VISCOELASTIC PROPERTIES OF WHEAT STRAW FIBER/TALC/POLYPROPYLENE COMPOSITES FOR AUTOMOTIVE APPLICATIONS

Mehdi Tajvidi, Arathi Mohan Sharma, Leonardo C. Simon

Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON, Canada, N2L3G1, mtajvidi@uwaterloo.ca; lsimon@uwaterloo.ca

Abstract

Under-the-hood applications of natural fiber thermoplastic composites represent a good opportunity for increasing the amount of renewable materials and reduce weight. Composites used in applications such as battery trays or air cleaner housing for example are subject to a wide range of temperatures affecting their viscoelastic properties as well as various load durations at different stress levels. Dynamic mechanical thermal analysis (DMTA) was used in this study to evaluate temperature dependent mechanical performance and viscoelastic properties of these thermoplastic composites. Isotactic polypropylene homopolymer and impact modified polypropylene copolymer were formulated with wheat straw fiber and with talc using twin-screw extrusion followed by injection molding. Different thermal transitions as well as mechanical performance of the composites were evaluated and the effects of fiber loading, matrix type, filler type and hybridization (combination of straw and talc) were studied. The modulus retention term (MRT) and the relative storage modulus (RSM) were used as parameters defining mechanical performance at various temperatures. Thermal transitions were evaluated over a wide range of temperatures. The short term creep behavior of selected composites was also studied at various stress levels. The composites with straw fiber are generally comparable to the composites with talc; composites with the straw fiber have better performance at low or at high temperatures. The power law model was used to evaluate the short term creep behavior. The results revealed the modulus dependent creep behavior of the composites where the total creep strain was more dependent on instantaneous creep than the time dependent fraction.

Introduction

Recently wheat straw has been used for natural fiber plastic composites production using polypropylene as the matrix aimed at automotive applications [1, 2]. Although present uses are limited to interior parts, future applications for under the hood components such as battery trays, air cleaner housing or resonators represent a good opportunity to increase the utilization of straw as a renewable feedstock.

Similar to many other composite materials, wheat straw polypropylene composites are viscoelastic materials whose mechanical performance is greatly influenced by temperature and time scale of deformation [3]. A study of under the hood temperatures measured in overhanging position in several cars in different operating conditions has shown that temperatures as high as 90 °C are possible [4]. Considering winter temperatures as low as -30 °C, the car component made of natural fiber plastic composites may undergo temperature variations in the range of 120 °C. Changes in temperature are associated with dimensional changes as well as changes in...
mechanical performance due to viscoelasticity [3, 5].

Apart from the traditional use of dynamic mechanical thermal analysis (DMTA) data for the study of thermal transitions in polymeric materials, variations in relative mechanical performance (stiffness) of the material over a range of temperatures can also be evaluated. This is normally carried out using two related quantified parameters, namely, Modulus Retention Term (MRT) and Relative Storage Modulus (RSM) defined as follows [3, 5, 6]:

\[
MRT = \frac{E_i'}{E_{ref}'} \times 100 \tag{1}
\]

where \( E_i' \) is the storage modulus of the composite at temperature \( i \) and \( E_{ref}' \) is the storage modulus at the reference temperature.

\[
RSM = \frac{E_{ci}'}{E_{mi}'} \tag{2}
\]

where \( E_{ci}' \) is the storage modulus of the composite at temperature \( i \) and \( E_{mi}' \) is the storage modulus of the matrix at the same temperature.

Thermal transitions in composites of natural fibers and polypropylene have been extensively studied [7]. Thermal transitions in wheat straw specimens are also studied by Stelte et al. (2011) who reported major transitions at around 5 and 90 °C for hemicelluloses and lignin components, respectively. However, not much data is available for the dynamic mechanical properties of wheat straw polypropylene composites especially over a wide range of temperatures [1].

Creep is one the fundamental properties of materials limiting their long-term application by excessive deformation or reduced stiffness over time [8]. Temperature dependent creep of natural fiber plastic composites has been studied and it was found that creep in such materials is more or less a modulus dependent phenomenon mainly controlled by the stiffness of the material at various temperatures [9]. Here the effect of stress levels on short term creep of selected formulations is presented to see if a similar behavior could be observed.

This paper will investigate the effect of type of matrix (homopolymer or copolymer) and compare straw fiber and talc with respect to thermal transitions, modulus retention term and relative storage modulus of these thermoplastic composites. The object is to identify the contribution of straw fiber to the mechanical behavior of the composites at different temperatures.

**Materials and Methods**

**Materials**

A total of twenty wheat straw/talc polypropylene composite formulations were evaluated. The % values reported in Table 1 are weight percentages. An isotactic homopolymer polypropylene (hereafter called PP1), grade D180M, Sunoco Chemicals, Inc., Philadelphia, with a melt flow index of 18g/10min and a high impact copolymer polypropylene (hereafter called PP2), grade TI6200N, Sunoco chemicals, Inc., Philadelphia, with a melt flow index of 18g/10min were used. Both resins were supplied by Braskem America.
Wheat straw was supplied by Omtec, Chatham, ON with an average fiber size of 520 microns and average aspect ratio of 4. Talc was BT 2207, and was supplied by Schulman Inc. (Akron, OH) and had a nominal particle size of 7 microns. In all formulations, antioxidants Irganox 1010 and Irgafos 168, both from CIBA Inc. (Switzerland), each at 0.25 wt% and MD-353D maleic anhydride grafted polypropylene coupling agent from DuPont, Canada at 2 wt% were used.

Table I. Composition of the evaluated formulations (wt%)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Polypropylene</th>
<th>Wheat Straw</th>
<th>Talc</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP1</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP2</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP1+20%talc</td>
<td>77.5</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>PP1+30%talc</td>
<td>67.5</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>PP1+40%talc</td>
<td>57.5</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>PP2+20%talc</td>
<td>77.5</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>PP2+30%talc</td>
<td>67.5</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>PP2+40%talc</td>
<td>57.5</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>PP1+20%mWS</td>
<td>77.5</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>PP1+30%mWS</td>
<td>67.5</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>PP1+40%mWS</td>
<td>57.5</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>PP2+20%mWS</td>
<td>77.5</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>PP2+30%mWS</td>
<td>67.5</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>PP2+40%mWS</td>
<td>57.5</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>PP1+10%talc+20%mWS</td>
<td>67.5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>PP1+15%talc+15%mWS</td>
<td>67.5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>PP1+20%talc+10%mWS</td>
<td>67.5</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>PP2+10%talc+20%mWS</td>
<td>67.5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>PP2+15%talc+15%mWS</td>
<td>67.5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>PP2+20%talc+10%mWS</td>
<td>67.5</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Methods

Raw materials were fed into a Haake Minilab Micro-compounder consisting of a co-rotating twin screw extruder (Thermo Scientific, Waltham, MA). Mixing process was conducted at 190°C and 40 rpm. The produced composites were injection molded using a Ray Ran Laboratory Injection Molding machine (Ray Ran Test Equipment Ltd., UK) at 190 °C and a pressure of 0.69 MPa to obtain rectangular bars according the dimensions set in the ASTM D-256 standard specification [10]. The specimens were then annealed in an oven to remove any thermal history.

DMTA was performed using a Rheometric Scientific DMTA V device (Rheometric Scientific, Piscataway, NJ). A single cantilever mode was selected and the samples were scanned over a temperature range of -100 to +140 °C at a heating rate of 2 °C/min. The frequency of oscillations was constant at 1 Hz. The samples were cooled using liquid nitrogen and a 10 minute soak time was allowed to ensure the equilibrium of the sample's internal temperature with that of the test chamber before the scans were initiated. A strain amplitude of 0.05% was used after determination of the linear viscoelastic region of the materials behavior using a strain sweep test at room temperature. The modulus retention term (MRT) and the relative storage modulus (RSM) values were calculated using Equations 1 and 2, respectively. The temperature of -80 °C was used as the reference temperature for the calculation of MRT.
The short term creep tests on selected formulations were performed using three point bending fixtures at room temperature at five stress levels ranging from 1 to 5 MPa. A two-parameter power law model (Equation 3) was used to model stress dependent creep behavior [9].

\[ \varepsilon_T = aT^b \]  

(3)

where \( \varepsilon_T \) is creep strain at time \( T \) and \( a \) and \( b \) are model parameters obtained by fitting the experimental data to the equation.

**Results and Discussion**

**Thermal Transitions**

The loss modulus spectra of formulations containing wheat straw fiber or talc and polypropylene homopolymer (PP1) or polypropylene copolymer (PP2) are presented in Figure 1. The vertical dashed lines on the graphs indicate the peaks for pure PP1 and PP2 so that shifts to lower or higher temperatures could be observed more easily. Two major transitions are observed for pure PP1 and its composites regardless of the dispersed phase type or content. The low temperature transition seen around 8 °C is related to the beta (glass) transition of amorphous polypropylene chains [3, 6-8, 11, 12]. Adding straw at 20% slightly reduces the glass transition temperature whereas it is again slightly increased when straw content increases. In contrast, 20% talc initially increases the glass transition temperature but it is reduced as the talc content increases. The second transition seen at around 75 °C for pure PP1 is alpha (crystalline) transition resulted in by the so called “defects” present in crystalline structure [7]. By the addition of 20% straw to PP1, a shift to higher temperatures is observed. However, at higher straw contents, a lower alpha transition temperature is seen. For talc filled PP1 composites, lower alpha transition temperatures are also resulted in when talc is added to the system.

Pure PP2 and its composites present three distinct thermal transitions over the temperature range studied (Figure 1c and d). In addition to the same alpha and beta transitions seen in PP1, a third low temperature transition peak is seen at around -48 °C for pure PP2 which is due to the impact modification of the copolymer [13-15]. Glass transition of pure PP2 is at a lower temperature as compared with that of PP1 which is attributed to the plasticization of polypropylene [8] and has been previously reported for various copolymers of polypropylene [16]. In straw filled PP2 composites, the glass transition is not significantly affected by the addition of fibers whereas it is shifted to slightly higher temperatures when talc is added. The alpha transition is shifted to higher temperatures in the presence of straw in PP2 composites whereas it is initially shifted to lower temperatures and subsequently to higher ones at 40% talc content. The lowest transition temperature associated with the impact modification experiences slight variations in both straw and talc formulations so that the highest values are observed at 30% content.

The beta transition, related to the glass-rubbery transition, is due to the molecular motions associated with unrestricted amorphous phase in polypropylene (PP) [17, 18]. Although it is expected that the presence of fibers should generally shift the glass transition to slightly higher temperatures due to restrictions in molecular chain mobility [8], different observations have been made regarding the effect of natural fibers on the glass transition of polypropylene whereas all three possible forms including no shifting [19], shifting to higher temperatures [20, 21] and shifting to lower temperatures [7, 22] have been reported. All in all, it seems that the position of
glass transition temperature in PP composites is a function of various variables and the direction of shifting depends on the dominant variable [7]. Generally, it seems that the temperature range between the glass and alpha transitions of PP is widened in all formulations so that most changes in the glass transition temperature are associated with increases in alpha transition temperature.

![Figure 1. Loss modulus spectra of different formulations (PP1-polypropylene homopolymer, PP2-polypropylene copolymer, mWS-wheat straw fiber)](image)

**Temperature Dependent Mechanical Behavior**

The modulus retention term (MRT) has been used by several authors as an indicator of the retention of mechanical properties at various temperatures [3, 5, 6, 21]. While comparing the absolute values of storage modulus at various temperatures might be misleading, the MRT works as a parameter for better comparison of the materials' behavior at various temperatures. The relative storage modulus (RSM) on the other hand, provides information on the reinforcing efficiency of fibers or fillers at various temperatures [6].

The above mentioned parameters for composites containing straw are plotted versus temperature in Figure 2. Comparing the trends in MRT for homopolymer and copolymer composites reveals that the values slightly decrease until around 0 °C for the homopolymer (PP1) composites but constantly reduce from -50 °C for the copolymer (PP2) composites. At temperatures above ambient, the MRT is higher for copolymer composites and at higher fiber contents, which can be explained by the lower stiffness of PP2 and the subsequent higher
reinforcing efficiency of the fibers. Comparing the RSM values however, reveals very different behaviors for the two polymer matrices. A somewhat quadratic increase in the RSM values is observed for all composite formulations with homopolymer (PP1) with slightly higher values at higher fiber contents. In contrast, the difference between straw content levels becomes more pronounced for the copolymer (PP2).

![Graphs showing Modulus Retention Term (MRT) and Relative Storage Modulus (RSM) for formulations containing wheat straw at various temperatures (PP1-polypropylene homopolymer, PP2-polypropylene copolymer, mWS-wheat straw fiber)](image)

**Figure 2.** Modulus Retention Term (MRT) and Relative Storage Modulus (RSM) for formulations containing wheat straw at various temperatures (PP1-polypropylene homopolymer, PP2-polypropylene copolymer, mWS-wheat straw fiber)

Figure 3 shows the MRT and the RSM curves for composites containing talc where similar to straw. The MRT is higher for copolymer (PP2) composites than for homopolymer (PP1) ones at any given temperature. While the MRT trends for talc filled composites are very similar to those for straw composites, Figure 5 shows that the RSM behaviors are not identical. As clearly seen for PP1 composites, talc has its highest reinforcing efficiency at around 0 °C which corresponds to the glass transition temperature of polypropylene. Addition of 20% talc also lowers the efficiency to values below unity at very low temperatures. A similar trend is seen for PP2 formulation with the difference that here the 30% talc composite has lower than unity values at low temperatures and the behaviors of composites containing 20 and 30% talc are similar at temperatures above -50 °C. The temperature dependent behavior of RSM for talc filled polypropylene composites has not been reported in the literature, although one study on composites of PP and clay also reported similar peaks but lower than unity RSM values at higher temperatures [23], which can be explained by the low level of clay content (<wt5%) in that study.
Formulation with Straw and Talc

The formulations with 30% dispersed phase (straw and talc) and polypropylene of either type were chosen to study the effects of varying compositions of straw and talc on different performance characteristics of the composites. The combination of straw and talc is called hybridization.

Figure 4 shows the effects of hybridization on storage modulus, loss modulus, MRT and RSM values for the homopolymer (PP1) composites. As seen in the storage modulus curves, below the glass transition temperature when the materials are still in the glassy state, straw filled composite has the lowest stiffness values. These are improved when talc is added to the system and the highest values correspond to the formulation with 20% talc. In the rubbery state, however, the difference between the formulations is less pronounced. Looking at the loss modulus curves in Figure 5, one observes that formulations containing talc generally have lower glass transition but higher alpha transition temperatures than the formulation with 30% of straw. The modulus retention term (MRT) was higher for the straw filled composite than the hybrid formulations or the talc/PP1 formulation almost throughout the entire temperature range studied.

In fact, the formulations having higher stiffness at sub zero temperatures experienced more significant drops in stiffness in the rubbery state leading to lower modulus retention values. The reinforcing efficiency measured by the RSM values shows lower efficiency for straw than talc over the temperature range. The peak in the RSM already observed for talc formulations in
Figure 3 is suppressed when the amount of talc is reduced in the formulations.

Figure 4. Effects of hybridization with talc on the mechanical properties of PP homopolymer composites (PP1-polypropylene homopolymer, mWS-wheat straw fiber)

Figure 5 exhibits the effects of hybridization on storage modulus, loss modulus, MRT and RSM values for the copolymer (PP2) composites. Unlike the homopolymer composites, no consistent variations could be observed as to the effect of hybridization on the storage modulus spectra. In fact, the behavior of the samples could be divided into four distinct temperature ranges. Below -50 °C that is the transition associated with the impact modification, the formulation containing 20% talc has the highest $E'$ values whereas the one with 10% talc has the lowest. In the region between -50 °C and 0 °C associated with the glass transition of polypropylene, the formulation with 30% talc exhibits the highest stiffness. In the temperature range of 0 to +50 °C which is the onset of alpha transition in polypropylene, all formulations seem to have more or less similar stiffness values, beyond which the behavior changes again with the formulation having 30% talc exhibiting the lowest values.

Comparing the loss modulus curves in Figure 5, one observes no significant change in transitions at around 0 °C or -50 °C. However, the alpha transition occurs at a considerably lower temperature when 30% talc is used. The modulus retention term (MRT) was higher for the composites containing 10 and 20% talc with the former maintaining this trend over all temperatures. The RSM values clearly show that at least at high temperatures, the impact copolymer (PP2) composites with 30% straw have considerably better reinforcing efficiencies.
than talc which might present better stiffness values at low temperatures.

![Figure 5](image)

**Figure 5.** Effects of hybridization with talc on the mechanical properties of PP impact modified copolymer composites (PP2-polypropylene copolymer, mWS-wheat straw fiber)

**Short Term Creep**

Selected creep curves for the composite with 20% straw and PP1 and PP2 as well as those for the PP2 composite with 40% straw are presented in Figure 6. Generally, the PP2 composite had higher creep strains at all stress levels as compared with the PP1 composite at the same straw content. Increasing the stress level almost linearly increased the creep strain in all formulations. Increasing the amount of straw significantly reduced the creep strain in PP2 composites.

The power law model described as Equation 3 was fitted onto the experimental data and coefficients of determination ($r^2$) values of 0.99 were obtained indicating the accuracy of the fit. The solid lines in Figure 6 show the model fits. Power law parameters $a$ and $b$ are plotted against stress level in Figure 7 where one can easily observe that while the $a$ parameter (which is the intercept of the curve on a logarithmic scale) is linearly stress dependent. The parameter $b$ (which is related to the slope of the deformation) is almost unchanged by the stress level indicating that creep rate is stress-independent. The PP2 composite shows higher parameters indicating higher creep whereas the values of both parameters are reduced when straw content is increased to 40%.
Figure 6. Short term creep behavior of selected formulations as a function of stress levels (PP1-polypropylene homopolymer, PP2-polypropylene copolymer, mWS-wheat straw fiber)

Figure 7. Dependence of power law model parameters on stress level for different formulations (PP1-polypropylene homopolymer, PP2-polypropylene copolymer, mWS-wheat straw fiber)
Conclusions

The glass transition of the straw and talc filled polypropylene composites was slightly affected by the presence of dispersed phase. A slight shift to lower temperatures was seen for straw whereas a shift to higher temperatures was observed for talc. An evident peak in the loss modulus spectra in the impact modified PP was observed at around -50 °C, which was not considerably affected by the presence of fibers. The alpha transition associated with crystalline PP was also slightly affected by the presence of fibers; shifts to higher temperatures were more evident with impact modified PP.

Both straw and talc significantly increased modulus retention term as compared to the pure polymers. Talc increased low temperature stiffness more than straw. However, better modulus retention terms were observed for straw composites at higher temperatures. The mechanical behavior of impact modified PP composites was strongly dependent on the transition associated with the impact modification. Talc generally resulted in the highest reinforcing efficiency around the glass transition of the polymer whereas that of straw constantly increased at higher temperatures.

The hybridization of the composites using both straw and talc resulted in different effects for homopolymer and copolymer composites. Improvements in stiffness values at low temperatures were more evident when the homopolymer was used. The short term creep of the studied formulations at room temperature was a modulus dependent phenomenon whose rate was not considerably affected by the applied stress level.

Acknowledgements

The authors would like to thank financial support by provided by NSERC Discovery, OMAFRA Bioproducts and Ontario BioCar Initiative. The authors would also like to thank OMTEC Inc., Braskem America Inc. and A. Schulman Inc. for the donation of materials.

References


