ABSTRACT

Polyurethane (PU) resin systems are generally characterized as aromatic and aliphatic. Aliphatic PU has lower mechanical properties than the aromatic resin system due to its chemical structure. The objective of the present work is to improve the mechanical properties of aliphatic resin system by exfoliating silicate nano particles. A pultrudable, soy-based, polyl-isocyanate aliphatic resin has been used as the base system. Nanocomposites were synthesized using the base resin and modified montmorillonite (MMT) clay. Modification of Na-MMT was confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy analyses. Increase in the basal spacing of the nanoclay was observed by wide angle X-ray diffraction. The curing mechanism of soy-based PU resin with 1wt% of triethanol amine/methyl iodide exchanged MMT clay was studied using differential scanning calorimetry as well as FTIR. Tensile testing of the nanocomposites showed improved modulus when compared to the neat aliphatic resin system. Soy-based nanocomposites hold great promise as environmentally friendly and low cost materials for structural and automotive applications.

INTRODUCTION

Biocomposites have either one or both the raw materials derived from natural/renewable resources. Raw materials derived from vegetable oils are of great interest due to their low cost when compared to petroleum based raw materials [1]. Biocomposites have been gaining great interest for the past few decades due to the ever increasing environmental concerns as well as depleting fossil fuels. PU resin system has been in use for a long time due to its high durability, low weight, no VOCs and higher cost effectiveness when compared to the conventionally used resin systems such as polyester and vinyl ester. Due to its versatile polymer chemistry and good properties, PU resin system is used to manufacture composites for various applications such as foams, sealants, automotive components etc [2]. Recently, work has been conducted on synthesizing PUs from renewable sources [3]. Guo et al. synthesized foams using polypropylene oxide based PU resin system derived from soybean oil [4]. Authors reported the mechanical and thermal properties of the soy-based PU foams which were comparable to that of the PU foams derived from petrochemical based raw materials. Hu et al. used PU derived from hydroxylated rape seed oil to manufacture rigid foams. These bio-based PU foams had lower
compression strength than the reference foam but the density of the foam increased by incorporating soybean component into the conventional polyol [5]. Dwan’isa et al. developed soy oil based fiber reinforced PU composites using hemp and glass fiber mats. PU composites with 20 wt% of fiber reinforcements showed significant improvements in the mechanical properties [6].

Polymer silicate nanocomposites are generally synthesized by dispersing phyllosilicates into the polymer resin system. Nanocomposites typically show significant improvements in various properties such as tensile strength, tensile modulus and gas permeability. Due to the hydrophilic nature and affinity towards forming a face-to-face stacking sequence of the layered silicates, it is difficult to disperse these silicate materials into the hydrophobic polymer. Dispersion can be improved by replacing the monovalent or divalent cations in the clay galleries with various organic surfactants. This process results in the increase of organophilic nature of the silicate layers. Ammonium, sulphonium and phosphonium ions are generally used to replace the exchangeable cations in the silicate galleries. Surface modification of the clays increases the basal spacing of the clay galleries by improving the compatibility between the clay and the hydrophobic polymer system [7, 8]. Kornmann et al. synthesized polyester nanocomposites using MMT modified with a methacrylate-silane coupling agent. The authors used X-Ray diffraction (XRD) and Transmission electron microscopy (TEM) to study the dispersion of clay platelets in the resin system [9]. Bharadwaj et al. prepared nanocomposites using polyester resin system and an organically modified MMT. Exfoliation of polyester resin in the modified clay was confirmed using XRD and TEM [10].

PU nanocomposites can be manufactured using melt intercalation, intercalation of polymer in solution and in-situ intercalative polymerization. Wang et al. manufactured PU silicate layered nanocomposites with improved properties by dispersing the clay materials into the polyol component of the PU resin system [11]. Yao et al. dispersed Na-MMT in a modified isocyanate system to form PU nanocomposites. Authors observed an increase in the d-spacing after dispersing the clay [12]. Berta et al. used polyols with varying molecular weight and functionality to synthesize PU nanocomposites. Authors observed that higher equivalent molecular weight of the polyols effects the exfoliation of the polymer chains into the clay galleries [13]. Xiong et al. modified the natural MMT with methylene-bis-ortho-choloroaniline and PU nanocomposites were synthesized using the modified MMT and polypropylene glycol based PU resin system. Authors observed exfoliated structures at low clay content while agglomerated nanocomposites were observed for clay contents greater than 3% by weight [14].

In the present work, a pultrudable soy-based, polyol-isocyanate, aliphatic PU resin has been used as the base system. Na-MMT was modified using triethanol amine and methyl iodide solution to make it compatible to the polyol component of the PU resin. Nanocomposites were synthesized using the base resin system and modified montmorillonite (M-MMT) clay. FTIR was used to confirm the ionic modification of Na-MMT. Increase in the basal spacing of the nanoclay was observed by XRD. PU nanocomposites synthesized using M-MMT showed improved tensile properties when compared to the base aliphatic PU resin system.
EXPERIMENTATION

Materials

A novel soy-based polyether polyol and an aliphatic isocyanate compatible with the pultrusion process were obtained from Bayer MaterialScience, USA. Na-MMT was received from Southern Clay Products Inc. Triethanolamine and Methyl iodide were obtained from Aldrich chemicals.

Surface Modification of Na-MMT and Preparation of PU Nanocomposites

10 g of Na-MMT was mixed with 0.2 M HCl solution using a magnetic stirrer for 12 hours. Methanol and centrifuge were used to wash out the excess HCl and NaCl from the above solution. 8.6g of methyl iodide was added to 9g of triethanolamine and the mixture was mixed overnight. Acidic clay was then reacted with the triethanolamine and methyl iodide solution for 12 hours using a magnetic mixer. Excess organic salt and HI were removed using methanol and centrifuge process. The resulting clay was dried at 120°C in an oven to remove the moisture present in the modified clay. Dried M-MMT was ground to 10 μm in a mortar and pestle and dried again under vacuum at 60°C before dispersing in the polyol. Final product was analyzed using FTIR to check for the additional organic groups added into Na-MMT.

Required quantity of the M-MMT was first mixed in the polyol component of the PU resin system using a high shear mixer for 5 minutes. Soon after the high shear mixing, the polyol/clay mixture was subjected to ultrasound until settling of the clay particles was not observed. PU nanocomposites were synthesized by adding the required quantity of aliphatic isocyanate into the exfoliated polyol in M-MMT and the mixture was mixed carefully in order to reduce the incorporation of air and moisture into the PU resin. Mixed PU resin was then poured into a preheated dog bone mold maintained at 60°C for one hour and then post cured at 110°C for one hour.

Acid Modification of Na-MMT:

\[ \text{MMT} - \text{Na} + \text{HCl} \rightarrow \text{MMT} - \text{H} + \text{NaCl} \]  

[1]

Formation of Surface Modifying Salt:

\[ \text{N} \left( \text{C}_2\text{H}_4\text{OH} \right)_3 + \text{CH}_3\text{I} \rightarrow \left[ \text{H}_3\text{CN}^+ \left( \text{C}_2\text{H}_4\text{OH} \right)_3 \right] \text{I}^- \]  

[2]

Surface Modification of Acidic MMT:

\[ \text{MMT} - \text{H} + \left[ \text{H}_3\text{CN}^+ \left( \text{C}_2\text{H}_4\text{OH} \right)_3 \right] \text{I}^- \rightarrow \text{MMT} - \text{H}_3\text{CN} \left( \text{C}_2\text{H}_4\text{OH} \right)_3 + \text{HI} \]  

[3]

Tensile Test

The tensile tests were carried out in accordance with ASTM D638 on an Instron universal testing machine. Tensile modulus, tensile strength, and the elongation at break values were obtained for the neat PU and PU nanocomposites. All the tensile tests were performed at a crosshead speed of 50 mm/min. At least five specimens were tested for the soy-PU neat resin and the soy-PU nanocomposites synthesized using M-MMT.
Fourier Transform Infrared Spectroscopy
FTIR at a 4 cm\(^{-1}\) resolution was conducted using a Nicolet Nexus 470 E.S.P. spectrophotometer over the 4000 to 400 cm\(^{-1}\) spectral range. The spectral absorption of Na-MMT, M-MMT and cured nanocomposites were obtained by using the powdered samples.

**X-ray Diffraction Analysis**
Thick film XRD pattern was obtained using a Philips X-Pert diffractometer equipped with Cu-K radiation with a wavelength of 0.15418 nm, accelerating voltage of 45 kV, and electric flow of 40 mA. The scanning range was from 2\(^\circ\) to 30\(^\circ\) with a rate of 0.02 degree/min. From the position of a peak, the corresponding d spacing was computed from the Bragg’s diffraction equation:

\[ n\lambda = 2dsin\theta \]  

where \( n \) is the order of reflection, \( \lambda \) is the wavelength of radiation, \( \theta \) is the angle of reflection and \( d \) is the interlamellar spacing.

**Differential Scanning Calorimetry**
Differential scanning calorimetry (DSC) was performed on TA Instrument model Q2000. Cured samples of neat aliphatic PU and M-MMT/PU nanocomposites were weighed to around 5g and were each placed in the aluminum crucible. The cell containing the samples was quickly cooled using a chiller mechanism and subjected to subsequent scanning from -30\(^\circ\)C to 200\(^\circ\)C to measure the resulting glass transition temperature. The glass transition temperature was reported as the inflection point on the glass transition region.

**RESULTS**

**Tensile Test**
Figure 1 shows the tensile test results of soy-PU base resin and soy-nano PU composite. Test results are tabulated in Table 1. Tensile modulus increased from 233 MPa to 280 MPa by the addition of just 1 wt% of M-MMT into the soy-PU resin system. Formation of an intercalated structure can be attributed to the increase in tensile modulus in the soy-nano PU. Due to the better interactions between polymer chains and the clay platelets with high aspect ratio, chain movement under applied load is decreased. This phenomenon results in the lower tensile failure strains for the soy-nano PU composites. In the present work, tensile failure strains decreased from 85% to 50% for the nano PU composite. Neat polymer exhibited ductile failure, whereas the additions of clay lead to brittle fracture in the PU resin system. The possible explanation to this phenomenon is that the silicate layers constrain the matrix so that plastic deformations are prevented in the nanocomposites. Lower tensile strength observed for nano-PU is due to the formation of micro voids during the synthesis of nano-PU.

**Fourier Transform Infrared Spectroscopy**
The IR spectra of Na-MMT and M-MMT are shown in Figure 2. M-MMT spectrum showed peaks at 2847 cm\(^{-1}\), 2920 cm\(^{-1}\), 1466 cm\(^{-1}\) and 1372 cm\(^{-1}\) representing symmetric, asymmetric, scissoring and wagging vibrations for the C–H bond respectively [15,16]. Peaks depicting the vibration of N-H bond were not observed in M-MMT spectrum due to the quaternary structure of the salt formed during the reaction between triethanolamine and methyl iodide. Intensity of peaks
at 3634 cm⁻¹, 3454 cm⁻¹, 1638 cm⁻¹, 1043 cm⁻¹, 524 cm⁻¹ and 466 cm⁻¹ for M-MMT is less when compared to that of Na-MMT. Presence of additional peaks and reduction in the intensity of characteristic peaks in M-MMT suggests the organic modification of Na-MMT using triethanolamine and methyl iodide.

![Graph showing tensile test results for soy-PU and nano soy-PU](image)

**Figure 1.** Tensile test results for soy-PU and nano soy-PU

<table>
<thead>
<tr>
<th>Tensile Test Results of Soy-PU Nanocomposites</th>
<th>Tensile Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat soy-PU</td>
<td>233.07±11.97</td>
<td>15.38±0.62</td>
<td>85.02±6.78</td>
</tr>
<tr>
<td>Soy-PU nanocomposite M-MMT-1%</td>
<td>280.54±8.73</td>
<td>12.24±0.86</td>
<td>50.08±8.93</td>
</tr>
</tbody>
</table>

**X-Ray Diffraction**

XRD is a useful method to measure and study the intercalation/exfoliation of polymer matrices into silicate layers. MMT consists of hundreds of individual layers and the distance between two adjacent layers is called d-spacing or basal spacing. The layers are approximately 1nm thick and possess high aspect ratios. The interlayer spacing of MMT clay can be calculated from the angle of diffraction using the Bragg equation. Whenever the distance between the galleries increases, the peak tends to shift towards the lower angle. Figure 3 shows the XRD spectrum of Na-MMT and M-MMT. Na-MMT had a diffraction peak at around 2θ=8.25° which corresponds to a basal spacing of 10.72 Å while M-MMT spectrum showed a sharp peak at an angle of 2θ=6.13° resulting in a gallery distance of approximately 14.43 Å.
These results show that the modification of Na-MMT with triethanolamine and methyl iodide solution increased the distance between the clay galleries which in turn results in better exfoliation of PU polymer chains inside the clay galleries. Figure 4 shows the XRD spectra of soy-PU nanocomposites when compared to the neat resin and the M-MMT clay. Soy-PU/M-MMT nanocomposite showed a peak of very low intensity corresponding to 14.43 Å. Low intensity peak for the soy-PU/M-MMT nanocomposites suggests an intercalated structure.

Figure 2. FTIR spectrum of organically modified MMT and Na-MMT
Figure 3. XRD spectrum of organically modified MMT and Na-MMT

Figure 4. XRD spectrum of PU nanocomposite
**Differential Scanning Calorimetry**

Glass transition temperature ($T_g$) of nanocomposites is mainly affected by (1) polymer chain movement inside the clay galleries (2) organophilic nature of organic modifiers in the silicate galleries (3) reduction in the cross linking density of the polymer system due to the presence of non homogenous silicate layers (4) high aspect ratio of clay galleries.

Polymer chain movements in the clay galleries depend on the reactivity of polymer with modifying surfactants in the clay galleries [16]. Higher the organophilicity, higher is the interaction between polymer chains and clay galleries resulting in better physical properties such as strength, modulus, degradation temperature, $T_g$ etc. Presence of interactions between polymer and the organic surfactants in the clay galleries decreases the cross linking density of polymer thus reducing the $T_g$. Clay galleries with their larger aspect ratio tend to act as soft segments rather than rigid plates. This results in the higher mobility of polymer chains thus affecting $T_g$ [17, 18].

Figure 5 shows the glass transition region of the neat soy-PU resin system and the soy-PU nanocomposites synthesized using triethanolamine and methyl iodide. $T_g$ for base soy-PU and soy-nano PU are tabulated in Table 5. $T_g$ was observed to be 32.95 °C, 39.22 °C for base PU resin system and soy-PU nanocomposite respectively. Increase in $T_g$ and tensile modulus suggests the high interaction between the PU polymer chains and clay galleries. Decrease in $T_g$ due to the decrease in cross linking density of the PU polymer was not observed which suggests that the stoichiometric ratio used during the synthesis of soy-PU nanocomposites was appropriate.

![Figure 5. DSC thermograms showing $T_g$ of soy-PU and soy-PU nanocomposite](image-url)
### Table 2. DSC test result for the aliphatic soy-PU and soy-PU nanocomposite

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat soy-PU</td>
<td>32.95</td>
</tr>
<tr>
<td>Soy-PU nanocomposite-</td>
<td></td>
</tr>
<tr>
<td>M-MMT-1%</td>
<td>39.22</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

Surface modification of Na-MMT was successfully conducted using triethanolamine and methyl iodide solution. FTIR results showed the presence of organic groups in M-MMT suggesting the organophilic nature of M-MMT. Soy-PU nanocomposites were synthesized by exfoliating the polyol component in the M-MMT and subsequently reacting with aliphatic isocyanate. Higher basal spacing of M-MMT and M-MMT/soy-PU nanocomposites confirmed the presence of intercalated structure in the soy-PU nanocomposites. Due to better intercalation of PU chains into the clay galleries, tensile properties increased by 20% with incorporation of just 1% of modified MMT clay into the soy-PU resin system. Better interaction between the polymer chains and the clay galleries resulted in higher $T_g$ for soy-PU nanocomposites. The addition of modified clay particles into the aliphatic PU resin system increased the mechanical properties as well as $T_g$ while being less brittle when compared to the aromatic resin system. Soy-based aliphatic PU nanocomposites synthesized using organically modified MMT will result in low cost, high performance and environmentally benign composite materials. These soy-based composites have huge prospects of being employed successfully in many areas such as transportation, infrastructure and naval applications.

### ACKNOWLEDGEMENTS

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REFERENCES


