CHARACTERIZATION OF VISCOELASTIC PROPERTIES OF FLAX REINFORCED POLYPROPYLENE COMPOSITES

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SUMMARY

The application of natural fibres is being targeted in various fields due to both environmental and economical benefits. Natural fibres are renewable, biodegradable, and have high specific strength to weight ratio. This paper deals with the investigation of dynamic mechanical properties of flax nonwovens reinforced polypropylene composites.

Keywords: Natural fibres, Composite, Viscoelastic Properties

INTRODUCTION

Natural fibres are hydrophilic in nature as they are lignocellulosic, which contain strongly polarized hydroxyl groups. These fibres, therefore, are inherently incompatible with hydrophobic thermoplastics, such as polyolefins. The major limitations of using these fibres as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fibres and non-polar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibres with the matrix. Therefore, it is imperative that natural fibres should be subjected to chemical modification to increase the compatibility and adhesion between fibres and matrix\textsuperscript{[1]}. It would also be desirable that the chemical agents used for the modification of natural fibres preserves the biodegradable nature of natural fibres. Ideally, the chemicals used for modification should also be from renewable resources. In this study, we have attempted to use zein as a coating on natural fibres to see if it influences the interfacial mechanism between fibre and matrix. Zein is a natural protein derived from corn and is composed of mainly amino acids and glutamic acid, leucine and alanine. Zein forms tough coatings and is resistant to microbial attack and possesses the additional benefits of being renewable and biodegradable. Recently Kim \textsuperscript{[2]} reported studies on the processing and properties of gluten-zein composites. The author observed the compressive yield strength of the composites to be around 40 MPa which was comparable to that of polypropylene. Although there have been many studies on lignocellulosic short fibre composites, only a few mention the use of needle punched nonwovens as reinforcement in composites. The biggest advantage of this type of composite is their low processing cost, combined with their ecological and technological benefits. This study attempts to investigate the
dynamic mechanical performance of polypropylene composites reinforced with flax nonwovens. The effect of zein coating on nonwovens is also analysed in terms of viscoelastic and thermal properties of composites.

2. EXPERIMENTAL

2.1 Materials

South African flax line fibres were cottonised on Temafa Cottonization line by processing flax fibres through 1 pass Lomy (at speed 680 rpm) and 1 pass Cottonizer (at 1470 rpm) to produce needle-punched nonwovens. The needle-punched nonwovens from 100% cottonised flax fibres with an area weight of 200 g/m² was used in this study. Polypropylene in sheet form (6 mm thickness), with a density of 0.9g/cc and melt flow index of 1.5g/10 min was procured from Ampaglas SA. Zein was obtained from Scientific Polymer Product Company, Ontario, NY. All other chemical reagents used in these studies were of analytical grade.

2.2 Preparation of composites

Composites were prepared from nonwoven flax and polypropylene on the basis of varying fibre content. The flax nonwoven mats were cut into small uniform squares (30 cm x 30 cm) and were dried in an air oven at the temperature of 110°C for 7 h. The dried nonwoven mats were placed between weighed polypropylene sheets. This was wrapped in Teflon® sheets and sandwiched between two aluminium plates. These two plates were then placed between the two platens of compression moulding press and cured at a pressure of about 35 bar for 20 minutes at 210°C, followed by cooling under pressure for 3 minutes.

2.3 Zein modification of flax nonwovens

Zein belongs to the characteristic class of proteins known as prolamin which occur specifically in cereals. The protein products from corn wet milling are corn gluten meal (CGM) and corn gluten feed (CGF) and zein is obtained as a by-product from corn gluten meal [3,4,5].

2 % of zein solution was prepared by mixing with an ethanol/water mixture in the ratio 80/20. The flax nonwovens were immersed in this solution and were allowed to stand for 2 hours. The ethanol/water mixture was drained out and the nonwoven was dried in air and then in an oven at 110°C until completely dry. These modified nonwovens were used to prepare the composites.

3. ANALYSIS

Dynamic mechanical analysis was carried out using the Perkin Elmer DMA 8000. Samples of dimensions 50 x 12 x 3 mm were used for testing. The testing temperature ranged from -20°C to 150°C and the experiment was carried out at frequencies 0.1, 1, 10 and 100 Hz. The samples were tested under dual cantilever mode at strain amplitude of 0.05mm.
TG was carried out using a Perkin Elmer TGA in an inert atmosphere at a heating rate of 10°C/min. The temperature range used for the analysis is 30°C to 700°C.

Scanning electron microscopic studies were conducted using Philips XL 30 SEM to analyse the fracture behaviour of the composites. The fracture ends of the tensile specimens were mounted on aluminium stubs and gold coated to avoid electrical charging during examination.

4. RESULTS

4.1 Effect of fibre content

Storage modulus (E’) provides valuable input into the stiffness of composites. The variation of storage modulus with temperature at different fibre loading at 1 Hz is given in Figure 1. It can be seen that storage modulus increases with increasing flax content at all temperatures when compared to the polypropylene. When fibres are incorporated in the polypropylene matrix, the stiffness of the composite increases resulting in high storage modulus. Also, the addition of fibres allows effective stress transfer at the interface, which consequently increases the storage modulus. Loss modulus (E”) measures the viscous response of materials and is related to amount of energy lost. The variation of loss modulus with temperature at different fibre loading is shown in Figure 2. It can be seen that loss modulus increases with the increase in fibre loading and reaches a maximum and then decreases. The maximum heat dissipation occurs at the temperature where the loss modulus is maximum indicating a relaxation phenomenon.

The increase in loss modulus is attributed to the increase in energy absorption caused by the addition of fibres. Damping is an important parameter related to the study of dynamic behaviour of fibre reinforced composite material. The major contribution to damping in composite is due to (a) nature of matrix and fibre (b) nature of interphase (c) frictional damping due to slip in the unbound regions between fibre and matrix interface or delaminations and (d) damping due to energy dissipation in the area of matrix cracks and broken fibres. The variation of tan δ with temperature at different fibre loading is given in Figure 3. It can be seen that upon incorporation of flax nonwovens, the position of β-relaxation is not significantly altered but the presence of flax nonwovens decreased the intensity (magnitude of tan δ values) of the relaxation region. Incorporation of nonwovens acted as barriers to the mobility of polymer chains, leading to lower degrees of molecular motion and hence lowers damping characteristics. Another reason for the decrease is that there is less matrix by volume to dissipate the vibration energy [6]. The width of the tan δ peak also becomes broader than that of the pure matrix as shown in Figure 3 suggesting that there are molecular relaxations occurring at the interfacial region of the composite. It can be observed that in the α-relaxation region, the position of the peak is shifted to higher temperatures and the magnitude of tan δ values is also seen to increase. This suggests that the molecular motions in the crystalline phase are affected by the increasing flax content.
Figure 1: Variation in storage modulus with temperature for composites at different fibre weight fractions at 1 Hz

Figure 2: Variation in loss modulus with temperature for composites at different fibre weight fractions at 1 Hz
4.2 Effect of zein coating

The variation of storage modulus with zein coating is given in Figure 4. It can be observed that storage modulus of the treated composites shows an increase which is more prominent in the rubbery plateau region at higher temperatures. This can be attributed to the better reinforcing effects which increase the thermal and mechanical stability of the material at higher temperatures. Figure 4 presents the damping peaks of untreated and zein treated composites. The position of β-relaxation was not found to be altered but in the α-relaxation region, a gradual narrowing of the peak shoulder was
detected. This could be attributed to the fact that the lamellar movement in the crystalline phase being strongly affected by the zein coupling agent.

![Graph showing variation in tanδ with temperature for untreated and treated composites at different fibre weight fractions at 1 Hz.]

Figure 5: Variation in tanδ with temperature for untreated and treated composites at different fibre weight fractions at 1 Hz.

The fibre/matrix interfacial adhesion can be indirectly quantified by estimating the damping term as it is a true indicator of the molecular motions in a material. When a composite material, consisting of fibres (essentially elastic), polymeric matrix (viscoelastic), and fibre–matrix interfaces is subjected to deformation, the deformation energy is dissipated mainly in the matrix and at the interface. If matrix, fibre volume fraction and fibre orientation are identical, then the damping term can be used to assess the interfacial properties between fibre and matrix. For a weak interface, more energy is dissipated during testing and this has been reported in studies by other researchers [7]. Therefore, an interfacial strength indicator, $B$, which may be used to characterize the interfacial bonding properties, is adopted in this study to assess the potential of zein as interface modifier.

The damping property results from the inherent damping of the constituents [8] and can be represented as

$$\tan \delta_c = V_m \tan \delta_m + V_f \tan \delta_f$$

[1]

As the contribution to damping from the natural fibers is negligible equation [1] reduces to

$$\tan \delta_c = \tan \delta_m (1 - V_f)$$

[2]

Where $\tan \delta$ is the damping value, $V$ is the volume fraction and $m$, $f$ and $c$ represents matrix, fibre and composite respectively.

Due to significant interaction between polymer and fibre, equation [2] is rewritten as
\[
\tan \delta_v = \tan \delta_m (1 - BV_f) \tag{3}
\]

Where B is a correction parameter related to effective thickness (which can be estimated from the dimensions of fibres) of the fibre-matrix interface, which was first introduced by Ziegel and Romanov [9]. Therefore

\[
B = \frac{\left(1 - \frac{\tan \delta_v}{\tan \delta_m}\right)}{V_f} \tag{4}
\]

Greater values of B indicate greater interfacial strength. The values of interfacial strength indicator B is shown in Table 2. It can be seen that interfacial strength increases with zein coating on the flax nonwovens.

**Table 1: \( \tan \delta \) and B values of composites**

<table>
<thead>
<tr>
<th>Composite</th>
<th>( \tan \delta )</th>
<th>( V_f )</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>0.0983</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.08519</td>
<td>0.22</td>
<td>0.606</td>
</tr>
<tr>
<td>2 % Zein Treated</td>
<td>0.08233</td>
<td>0.20</td>
<td>0.812</td>
</tr>
</tbody>
</table>

4.3 Effect of frequency

![Graph](image)

**Figure 5:** Variation in storage modulus with temperature for 20% composites at different fibre weight fractions at 1 Hz

The visco-elastic properties of a composite are dependent on temperature, time and frequency. A material that is subjected to constant stress will experience a decrease in
elastic modulus over a period of time. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimize the localized stresses. The variation of storage modulus with temperature at different frequencies of samples with 20% fibre loading is given in Figures 5. It can be seen that as frequency increases, storage modulus increases and this is more prominent at lower temperatures. This can be attributed to the lesser mobility of the polymer chains when the speed of cyclic stress is too fast to bring about deformation. The molecules will not get time to undergo permanent deformation (irreversible flow) and so the material exhibits elastic behaviour resulting in an increase of E’ value.

4.4 Thermal studies

Thermogravimetric analysis is a useful technique to determine the thermal stability of the materials. In addition it is possible to quantify the amount of moisture and volatiles present in the composite. Figure 6 and 7 presents the thermo grams of the composites based on fibre content and modification. It can be seen that thermal stability increases upon fibre content.

![Figure 6: Thermograms of flax-PP composites based on fibre content](image-url)

Figure 6: Thermograms of flax-PP composites based on fibre content
4.5 Scanning electron microscopic studies

Scanning electron microscopy is a common method to analyze the level of fibre/matrix adhesion. Enormous amount of studies has been conducted to evaluate the bonding between matrix and fibre. Analysis of the morphological features of fracture surfaces by SEM is an important tool for observing the surface morphology of fibres, the cause of crack initiation and the failure process in composites. Figure 6(a) shows the tensile fractured surface of untreated flax nonwoven composite at 30%. The presence of cavities is clearly visible. This indicates that the level of adhesion between the fibres and the matrix is poor and when stress is applied it causes the fibres to be easily pulled out from the matrix, leaving behind gaping holes. Figure 8(b) shows the tensile fracture surface of zein treated flax nonwoven composite at the same fibre loading. The figure shows the presence of a number of short broken fibres projecting out of the polypropylene matrix indicating that zein modification definitely improves the bonding between the fibres and matrix.
Conclusions
Viscoelastic properties like storage modulus increased while damping properties were found to decrease with incorporation of flax nonwovens. Zein modification resulted in increase of storage modulus indicating better interfacial adhesion. The variation of excitation frequency was found to affect the storage modulus and secondary relaxations of the composites significantly. Thermal stability increased with incorporation of flax nonwovens. Scanning electron microscopic studies revealed fibre breakage in treated composites as opposed to fibre pull out in untreated composites.

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References:

Figure 8(a) and (b): Scanning electron micrograph of tensile fractured specimen of (a) untreated and (b) 2% zein treated composites.