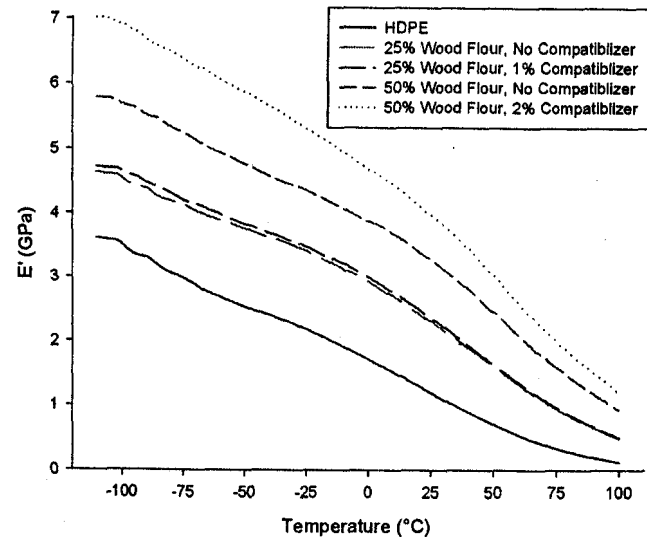

Figure 7. ~ *Effect of compatibilizer on the storage modulus of HDPE-woodflour composites. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*

when the compatibilizer is added. As in the case of storage modulus, effect of compatibilizer seems to be more pronounced at 50 percent fiber content.

The effect of compatibilizer on the mechanical loss factor of HDPE-woodflour composites is presented in **Figure 9.** Below the onset of a transition, all formulations have similar tan **d** values. After this point, coupled and uncoupled 50 percent WPC curves start deviating from each other. However, at 25 percent fiber content such an effect is not observed and the curves overlay throughout the tem-
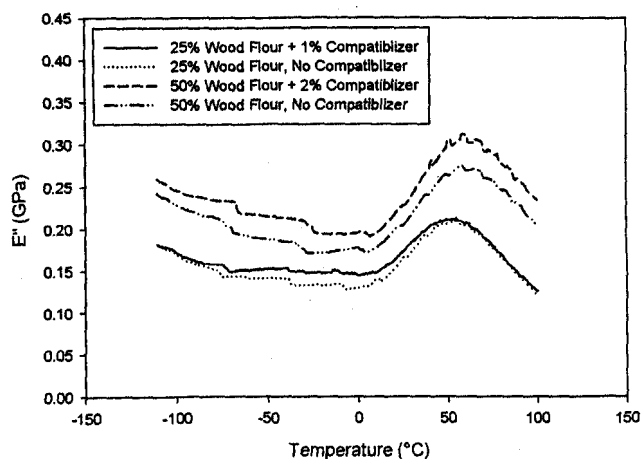
Figure 8. ~ *Effect of compatibilizer on the loss modulus of HDPE-woodflour composites. Frequency is 1 Hz, and maximum fiber strain is 0.1%.*

Figure 9. ~ *Effect of compatibilizer on the mechanical loss factor of HDPE-woodflour composites.*

perature range. It could therefore be concluded that energy loss becomes more pronounced at temperatures above the a transition, and this is particularly true in the case of 50 percent wood flour.

As mentioned previously, in this study a slight loss modulus peak can be detected at temperatures around $-30°C$, which seems to be the **b** transition. Introduction of fibers into the system apparently masked this slight transition, indicating changes in the morphology of the system. This shows that in natural fiber-HDPE composites, **b** transition is a minor transition and plays no significant role in the material properties.

The a transition, on the other hand, is considerable in HDPE. As mentioned previously, the high temperature a process is commonly considered to be connected with the crystal fraction in the semicrystalline material (15). Sirotkin et al. (16) suggest that in polyethylene, the a relaxation temperature increases with the lamellar thickness, irrespective of grade or crystallinity, and is associated with c-shear within the crystalline lamellae. Oksman et al. (19) studied the influence of thermoplastic elastomers (including SEBS-MA) on adhesion in polyethylene-woodflour composites. Dynamic mechanical thermal analysis was used to determine dynamic properties. Tan **d** peak temperatures for the various combinations showed interaction between the ethylene/butylene (EB) part of the copolymer and the wood flour in the maleated system as it was moved to higher temperatures, while the same was unaffected in SEBS systems (by adding wood flour). The shift to higher
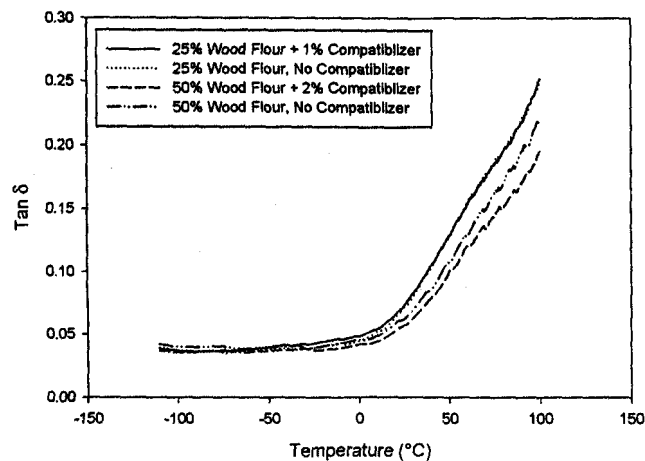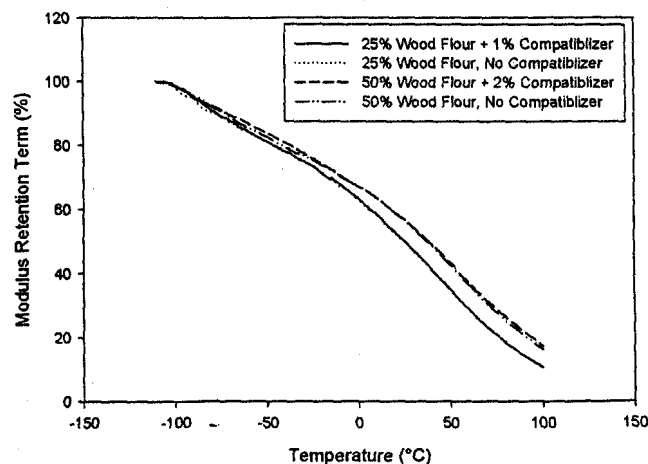

Figure 10. ~ *Effect of compatibilizer on the HDPE-woodflour composites modulus retention term.*

temperature is an indication of an interaction between the polymer and the wood filler and that the mobility of the EB was restricted.

As discussed previously, in the present study, the a transition in all HDPE composites shifted to higher temperatures when natural fibers were added, and the intensity of the transition seems to be more or less proportional to the fiber content. A shift to higher temperatures is an indication of the presence of some process that has restricted the mobility of the chains in the crystalline phase so that more energy is required for the transition to occur. Therefore it seems that natural fibers restricted the matrix polymer chains and increased the a transition temperature. On the other hand,

an increase in the intensity or amplitude of the transition means that the number of molecular portions responsible for this transition increased. Thus it could be concluded that the number of "defects" in the crystalline zone increased when fibers were added. This seems to be in close relation with the fiber surface area, which increases with fiber content.

Conclusions

The following conclusions could be drawn based on the results of the present study:

l All composites had higher storage and loss modulus values than did the base polymer throughout the temperature ranges used in this study.

l Mechanical loss factor (tan **d**) was lower in composites. This was attributed to less viscous behavior of the materials when natural fibers are present. Kenaf fiber composites proved to have the highest storage modulus of all the formulations.

l The a transition occurred at about 50°C and was shifted to higher temperatures when fibers were present. The intensity of this transition was also greater at higher fiber contents. This was attributed to possible restrictions that fibers impose on polymer molecules, supported by the fact that the a transition occurred at higher temperatures at higher fiber contents. The higher intensity of this transition was attributed to the possibility of more defects in the crystalline zone. The a transition is a major transition for HDPE composites.

• The **b** transition was hard to detect. However, a very weak loss modulus peak was observed for pure HDPE at about –30°C, which is considered by some in the literature to be the **b** transition. This was masked when fibers were present. Tan **d** values of the composites were very close to those of the pure plastics below the onset of a transition.

l Coupled composites had higher storage modulus values than did uncoupled composites. This was attributed to the improved interface quality due to the presence of the compatibilizer. Neither temperature nor intensity of the a transition was significantly changed by the addition of compatibilizer. Compatibilizer was much more effective at 50 percent fiber.

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