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CENTER FOR TRANSPORTATION INFRASTRUCTURE AND SAFETY

Soy-Based UV Resistant Polyurethane Pultruded Composites

by

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NUTC R263

A National University Transportation Center
at Missouri University of Science and Technology

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16. Abstract

Aliphatic polyurethane (PU) nanocomposites were synthesized using organically modified nanoclays. X-Ray diffraction results confirmed good exfoliation of nanoclay particles in the PU resin system. With the addition of just 1% of nanoclay in the base resin, PU nanocomposites showed significantly higher strength and modulus. Soy-PU resin system with increased soy content (30% Soy-PU) was obtained from Bayer MaterialScience. Neat resin samples were manufactured using the aliphatic and aromatic 30% Soy-PU resin system. Results show that there is no significant change in the glass transition temperature for the Soy-PU with 30% soy content when compared to the 20% Soy-PU and base PU resin systems. Glass fiber reinforced polyurethane composites were manufactured using aromatic 30% Soy-PU resin system and modified pultrusion process. Low velocity impact tests were conducted on the pultruded PU composites. Results indicate that increase in the soy content in PU resin system does not result in the degradation of composite properties. Incorporation of pigments during the pultrusion of PU composites was also studied. Pigments such as zinc oxide and zinc sulphide (ZnS) were studied to obtain the required “white” coloration to the PU composites. ZnS was chosen for the pultrusion process due to its low corrosive property. Pigmented pultruded composites were manufactured using the base PU resin and ZnS. Soy-based, pigmented pultruded PU composites manufactured during this study will have higher UV resistance and comparable mechanical properties when compared to the conventional PU pultruded composites. These Soy-based composites will find numerous applications in the automotive, marine and housing industries.

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ADVANCED MATERIALS AND NON-DESTRUCTIVE TESTING TECHNOLOGIES

Sequential #: (UTC Office will assign #)

Project Title: Soy-Based UV Resistant Polyurethane Pultruded Composites

Matching Research Agency: United Soybean Board

Principal Investigator: K. Chandrashekhara, Curators' Professor, Department of Mechanical and Aerospace Engineering

Project Duration: 09/01/2010 – 12/31/2011

Project Summary:

Aliphatic polyurethane (PU) nanocomposites were synthesized using organically modified nanoclays. X-Ray diffraction results confirmed good exfoliation of nanoclay particles in the PU resin system. With the addition of just 1% of nanoclay in the base resin, PU nanocomposites showed significantly higher strength and modulus. Soy-PU resin system with increased soy content (30% Soy-PU) was obtained from Bayer MaterialScience. Neat resin samples were manufactured using the aliphatic and aromatic 30% Soy-PU resin system. Results show that there is no significant change in the glass transition temperature for the Soy-PU with 30% soy content when compared to the 20% Soy-PU and base PU resin systems. Glass fiber reinforced polyurethane composites were manufactured using aromatic 30% Soy-PU resin system and modified pultrusion process. Low velocity impact tests were conducted on the pultruded PU composites. Results indicate that increase in the soy content in PU resin system does not result in the degradation of composite properties. Incorporation of pigments during the pultrusion of PU composites was also studied. Pigments such as zinc oxide and zinc sulphide (ZnS) were studied to obtain the required "white" coloration to the PU composites. ZnS was chosen for the pultrusion process due to its low corrosive property. Pigmented pultruded composites were manufactured using the base PU resin and ZnS. Soy-based, pigmented pultruded PU composites manufactured during this study will have higher UV resistance and comparable mechanical properties when compared to the conventional PU pultruded composites. These Soy-based composites will find numerous applications in the automotive, marine and housing industries.

Summary of Results:

Nanoclay materials compatible for the PU resin system were synthesized using ion exchange process. Nanocomposites were manufactured using the modified clay and the Soy-based PU resin system. Significant increase in the properties

was observed for the PU nanocomposites. Pultruded PU composites were manufactured using Soy-PU resin system with increased soy content (30%). Pigmented PU composites were also manufactured using ZnS as a pigment. UV resistant, bio-based PU composites manufactured at Missouri S&T have comparable properties to that of the base PU composites. Hence, Soy-PU can be used as an alternative to the conventional petroleum based PU resin system without any property degradation.

Synthesis of PU Nanocomposites:

Dispersion of commercially available montmorillonite clay (MMT) in the PU raw materials involved ultrasonication which resulted in the rapid increase in temperature. This resulted in the inferior properties of the PU nanocomposites. Hence, different approach was followed to synthesize aliphatic nanocomposites. The base MMT was modified using triethanolamine and methyl iodide mixture to make Na-MMT more organophilic.

FTIR tests were conducted using a Nicolet Nexus 470 E.S.P. spectrophotometer over the 4000 to 400 cm-1 spectral range. The spectral absorption of Sodium montmorillonite (Na-MMT) and surface modified montmorillonite (M-MMT) is shown in Figure 1. 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. Peaks corresponding to 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.

XRD is an useful method to measure and study the intercalation/exfoliation of silicate layered nanocomposites. The interlayer spacing of MMT clay can be calculated from the peak intensity angle of diffraction using the Bragg equation. 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. Whenever the distance between the galleries increases, the peak tends to shift towards the lower angle.

Figure 2 shows the XRD spectrum of M-MMT and commercially available MMT clays. Na-MMT shows a peak around $2\theta=8.25^{o}$ which corresponds to a basal spacing of 10.72 Å while M-MMT spectrum shows a sharp peak at an angle of $2\theta=6.125^{o}$ 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. Figure 3 shows the XRD spectra of Soy-PU nanocomposites (with 1% by wt of M-MMT) 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.

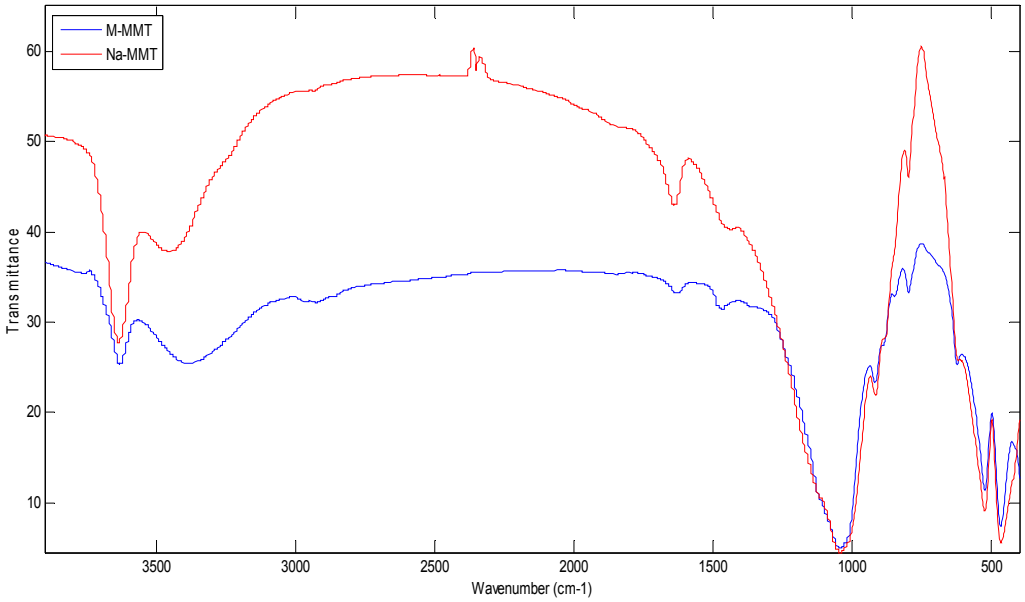

Figure 1. FTIR spectrum of organically modified MMT and Na-MMT

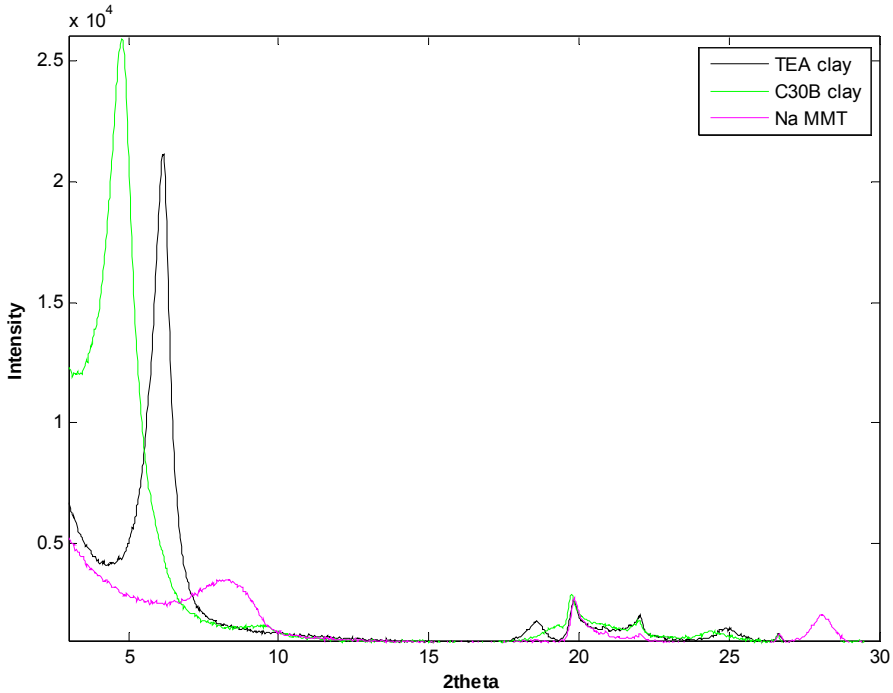

Figure 2. XRD spectrum of Modified clays and Na-MMT

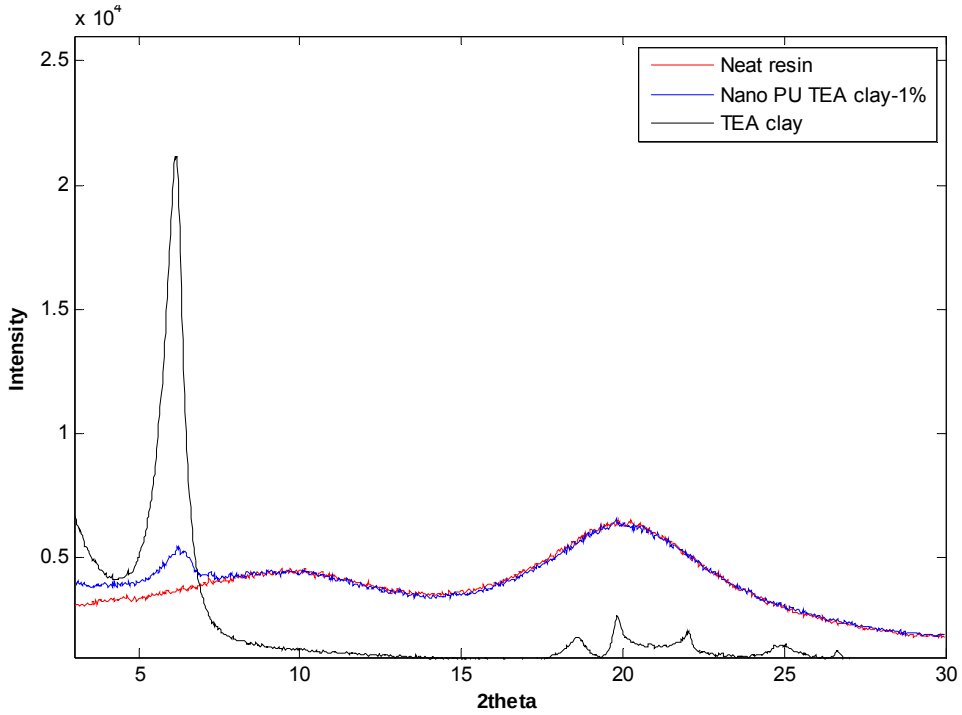

Figure 3. XRD spectrum of PU nanocomposite

Differential Scanning Calorimetry (DSC) tests were performed using a TA Instrument model Q2000. Cured neat aliphatic PU and M-MMT/PU nanocomposites were weighed to around 5mg 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 -30ºC to 200ºC to measure the resulting glass transition temperature. The glass transition temperature was reported as the inflection point on the glass transition region.

Polymer chain movements in the clay galleries depend on the reactivity of polymer with modifying surfactants in the clay galleries. Higher the organophillicity, higher is the interaction between polymer chains and clay galleries resulting in better physical properties such as strength, modulus, degradation temperature, glass transition temperature (Tg) etc. Presence of interactions between polymer and the organic surfactants in the clay galleries decreases the cross linking density of polymer thus reducing the Tg. Clay galleries with their larger aspect ratio tend to act as soft segments rather than rigid plates. The change in the softness of the segments results in the higher mobility of polymer chains thus affecting Tg. Figure 4 shows the glass transition region of the neat Soy-PU resin system and the Soy-PU nanocomposites synthesized using triethanolamine and methyl iodide. Tg for base Soy-PU and Soy-nano PU are tabulated in Table 1. Tg was observed to be 32.95°C, 39.22°C for base PU resin system and Soy-PU nanocomposite respectively.

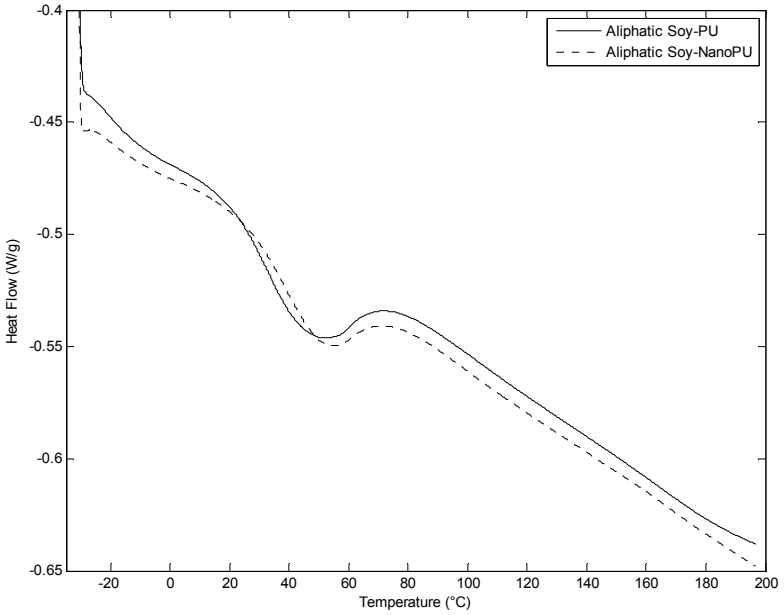

Figure 4. DSC thermograms showing Tg of Soy-PU and Soy-PU nanocomposites

Table 1. DSC test results for the aliphatic Soy-PU and Soy-PU nanocomposites

	Glass Transition Temperature (ºC)
Neat Soy-PU	32.95
Soy-PU nanocomposite-M-MMT-1%	39.22

Tensile tests were conducted on the aliphatic PU nanocomposites in accordance with ASTM D638 standard. Five specimens each were tested. A cross head speed of 2 in./min (50 mm/min) was used during the testing. Figure 5 shows the tensile properties of the 20% Soy-based PU and 20% Soy-based PU nanocomposite. Table 2 tabulates the tensile properties of the base Soy-PU and Soy-PU nanocomposite. Tensile modulus of Soy-PU nanocomposite increased by nearly 75% whereas, tensile strength was found to increase by 125% when compared to the base Soy-PU resin system. This considerable increase in the tensile properties can be attributed to the proper dispersion of the nanoparticles in the PU resin system. This phenomenon results in the lower tensile failure strains for the Soy-PU nanocomposites. The possible explanation to this phenomenon is that the silicate layers constrain the matrix so that plastic deformations are prevented in the nanocomposites. Increase in tensile strength and tensile modulus suggests the high interaction between the PU polymer chains and clay galleries. Decrease in Tg 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.

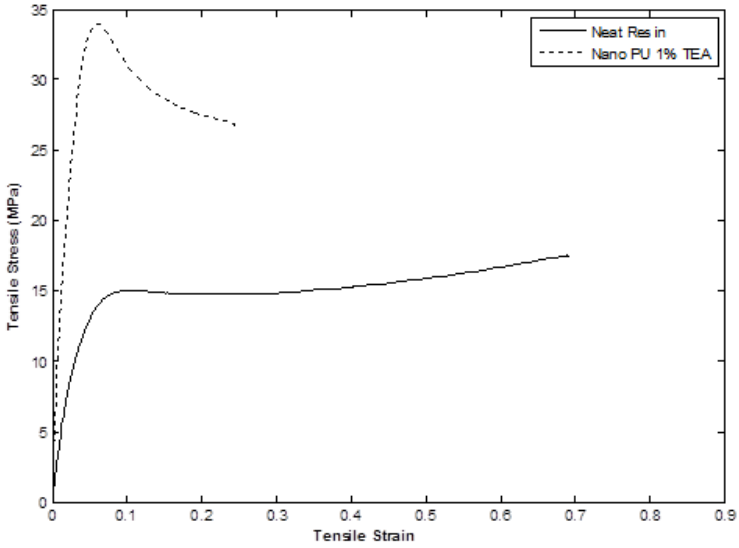

Figure 5. Tensile stress vs strain curve for aliphatic Soy-PU nanocomposite

Table 2. Tensile test results of Soy-PU nanocomposites

	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain to Failure (%)
Neat Soy-PU	353.23±40.8	18.73±1.41	66.2±5.42
Soy-PU nanocomposite M-MMT-1%	791.49±31.46	32.86±1.21	25.3±0.52

Degradation of base clay (Na-MMT) and the modified clay synthesized at Missouri S&T with increase in temperature is calculated using Thermogravimetric Analysis. Clays were heated to 800°C with a ramp rate of 10°C/min. Modified clay showed the evolution of organic groups at around 290°C and 575°C (Figure 6). Intensity of peaks for the modified clay is higher than that of the Na-MMT. This suggests the presence of organic groups in the modified MMT clay thus making the modified clay organophillic. Increase in the organophillic nature of the clay material results in the better interaction of clay particles in the polyol system.

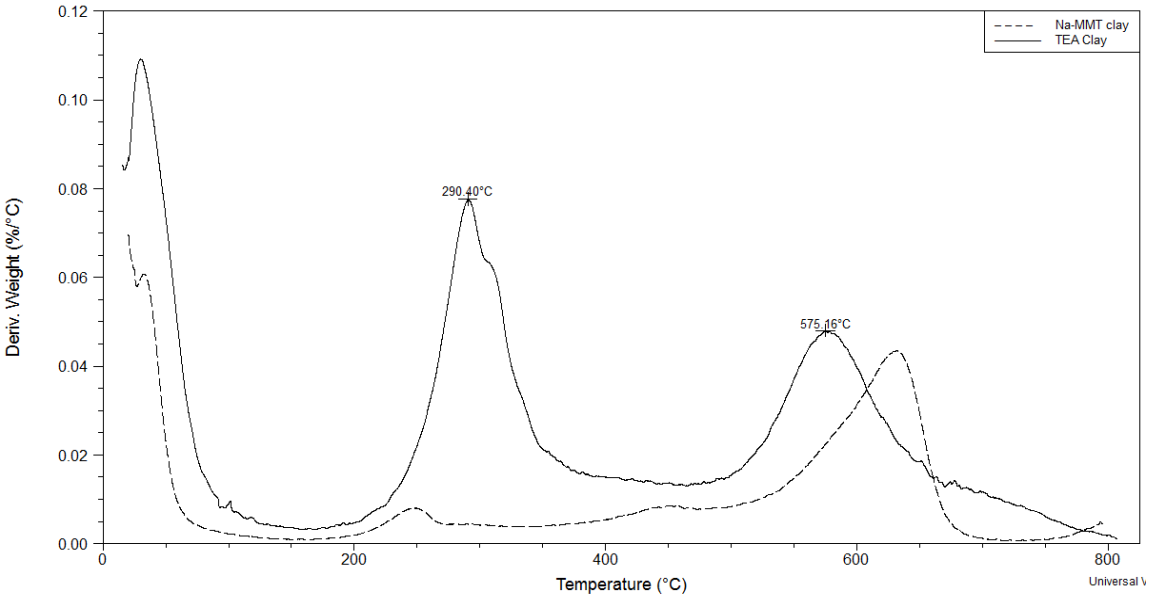

Figure 6. Thermogravimetric analysis of modified clay synthesized

Soy-based PU samples with 30% soy content:

Soy-based PU specimens were prepared using the polyol with higher soy content (30%). This polyol has been recently obtained from Bayer MaterialScience and it is a blend of 30% soybean raw material and polyether polyol. Aromatic and aliphatic PU dog-bone specimens were cast using these new polyol and the isocyanate raw materials. Process variables used during this process are tabulated in Table 3.

Table 3. Process variables

	Aliphatic PU	Aromatic PU
Stoichiometric ratio (polyol : isocyanate) by weight	1.56	1.15
Preheating temperature of the mold	110°C	50°C
Cure cycle	80°C for 1 hour and 125°C for 10 hours	50°C for 1 hour and 110°C for 1 hour

DSC tests were performed using a TA Instrument model Q2000. Cured aliphatic PU samples were weighed to around 5 mg and were each placed in an aluminum crucible. The cell containing the samples was quickly cooled using a chiller mechanism and subjected to subsequent scanning from -40ºC to 150ºC at a rate of 10˚C/min to measure the glass transition temperature. The glass transition temperature was reported as the inflection point on the glass transition region. Figure 7 shows the DSC scan of PU polymer samples. Table 4 shows the glass

transition temperatures of aliphatic PU polymer samples. Results show that there is no significant change in the glass transition temperatures of the aliphatic PUs with increase in the soy content.

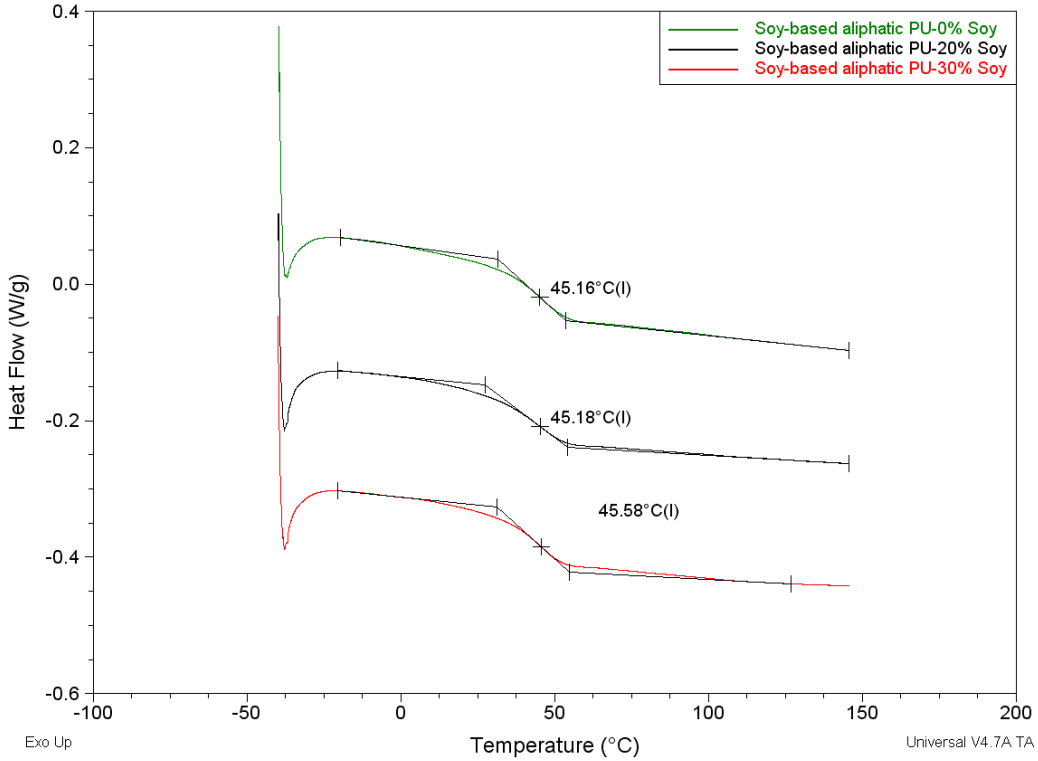

Figure 7. DSC scanning of PU polymer samples depicting glass transition temperature

Table 4. Glass transition temperature of PU polymer samples

	Glass Transition Temperature (˚C)
Base aliphatic PU	44.4±0.93
20% Soy-based aliphatic PU	45.53±1.30
30% Soy-based aliphatic PU	44.46±1.31

Figure 8 shows the glass transition behavior of aromatic PU polymer samples. Tg of aromatic PU samples are tabulated in Table 5. Base aromatic PU has the highest Tg, closely followed by 30% Soy-PU and 20% Soy-PU. 30% Soy-PU aromatic resin showed almost equivalent Tg to that of the base aromatic PU resin.

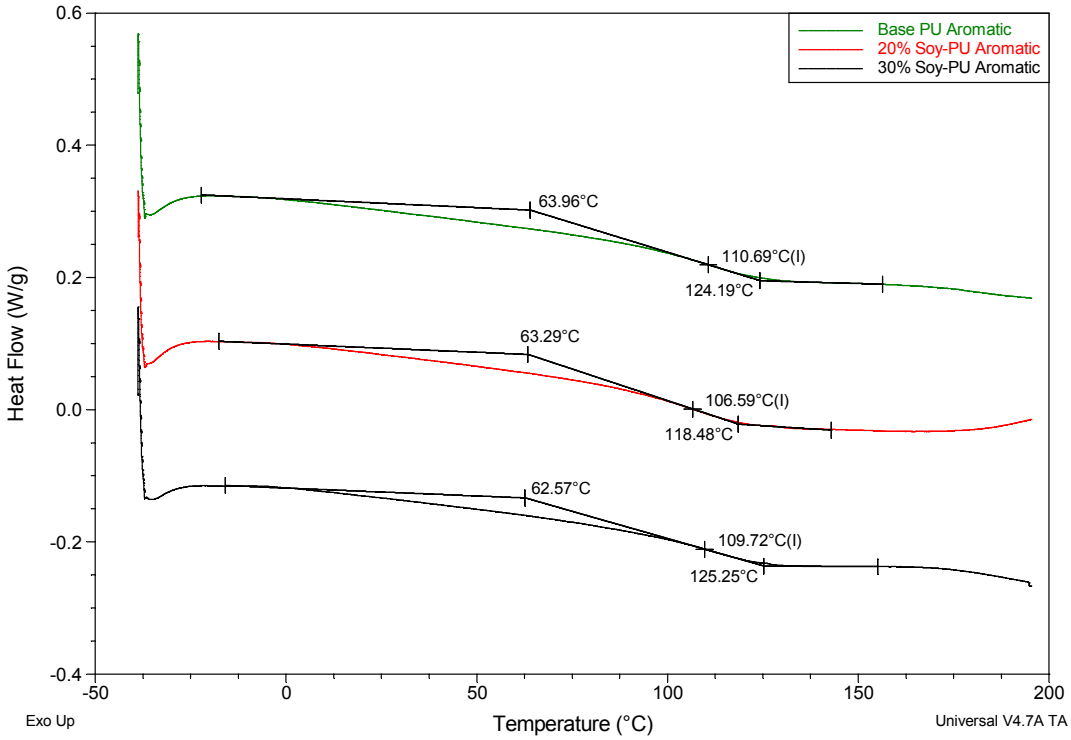

Figure 8. Glass transition behavior of aromatic PU resin systems compatible for pultrusion

Table 5. Glass transition temperatures of pultrudable aromatic Soy-PU resin systems

	Glass Transition Temperature (˚C)
Aromatic Base PU	110.69
Aromatic 20% Soy-PU	106.59
Aromatic 30% Soy-PU	109.72

Manufacturing of pultruded 30% Soy-PU composites:

Pultruded PU composite parts were manufactured using the modified pultrusion process and aromatic 30% Soy-PU resin system. The glass fibers were passed through preforming guides into the injection box and then pulled through the die to avoid the entanglement and achieve uniform fiber distribution. The pultrusion die cavity is 2 in. (50 mm) wide and 0.125 in. (3 mm) thick. Sixty fiber tows were used to obtain a fiber volume fraction of approximately 64%. Polyol and isocyanate were fed into the two resin tanks of the metering unit. The die was maintained at 270°F (132°C).

Bio-based aromatic PU composites were tested for their impact properties. A Dynatup Instron Model 9250 Impact Testing Machine with impulse control and data system was used to carry out the low velocity impact tests. As the pultruded

samples were only 2 in. (50 mm) wide, a fixture with an opening of 1.75 in. (44.5 mm) x 1.75 in. (44.5 mm) was used for the impact tests. The impactor had a mass of 6.48 kg and a diameter of 0.5 in. (12.5 mm). Three energy levels of 15 J, 20 J and 25 J were considered to induce barely visible damage, clearly visible damage and significant damage on the specimens. Five specimens were tested for each resin formulation at each energy level.

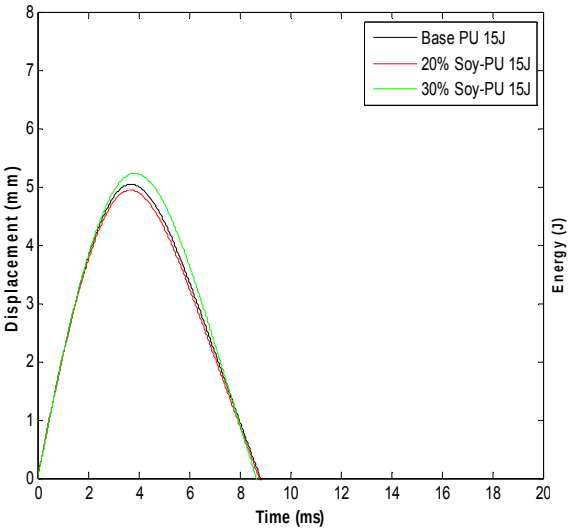

Figure 9. Energy vs Time at 15J of Impact Energy

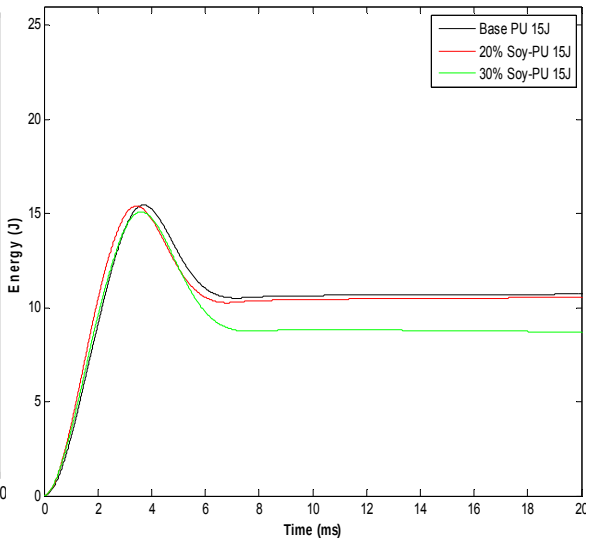

Figure 10. Displacement vs Time at 15J of Impact Energy

Figure 9 shows the energy vs time curves for base PU, 20% Soy-PU and 30% Soy-PU at 15 J of energy. The loading phase of the curve indicates the amount of energy absorbed by the specimen and the unloading phase depicts the amount of energy given out by the specimen to the impactor due to its elasticity. Flat region of the energy curves indicates the net energy absorbed by the specimen. 30% Soy-PU aromatic composites absorbed more energy due to their elastic nature. Displacement vs time curves for the pultruded PU composites at 15 J are shown in Figure 10. Pultruded composites manufactured using 30% Soy-PU showed more deflection when compared to other PU composites. This suggests that 30% Soy-PU absorbed more energy by elastic deformation at low impact energies.

Manufacturing of pigmented PU composites:

Pigmented PU pultrusion was conducted to manufacture white colored PU composites. Titanium dioxide (TiO_2) is generally used as a primary pigment to manufacture white colored composites. However, due to its high abrasive properties TiO_2 is not preferred in the pultrusion process thus causing damage to the pultrusion die. ZnS is generally used as a secondary pigment to manufacture pigmented composites. In the present work, ZnS is used for manufacturing the pigmented PU composites. Various percentages of ZnS loading by weight were

used to manufacture pigmented PU samples. 6 wt% was chosen for the present work. Prior to the pultrusion process, ZnS was dispersed in the base polyol using high shear mixing and ultrasound to achieve uniform coloration in the polyol component. Pigmented polyol was then transferred into the polyol raw material container in the metering unit. Viscosity of the PU resin system increased due to the addition of ZnS. This resulted in the decrease in pultrusion speed during the manufacturing. Figure 11 shows the unpigmented and pigmented glass fiber reinforced PU composites manufactured at Missouri S&T.

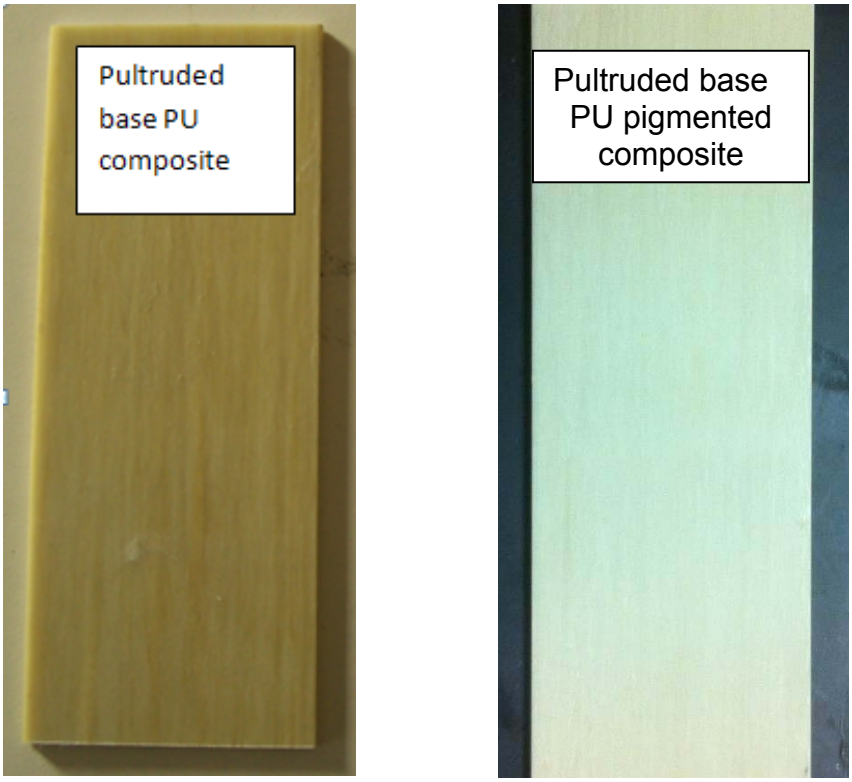

Figure 11. PU composites manufactured at Missouri S&T

Publications:

1. R. R. Vuppalapati, V. G. K. Menta, T. Schuman and K. Chandrashekhara, "**Synthesis and Characterization of Soy-based Aliphatic Polyurethane Nanocomposites Compatible for Pultrusion**," *SAMPE Technical Conference*, Long Beach, CA, pp.1-12, May 23-26, 2011

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