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Viscoelastic and thermal analysis of lignocellulosic material filled polypropylene bio-composites

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Abstract In this study, we investigated the viscoelastic and thermal properties of lignocellulosic material filled polypropylene (PP) bio-composites. Lignocellulosic fillers are totally bio-degradable and PP is a thermoplastic polymer which has good stiffness, tenacity, flexural strength and thermal properties. The thermal and viscoelastic properties of the composites with different filler contents were examined using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), respectively. The effects of the compatibilizing agent were also evaluated. The glass transition (T_g) and melting (T_m) temperatures of the composites did not vary significantly with the filler content, because no chemical bonding occurred at the interface between the matrix and filler. However, the compatibility between the filler and PP matrix was increased by the incorporation of the compatibilizing agent. The storage modulus (E') of the composites was higher than that of the neat PP, indicating that the incorporation of the natural filler increased their stiffness. The thermal properties of the composites should be considered as an important factor in the manufacturing process and the use of the final products.

Keywords Lignocellulosic material · Bio-composites · Thermal properties · Viscoelastic properties · Glass transition temperature (T_g) · Melting temperature (T_m) · Storage modulus (E')

Introduction

Recently, lignocellulosic material filled thermoplastic polymer bio-composites have been widely researched and developed. Petroleum-based synthetic thermoplastic polymers can be used in a variety of applications and have excellent chemical resistance, good mechanical properties and low cost. However, most synthetic polymers are extremely resistant to microbial attack and are therefore detrimental to the ecosystem, because their consequent non-biodegradability leads to environmental problems associated with their disposal. A consequence of the current phenomenal use of plastics is their increasing presence in municipal solid waste throw-away products [1, 2]. Consequently, lignocellulosic material filled thermoplastic polymer bio-composites offer at least a partial solution to the problem of non-biodegradable plastic waste pollution. These bio-composites can be used as house-wares, dashboard for car interiors and construction materials, etc. They combine the favorable performance and low cost attributes of both lignocellulosic materials and plastics. The convenience of these composites lies in the fact that the ingredients can be readily obtained from natural resources and they can be made relatively easily [3]. These bio-composites have received increasing attention because they contain naturally degradable fillers. Lignocellulosic materials such as rice husks, cotton, hemp, and wood fiber/flours are a particularly important resource of natural fillers. Rice-husk flour (RHF) and wood flour (WF) are totally

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biodegradable fillers which can be used in bio-composites and whose combustion does not produce any hazardous by-products [2, 4]. The benefits offered by natural fillers include the lightness of the final product, the decrease in the wear of the machinery used, low cost, biodegradability, and the absence of toxic by-products, merits which inorganic materials such as glass fiber, carbon fiber, talc, clay and synthetic fiber, cannot offer [3, 5, 6]. One of the most important issues related to these composites is the interfacial adhesion between the natural fillers and matrix polymers. In order to obtain good properties by improving the compatibility between the hydrophilic lignocellulosic material and the hydrophobic matrix polymer, reinforcing fillers are chemically modified. The strong interfacial bonding strength afforded by the improved compatibility between the hydrophilic filler and hydrophobic matrix polymer can improve the physical, mechanical and thermal properties of the composite system [3, 6, 7].

Thermal analysis is used to measure the thermal behavior of a composite material as a function of temperature. The processing temperature and other factors involved in the manufacturing of polymer composites are determined by their thermal characteristics. In this research, the thermal and viscoelastic properties of the bio-composites were examined. Differential scanning calorimetry (DSC) is the simplest and most widely used thermal analysis technique. DSC can be used to measure the melting temperature (T_m) and glass transition temperature (T_g) of bio-composites [2, 8]. Dynamic mechanical thermal analysis (DMTA) has been widely used to investigate the structures and viscoelastic behaviors of composite materials as determined by their storage modulus (E'), loss modulus (E'') and loss factor (tan δ). This analysis technique can provide information on the stiffness of the composites [2, 9].

This work addresses the question of how the lignocellulosic filler and compatibilizing agent, such as maleated polypropylene, affect the thermal and viscoelastic properties of bio-composites. The current study focuses on the effects of the lignocellulosic filler content and presence of the compatibilizing agent on the thermal properties and viscoelastic behaviors of the bio-composites.

Materials and experimental procedure

The polypropylene was supplied by Hanwha L&C Corp., in the form of homopolymer pellets with a density of 0.91 g/cm^3, melt flow index of 12 g/10 min (230 °C/2,160 g). The lignocellulosic fillers were rice-husk flour (RHF) and wood flour (WF), with particle sizes of 80–100 mesh. These fillers were both supplied by Saron Filler Co. and were stored in sealed packs containing a desiccant after being oven dried for 24 h at 100 °C. The chemical constituents are shown in Table 1. The compatibilizing agent, maleated polypropylene (MAPP), was obtained from Eastman Chemical Products, Inc., in the form of Epolene G-3003$^{\mathrm{TM}}$ which has an acid number of 8 and a molecular mass of 103,500.

Table 1 Chemical constituents of the lignocellulosic fillers (rice-husk flour and wood flour)

	Holocellulose	Lignin	Ash	Others
RHF	59.9	20.6	13.2	6.5
WF	62.5	26.2	0.4	10.9

Values are percentage by mass (%)

The reinforcing fillers, RHF and WF, were dried to a moisture content of 1–3 wt% using an oven at 100 °C for 24 h and then stored over a desiccant in sealed containers in an environmental controller prior to compounding. The matrix polymer, PP, was blended with the fillers and the compatibilizing agent, MAPP. A laboratory-scale twin-screw extruder was employed to compound the RHF and WF with the polypropylene. Compounding was performed at 180 °C for 3 min with a screw speed of 300 rpm. The extruded strand was quenched in a water bath and then pelletized and stored in sealed packs containing a desiccant to avoid moisture infiltration after being oven dried for 24 h at 70 °C. Four levels of filler loading (10, 20, 30 and 40 wt%) and a fixed compatibilizing agent content of 3 wt% were used in the sample preparation.

The samples used for the dynamic mechanical thermal analysis test were injection molded at 200 °C, an injection pressure of 1,200 psi and a device pressure of 1,500 psi. The width, length and depth of the DMTA test samples were 1/5, 1/2 and 1/16 inches, respectively. After being molded, the test samples were conditioned before testing according to ASTM D 618-99 [10].

DSC analysis was carried out using a TA Instrument DSC Q-1000 with a sample mass of 5–8 mg. Each sample was scanned from −80 to 200 °C at a heating rate of 10 °C/min and then cooled at the same rate under a nitrogen atmosphere. The thermal properties were determined from the second scan. The T_m value was taken as the maximum of the endothermic melting peak in the second heating scan and the T_g value as the deflection of the baseline in the second cooling scan.

The viscoelastic properties of the bio-composites were measured using a Rheometric Scientific DMTA IV. Rectangular samples were examined in the single cantilever mode. The measurements were performed at a frequency of 10 Hz and at a strain rate of 0.1%. The temperature range was from −80 to 150 °C at a scanning rate of 5 °C/min. The storage modulus (E'), loss modulus (E'') and loss factor (tan δ) of the samples were measured as a function of temperature.

Results and discussion

Differential scanning calorimetry analysis

The effect of the lignocellulosic filler and compatibilizing agent on the thermal properties of the bio-composites was examined in the non-isothermal DSC tests. Figure 1 presents the second cooling curves of the neat PP and lignocellulosic filler incorporated bio-composites at a cooling rate of 10 °C/min. An endothermic T_g peak can be seen in the cooling scan. The glass transition in the bio-composites is accompanied by an abrupt change in the baseline position resulting from the change in heat capacity that occurs during the transition from the glassy to the rubbery state [11]. This figure shows that as the filler loading increased, the T_g of the bio-composites slightly increased, but only marginally. This implies that no chemical bonding occurs at the interface between the matrix and filler. In other words, the lignocellulosic fillers are physically encapsulated by the melted matrix polymer and physically inhibit the mobilization of the polymer chain. If interfacial adhesion such as chemical bonding were to occur between the matrix and filler, the T_g of the bio-composites would be substantially changed, and such is the case for the compatibilizing agent incorporated composites, where the glass transition temperature changes appreciably as compared with that of the non-compatibilized composites, as shown in Fig. 2. The T_g of the maleic anhydride modified polypropylene (MAPP) treated bio-composites is shifted to a lower temperature, because the fillers do not physically inhibit the mobilization of the polymer chain, but are chemically bonded to the matrix polymer. Therefore, the filler-matrix interface is chemically blended due to the enhanced adhesion afforded to act as a same blend by the compatibilizing agent. Figure 3 shows the typical DSC curves corresponding to the second heating scans of the neat PP and bio-composites containing 10, 20, 30 and 40 wt% of filler from which the T_m values were obtained. The melting point was taken as the main peak of the endothermic curve. The effect of the lignocellulosic filler content on the T_m of the bio-composites is presented in this figure and no significant change is observed. The addition of the natural filler to PP has no effect on the melting temperature and no correlation of the results with the filler loading can be established. This result means that the presence of the natural filler does not affect the T_m of the bio-composites. From these results, it can be concluded that the T_g and T_m values of the bio-composites were strongly influenced by the matrix polymer. Furthermore, the T_m of the bio-composites plays an important role in determining their processing temperature and their critical environmental conditions are strongly related to their thermal properties.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis has been widely used to investigate the structures and viscoelastic behavior

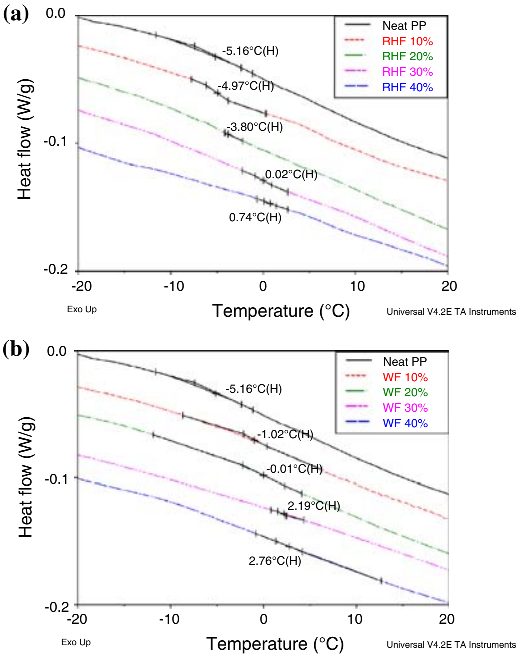

Fig. 1 DSC curves of lignocellulosic filler filled polypropylene bio-composites. **a** RHF filled bio-composite; **b** WF filled bio-composite

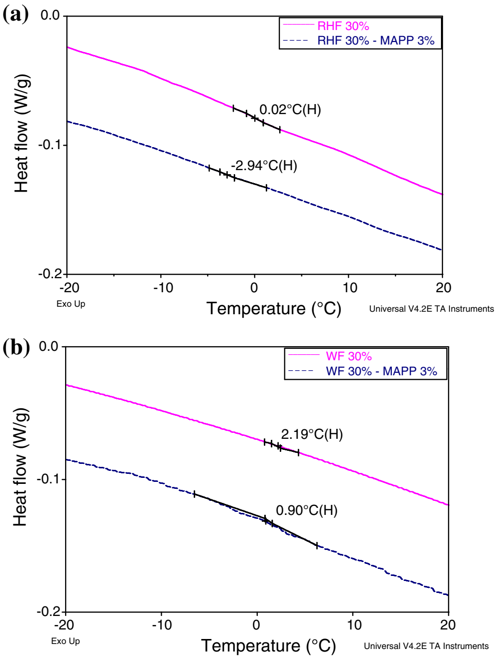

Fig. 2 DSC curves of compatibilizing agent incorporated bio-composites. **a** RHF filled bio-composite; **b** WF filled bio-composite

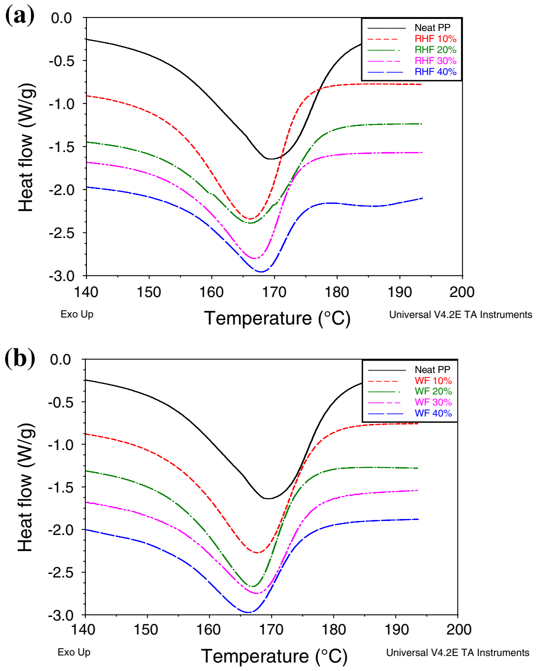

Fig. 3 DSC curves corresponding to second heating scans of neat PP and bio-composites. **a** RHF filled bio-composite; **b** WF filled bio-composite

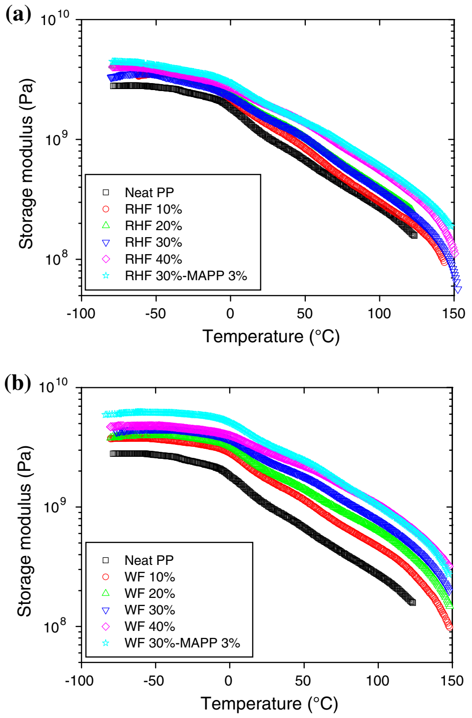

Fig. 4 Storage modulus of bio-composites from −80 to 100 °C as a function of temperature. **a** RHF filled bio-composite; **b** WF filled bio-composite

of composite materials. Damping (tan δ) measurements give practical information on T_g, while E' determines their relevant stiffness [2]. The dynamic mechanical thermal properties of the neat PP and bio-composites were evaluated. The variation of the E' value of the bio-composites as a function of temperature in the range from −80 to 150 °C is shown in Fig. 4 for different filler loading and in the presence of the compatibilizing agent. The stiffness of the composites is greater than that of the neat PP in the whole temperature range, and this trend is more significant in the higher temperature range. The storage modulus steadily decreases with increasing temperature until the matrix melts, where upon it abruptly decreases. A slight drop in the modulus occurs in the 60–80 °C region, possibly due to the reordering of the small crystals [9].

The WF-filled composites are stiffer than the RHF-filled ones because WF has a higher holocellulose and lignin content. In the case of the neat PP, E' decreases with increasing temperature due to the increased segmental mobility. During the glass transition of semicrystalline material such as PP, only the amorphous part undergoes segmental motion, while the crystalline region remains solid until its melting temperature [12]. The E' values of the bio-composite systems are higher than those of the neat PP and increase with increasing filler content. This is because the reinforcement effect of the lignocellulosic filler facilitates the transfer of stress across the interface from the PP to the filler. The WF-filled composites show almost the same result as the RHF-filled composites, indicating that the incorporation of the lignocellulosic filler also increases their stiffness [13]. Fillers play an important role in increasing the storage modulus of polymeric materials. The storage modulus decreases with increasing temperature, which is associated with the softening of the matrix polymer at higher temperature. At low temperature, the fillers do not impart a great deal of stiffness to the material. As the temperature increases, however, the decrease in the modulus of the matrix polymer is compensated for by the debonding of the filler due to the increased viscoelastic deformation of the matrix polymer at higher temperatures. As the temperature is increased, relaxation process of the molecular matrix is initiated. Also, thermal expansion occurs which decreases the intermolecular forces [14]. At higher temperatures and higher filler loadings, the modulus, E' of the lignocellulosic filler-PP composite system becomes higher than that of neat PP. This is due to the reinforcement effect of the filler which allows the transfer of stress from the matrix to the filler [15]. At any particular temperature, the storage moduli increase with increasing filler loading. At a low filler loading, the matrix is not restrained by sufficient filler and highly localized strains occur in the matrix polymer at low stresses, causing the bond between the matrix polymer and filler to break and leaving the matrix polymer diluted by non-reinforcing debonded filler [16]. As the filler loading increases, the stress is more evenly distributed throughout the composite and hence the modulus increases. As the temperature increases, the presence of fillers restricts the flow of the matrix polymer and this restriction increases with increasing filler loading [12]. In the tan δ versus temperature plot in Fig. 5, a peak is observed at around 10 °C which corresponds to the glass transition temperature of PP [12]. Thereafter, the tan δ values for the composites increase with increasing temperature. As the filler loading increases, a greater decrease in the tan δ values is observed at higher temperature. On the other hand, the tan δ values of the composites are slightly higher than that of neat PP at low temperatures. At higher temperatures, however, this difference is more predominant. At temperatures above 30 °C, tan δ increases with increasing temperature. This may be due to the increasing ductility of PP at higher temperature. As the filler loading increases, the damping characteristics of the composite system decrease. From the peak in the tan δ curve, we can see that the incorporation of natural filler does not significantly affect the glass transition temperature, but it does have a significant effect on the tan δ values. The α-peak values of the bio-composites were significantly decreased around the glass transition temperature, due to the restriction in the chain segment mobility in the amorphous phase of the matrix polymer caused by the incorporation of the natural filler. Figure 6 shows the relationship between the filler loading to the tan δ_{max} peak of the composites. The neat PP presents a tan δ_{max} peak temperature of about 12 °C. The tan δ_{max} peak values can be considered to correspond to the glass transition temperature and these values are not significantly changed as the filler content is increased [12, 15], because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. However, the dynamic mechanical thermal properties of the composites are influenced by the chemical treatments to which the filler surfaces are subjected. The tan δ_{max} peak temperature of the compatibilized composite is lower than that of the untreated composite in the case of a filler loading of 30 wt%, due to the improved interfacial adhesion which prevents the pulling out and debonding of the fillers from the matrix polymer. The effects of the chemical treatment on the storage modulus and tan δ of the bio-composites at a filler loading of 30 wt% are shown in Fig. 7. An appreciable improvement in the storage modulus and decrease in tan δ are observed for the compatibilizing agent incorporated composite, due to the increase in the interfacial stiffness brought about by the more intense filler-matrix interaction. The compatibilizing agent improves the interfacial adhesion and this lessens the molecular mobility in the interfacial region. In a previous study, the beneficial effects of maleated polypropylene on the strength properties of lignocellulosic filler-polypropylene composites were

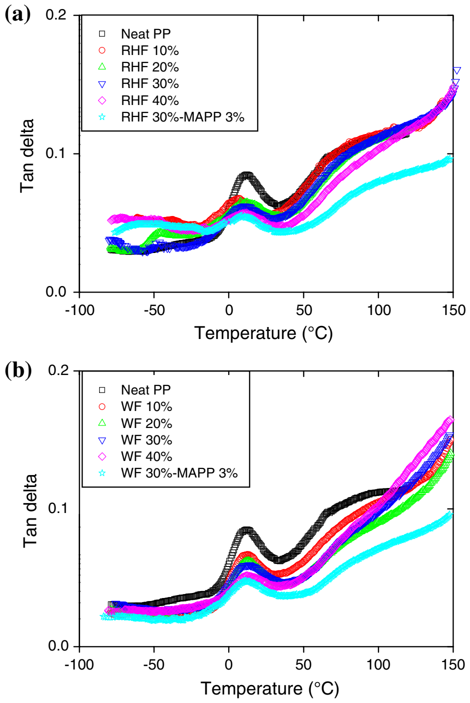

Fig. 5 Tan δ versus temperature plot of bio-composites from −80 to 100 °C. **a** RHF filled bio-composite; **b** WF filled bio-composite

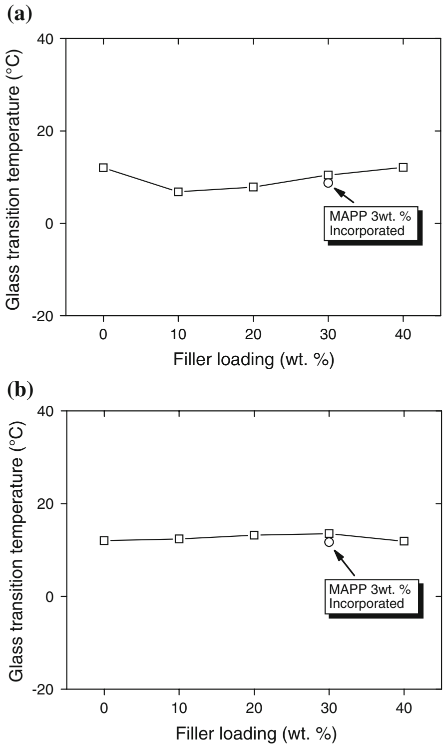

Fig. 6 Tan δ_{max} peak temperatures of the composites at different filler loadings. **a** RHF filled bio-composite; **b** WF filled bio-composite

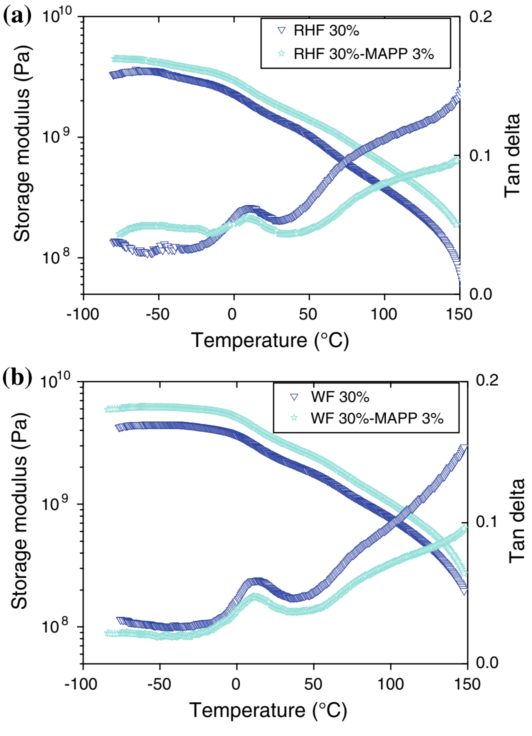

Fig. 7 The differences between the storage modulus and tan δ of the chemically treated (MAPP 3 wt% incorporated) and untreated bio-composites at a filler loading of 30 wt%. **a** RHF filled bio-composite; **b** WF filled bio-composite

attributed to the esterification reaction between the hydroxyl groups of the lignocellulosic filler and the anhydride functionalities of the maleated polypropylene [17].

Conclusions

There was no significant change in the glass transition and melting temperatures of the bio-composites with increasing filler loading. This means that no chemical bonding occurs at the interface. However, when the compatibilizing agent is added, a change occurs because of the enhanced interfacial adhesion between the matrix and natural filler. Based on these results, we can conclude that the T_g and T_m values of the bio-composites were strongly influenced by the matrix polymer. Furthermore, the T_m value of the bio-composites plays an important role in determining their processing temperature and their critical environmental conditions are strongly related to their thermal properties. The storage modulus of the bio-composites was higher than that of neat PP and increased with increasing filler content, because of the resultant increasing stiffness of the bio-composites. This is because the reinforcement effect of the lignocellulosic filler facilitates the transfer of stress across the interface from the matrix to the natural filler. The compatibilizing agent improves the interfacial adhesion, thereby lessening the molecular mobility in the interfacial region. The damping characteristics of the composites decrease with increasing filler loading, but their dynamic mechanical thermal properties are influenced by the chemical treatments to which the filler surface are subjected.

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