

DYNAMIC MECHANICAL ANALYSIS OF COMPATIBILIZER EFFECT ON THE MECHANICAL PROPERTIES OF WOOD FLOUR – HIGH-DENSITY POLYETHYLENE COMPOSITES

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(Received: August 6, 2003 – Accepted in Revised Form: January 25, 2004)

Abstract In this study, effect of MAPE (maleic anhydride polyethylene) as the compatibilizer on the mechanical properties of wood-flour polyethylene composites has been investigated by using Dynamic Mechanical Analysis (DMA). Composites were made at 25% and 50% by weight fiber contents and 1% and 2% compatibilizer respectively. Controls were also made at the same fiber contents without the compatibilizer. Static mechanical tests including tensile and bending tests were performed. Temperature scans in the range of -110 to $+100^{\circ}\text{C}$ was also conducted. Results indicated improvements in the mechanical properties due to the compatibilizer addition. Storage modulus values were higher in the case of coupled composites especially at 50% fiber loading. Glass transition was hard to detect in all composite systems while increasing fiber content slightly shifted alpha transition to higher temperatures. MAPE had negligible effects on the main transitions but the effect of fiber content on the intensity and temperature of alpha transition seemed to be proportional to the fiber content. Mechanical loss factor spectra showed that at 50% fiber content, the compatibilizer caused a reduction in $\tan\delta$ values indicating less energy loss when the compatibilizer was present.

Key Words Composites, Wood flour, High-density Polypropylene, Compatibilizer, Dynamic Mechanical Analysis

چکیده در این مقاله اثر استفاده از سازگار کننده MAPE (پلی اتیلن سنگین با اصلاح شده با انیدرید مالئیک) بر خواص مکانیکی مواد مرکب حاصل از آرد چوب و پلی اتیلن سنگین با استفاده از تحلیل دینامیکی مکانیکی (DMA) مورد بررسی قرار گرفته است. مواد مرکب با درصد های وزنی ۲۵٪ و ۵۰٪ آرد چوب و به ترتیب ۱٪ و ۲٪ سازگار کننده ساخته شدند و نمونه های شاهد با درصد های وزنی مشابه بدون سازگار کننده تهیه گردیدند. آزمونهای مکانیکی استاتیکی شامل آزمونهای کشش و خمش بر روی نمونه ها انجام پذیرفت. اسکن دما در دامنه ۱۱۰- تا ۱۲۰+ درجه سانتیگراد نیز انجام گردید. نتایج حاکی از بهبود خواص مکانیکی و اثر افزودن سازگار کننده بودند. مدول ذخیره ترکیبات دارای سازگار کننده بویژه در سطح ۵۰٪ الیاف بالاتر بود. تشخیص دمای انتقال شیشه ای در همه سیستمهای مواد مرکب دشوار بود. در حالی که افزایش درصد الیاف انتقال آلفا را اندکی به سمت دماهای بالاتر جابجا نمود. MAPE بر انتقالهای عمده تاثیر ناچیزی داشت لیکن اثر الیاف بر دما و شدت انتقال آلفا متناسب با مقدار الیاف ملاحظه گردید. طیف فاکتور اتلاف مکانیکی نشان داد که در سطح ۵۰٪ الیاف استفاده از سازگار کننده موجب کاهش مقادیر $\tan\delta$ و اتلاف انرژی می گردد.

1. INTRODUCTION

In recent years, the use of natural fibers as reinforcers and/or fillers in the manufacture of

fiber-thermoplastic composites has been of great interest, particularly to automotive industry [1]. These fibers have many advantages such as low density, high specific strength and modulus,

TABLE 1. Composition of Evaluated Formulations (%wt).

Formulation	Code	Fiber Content (%)	Resin Content (%)	Compatibilizer Content (%)
1	PE	0	100	0
2	PE-WF-25	25	74	1
3	PE-WF-50	50	48	2
4	PE-WF-25-0	25	75	0
5	PE-WF-50-0	50	50	0

relative non-abrasiveness, ease of fiber surface modification, wide availability and renew ability. The main disadvantages of natural fibers in composites are the lower processing temperatures allowable, incompatibility between the hydrophilic natural fibers and hydrophobic polymers, and potential moisture absorption of the fibers and in turn, the manufactured composite [2,3]. To enhance the compatibility of the two phases in such composites, a compatibilizer or coupling agent is normally added to the mixture or fiber surface is modified prior to compounding. Gauthier et al. (1998) [4] state that a compatibilizer must be highly reactive to cellulose hydroxyl groups while at the same time having a non-polar chain preferably of the same type as the matrix [4]. While for polypropylene based composites, use of maleic anhydride modified polypropylene (MAPP) has been reported for this purpose, a similar material (MAPE) has proved equally well for polyethylene composites. Conventional static tests are normally used to evaluate the performance of the compatibilizers [5-9]. However, Tajvidi et al. (2003) [10] have successfully used dynamic mechanical analysis to study the compatibilizer effect on the mechanical performance of wood flour PP composites [10].

Dynamic Mechanical Analysis (DMA) 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. Mechanical loss factor ($\tan \delta$) is another useful parameter, which can be very useful

in order to compare viscoelastic responses of different materials. The technique has gained a great amount of popularity thanks to its speed and high accuracy and the ability of scanning the materials over a wide range of temperatures and frequencies.

Polyethylene is a commodity thermoplastic polymer and its use is preferable over many other thermoplastics due to the lower melting point, for the processing temperatures for natural fibers are limited to temperatures below 200° C. However, not many researchers have focused on the dynamic mechanical properties of natural fiber HDPE-based composites.

The objective of this research was to study the compatibilizer effect on the dynamic mechanical properties and the temperature and intensity of the main thermal transitions of wood flour-HDPE composites.

2. MATERIALS AND METHODS

2.1. Materials High-density polyethylene, Chevron HiD® 9035 with a melt flow index of 40g/10 min (190°C, 2.16 Kg) and a density of 0.952 g/cm³ was used as the polymer matrix in this study. Wood flour was 40-mesh maple flour and was supplied by American Wood fibers Inc., Schofield, WI, USA. MAPE (Maleic Anhydride Polyethylene) was Fusabond® C modified polyethylene, product MB-100D and was supplied by DuPont Industrial Corporation.

2.2. Methods

Composites Preparation Polymer, wood flour and the compatibilizer were initially weighed and bagged according to the various fiber contents

indicated in Table 1. They were then mixed in the proprietary mixing equipment of Teel Global Resources Inc., Baraboo, Wisconsin, USA. The compounded materials were then ground using a pilot scale grinder to prepare the granules.

Preparation of the Specimens The granules of the various composite formulations were injection molded to produce standard ASTM 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 93.3° C and barrel and nozzle temperature were set to 187.8° C. Specimens for DMA testing were cut out of the impact specimens using a table saw. They were further 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 hours prior to performing the tests.

Tensile Test Tensile tests were performed according to ASTM D 638M-89. A type M-I dog-bone specimen was selected. Tensile tests were performed using an Instron 5566 testing machine with computer data acquisition system and load cell capacity of 908 kgf. Loading speed was 5.08 mm/min and strain measurements were performed using an MTS strain gauge mounted on the samples. The gauge length was 2.54 cm. Ten specimens of each formulation were tested and the results were analyzed in a completely randomized design and Duncan's multiple range tests was performed to group means. All comparisons were made at 95% confidence level.

Three-Point Bending Bending tests were

carried out on the specimens according to ASTM D 790-90, test method I. The specimens' nominal dimensions were 130 mm by 13 mm by 3.2 mm. The span was 100 mm, which resulted in a span-to-depth ratio of 32. Crosshead speed was 5.08 mm/min. Three-point bending tests were carried out using an Instron 5544 testing machine with data acquisition system. Ten specimens of each formulation were tested. The same statistical approach was followed.

Temperature Scan Dynamic mechanical analysis was performed using a Rheometric Scientific DMTA V analyzer. A dual cantilever mode was selected and the specimens were scanned over a temperature range of -110 ° C to +100 ° C. Frequency of the oscillations were 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 ($\tan\delta$) were collected during the test and were plotted versus temperature.

3. RESULTS AND DISCUSSION

3.1. Static Tests Figure 1 shows the effect of compatibilizer on the composites' tensile modulus. At both fiber contents an improvement in the modulus values is observed due to the addition of the compatibilizer and the differences are statistically significant. Thus the adding the compatibilizer has improved the quality of the interface and in turn, resulted in higher modulus values. Another point to notice is that for both coupled and uncoupled composites, doubling the fiber content has drastically increased modulus values.

A completely different trend is seen in the case of tensile strength. As it is clearly seen in Figure 2, for the coupled composites, tensile strength increases with fiber content while for uncoupled composites a declining trend in tensile strength values is observed at both 25% and 50% fiber contents. This shows the effectiveness of the compatibilizer on enhancing the quality of the interface and in turn improving stress transfer and eventually tensile strength [5].

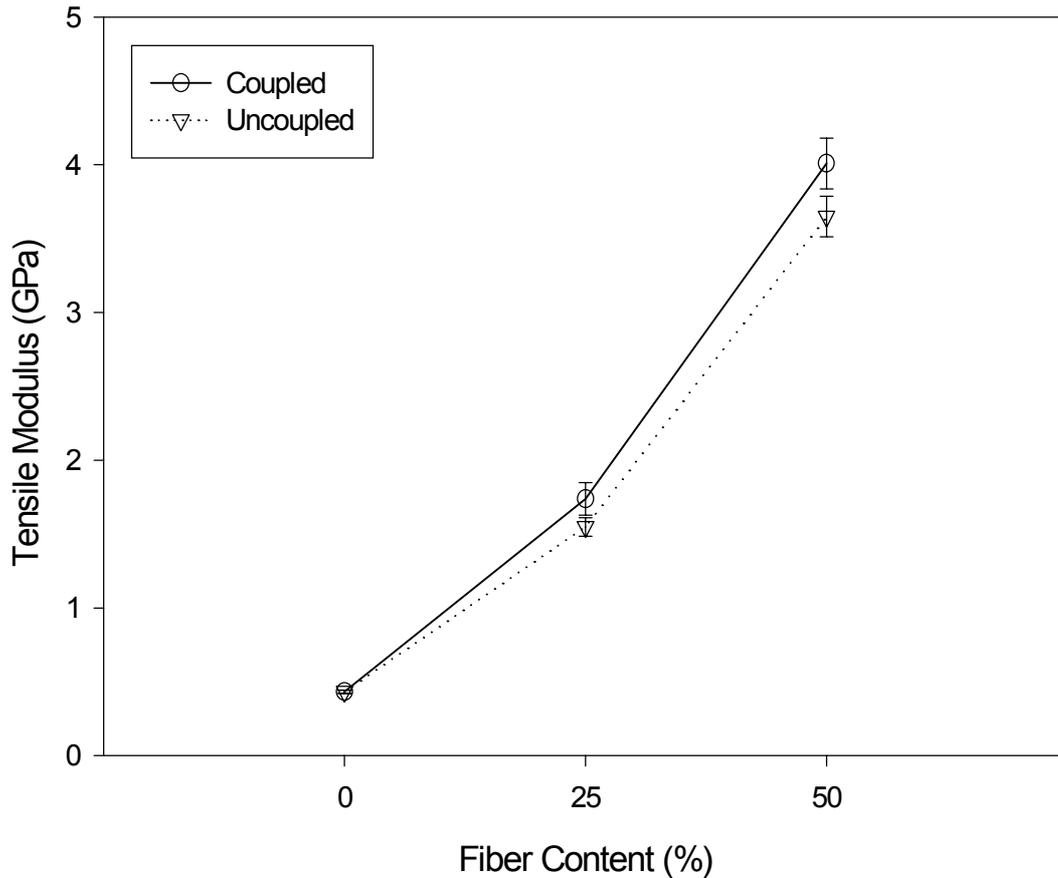


Figure 1. Effect of compatibilizer on the wood flour/HDPE composites tensile modulus.

Effect of compatibilizer on the composites flexural modulus is presented in Figure 3. A very similar trend is seen for both coupled and uncoupled composites. At 25% fiber content, no significant difference is observed between the coupled and uncoupled composites. At 50% fiber content, coupled composites show a slight improvement and are significantly different from uncoupled ones. It seems that at higher fiber contents, the presence of compatibilizer becomes more effective on enhancing the modulus values.

Figure 4 shows the effect of compatibilizer on the composites' flexural strength at maximum load. A relatively straight line is obtained for the coupled composites while in the case of uncoupled composites a very slight improvement in the flexural strength values is observed when

the fiber content is doubled. Duncan's multiple range tests indicate significant differences between the coupled and uncoupled composites at both fiber content levels.

Dynamic Mechanical Analysis Effect of compatibilizer on the storage modulus of HDPE/wood flour composites is presented in Figure 5. A general declining trend for all curves is observed when the materials go through higher temperatures. The only noticeable transition can be detected at around 40°C (indicated by an arrow), which is the alpha transition. As it is seen, in the case of 25% wood flour, no significant difference between the storage modulus of coupled and uncoupled composites is observed while in the case of 50% wood flour; a very significant

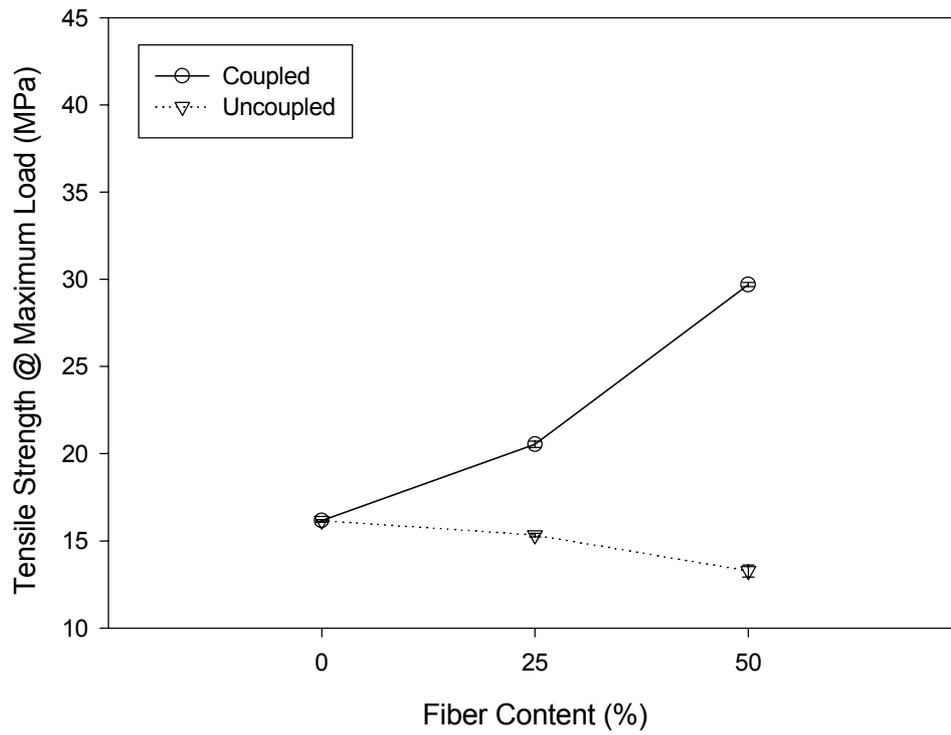


Figure 2. Effect of compatibilizer on the wood flour/HDPE composites tensile strength at maximum load.

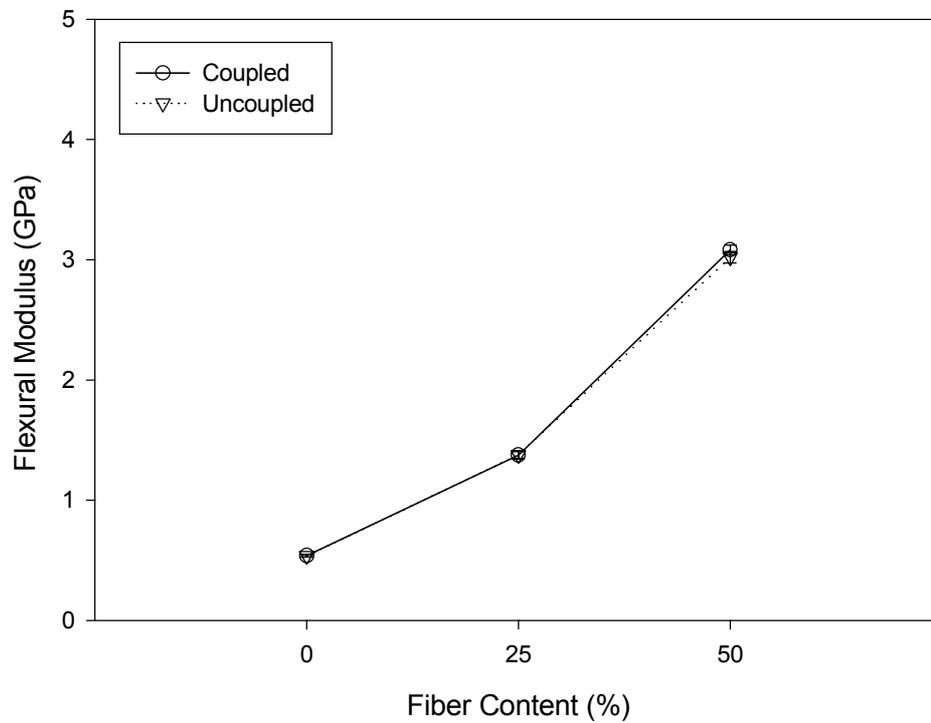


Figure 3. Effect of compatibilizer on the wood flour/HDPE composites flexural modulus.

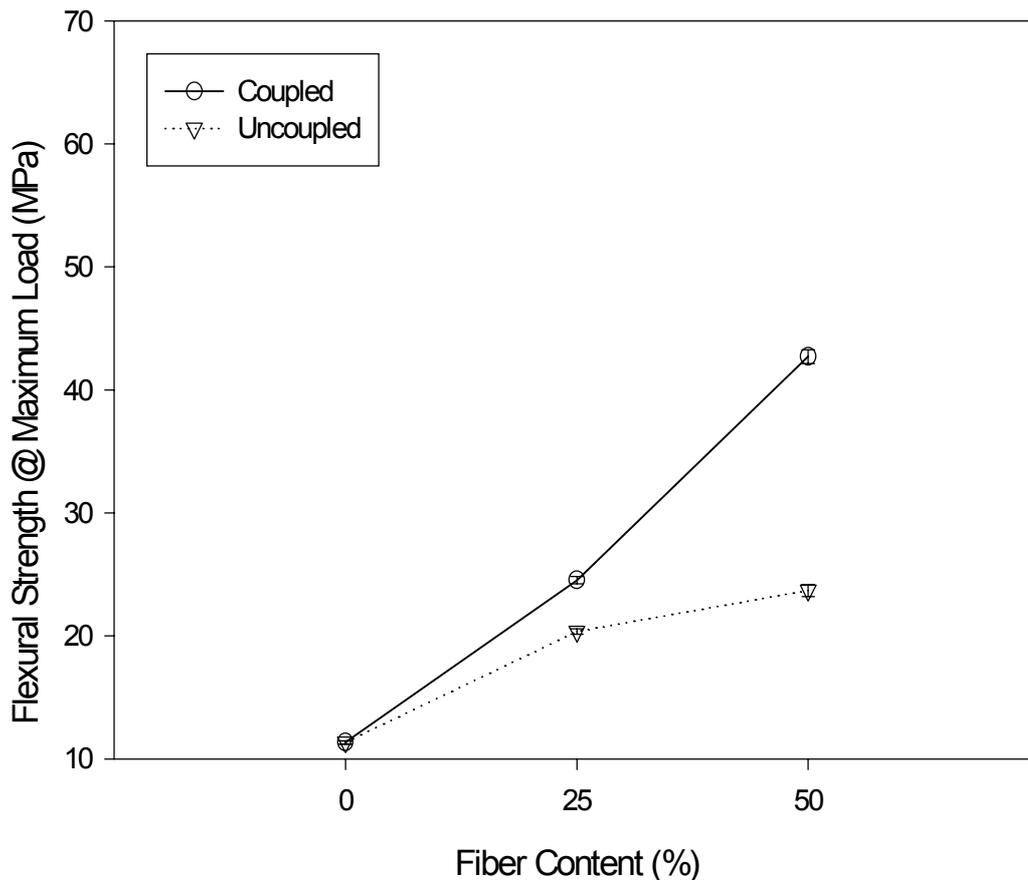


Figure 4. Effect of compatibilizer on the wood flour/HDPE composites flexural strength at maximum load.

improvement due to the addition of the compatibilizer can easily be seen. It can also be seen that as the materials go through higher temperatures, the difference between coupled and uncoupled composites becomes negligible. This is a scaling effect and the compatibilizer is as effective at higher temperatures as at lower temperatures.

Effect of compatibilizer on the loss modulus of HDPE/wood flour composites is shown in Figure 6. Here, the alpha transition can be better studied. Generally, coupled composites have higher loss modulus. As it is seen, while it is evident that the alpha transition peak is significantly shifted to higher temperatures by the addition of more fibers, no significant shifting in the transitions peaks can be observed when the compatibilizer is added. This clearly shows that the presence of the compatibilizer in the system does not affect the

alpha transition temperature. Alpha transition intensity is also higher at 50% fiber content. However, it seems that the alpha transition intensity is somewhat higher in the case of coupled composites at 50% fiber content. As in the case of storage modulus, effect of compatibilizer is more pronounced at 50% fiber content.

Effect of compatibilizer on the mechanical loss factor of HDPE/wood flour composites is presented in Figure 7. As it is clearly seen, below the onset of alpha transition, all formulations have relatively the same $\tan\delta$ values. It is after this point that coupled and uncoupled 50% wood fiber composites curves start deviating from each other. However, at 25% fiber content such an effect is not observed and the curves overlay throughout the temperature range. Therefore it could be concluded that energy loss becomes more

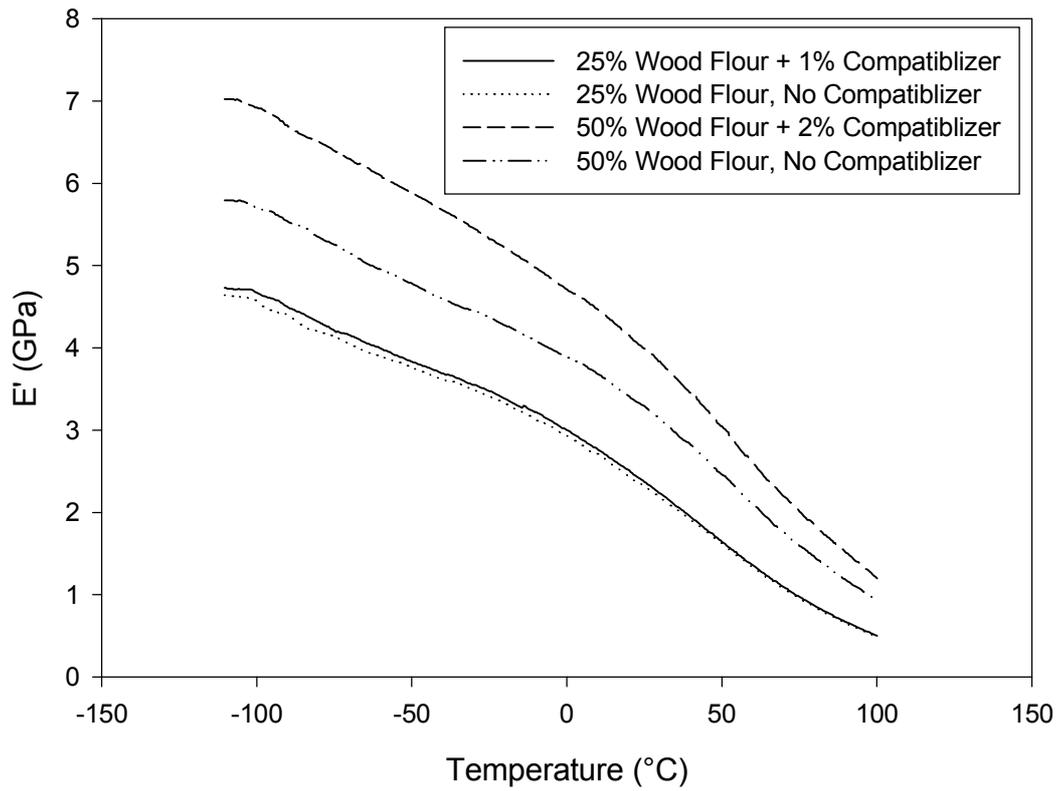


Figure 5. Effect of compatibilizer on the storage modulus of HDPE/wood flour composites.

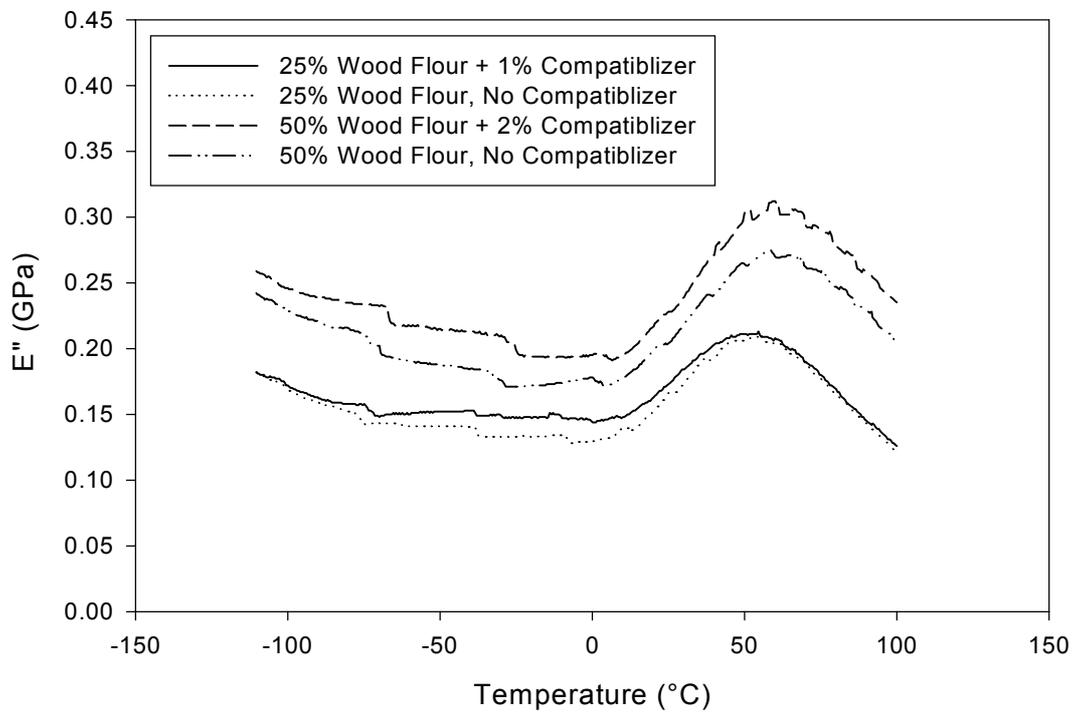


Figure 6. Effect of compatibilizer on the loss modulus of HDPE/wood flour composites.

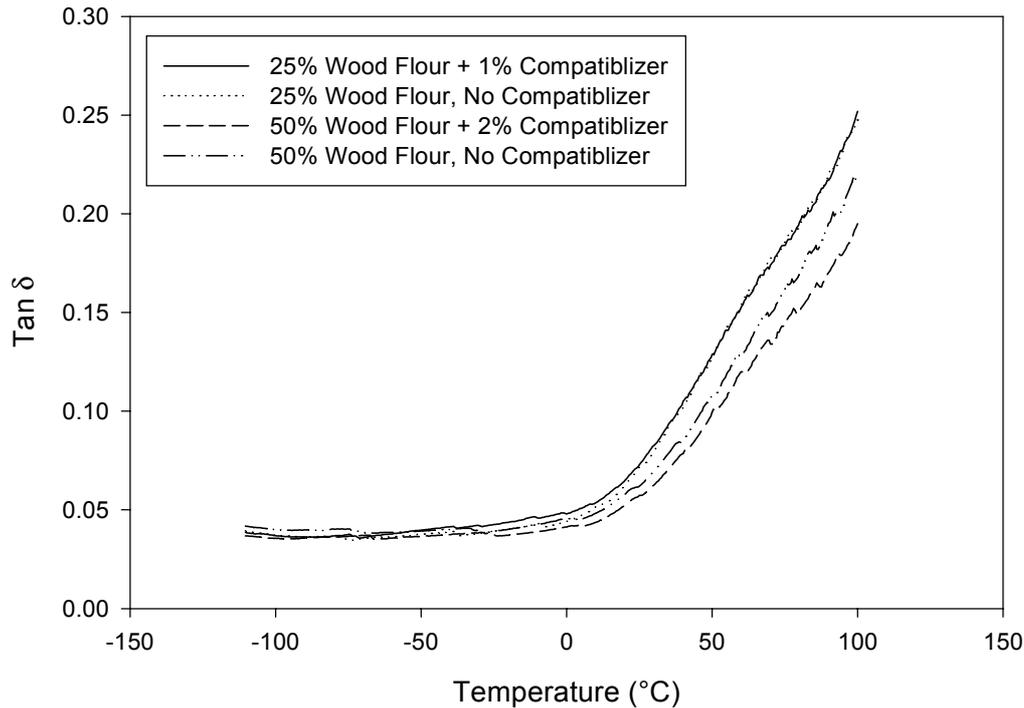


Figure 7. Effect of compatibilizer on the mechanical loss factor of PP/wood flour composites.

pronounced at temperatures above alpha transition and this is particularly true in the case of 50% wood flour.

Glass transition in highly crystalline polymers is difficult to identify [12]. 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 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, $\sim 240^\circ\text{K}$ (-33°C), $\sim 190^\circ\text{K}$ (-83°C) and $\sim 150\text{K}$ (-123°C). Turi (1997) [12] suggests that evidence favoring the $\sim 240^\circ\text{K}$ (-33°C) temperature range has gained considerable credibility in recent years [12]. On the other hand, it is suggested that beta relaxation is associated with the relaxation of branch points. This seems to be true as in low-density polyethylene, which is a branched polymer, a clear beta transition peak can be detected [13]. Sirotkin et al. (2001) [14] report that for high-density polyethylene the beta relaxation is usually absent. This relaxation is,

therefore, generally attributed to segmental motions in the non-crystalline phase [14]. Because glass transition is a minor phenomenon in the composites studied here the effect of compatibilizer on it could not be judged properly. However, it can still be concluded that beta (glass) transition in wood flour-HDPE composites does not have any important role as far as mechanical performance of the final product is concerned.

Alpha transition, on the other hand, is quite considerable in high-density polyethylene. As mentioned earlier, the high-temperature α process is commonly considered to be connected with the crystal fraction in the semi crystalline material [12]. Sirotkin et al. (2001) [14] suggest that in polyethylene α relaxation temperature increases with the lamellar thickness, irrespective of grade or crystallinity and is associated with c-shear within the crystalline lamellae [14]. Oksman et al. (1998) [15] studied the influence of thermoplastic elastomers (including SEBS-MA) on adhesion in polyethylene-wood flour composites. Dynamic mechanical thermal analysis was used to determine dynamic properties. $\text{Tan}\delta$ peak temperatures for the

various combinations showed interaction between the ethylene/butylenes (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 temperature was concluded to be an indication of an interaction between the polymer and the wood filler and that the mobility of the EB was restricted [15].

As discussed earlier, in the present study, alpha transition in all HDPE composites has been shifted to higher temperatures 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 processes, which have 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 somehow restricted the matrix polymer chains and increased the alpha 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 has increased. Thus it could be concluded that the number of so-called "defects" in the crystalline zone has increased when fibers are present. This seems to be in close relation with the fiber surface area, which increases with fiber content. However, as mentioned earlier, no significant shifting in alpha transition temperature was detected by adding MAPE to the system. This indicates that improving interface quality (seen as improvement in storage modulus values) does not have any effects on alpha transition temperature.

4. CONCLUSIONS

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

- Dynamic mechanical analysis is a very effective technique to determine the performance of compatibilizers in wood flour-thermoplastic composites over a wide temperature range.
- Tensile and flexural modulus values only marginally increased in the presence of the compatibilizer while the compatibilizer had

a very significant effect on increasing the composites tensile and flexural strengths. This was attributed to the improvement of the interface between the two phases due to the better compatibility of the phases.

- Alpha transition is the only major transition detectable over the temperature range of the study.
- The compatibilizer was much more effective on storage modulus at 50% fiber content.
- The compatibilizer had no significant effect on the temperature and intensity of alpha transition.
- Mechanical loss factor spectrum of 50% uncoupled composite significantly deviated from the coupled composite's curve at temperatures above the onset of alpha transition.

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