Center for Transportation Infrastructure and Safety

Soy-Based UV Resistant Polyurethane Pultruded Composites

by

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Technical Report Documentation Page

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16. Abstract

Polyurethane (PU) resin systems exhibit superior strength and damage tolerance relative to unsaturated polyester and vinylester pultrusion resins. Also, high pultrusion line speeds can be achieved using PU resins. In our previous study, we have successfully evaluated pultrudable PU with aromatic isocyanate and soy-based polyol (with 20% soy content). The performance of the soy-based resin is comparable to the base PU resin. However, aromatic PU based composites have poor environmental stability under UV light exposure and require specialized painting to provide protection. Aliphatic PU resins provide improved UV resistance but exhibit lower mechanical performance in comparison to aromatic polyurethanes. In the proposed work, we will investigate pultrudable PU resin systems with aromatic and aliphatic isocyanates, and soy-polyol. Neat resin coupons and pultruded composite parts will be manufactured using the developed aromatic and aliphatic PU resin systems. Also, parts will be manufactured by incorporating nano-engineered fillers in the aliphatic soy-based PU resin system to compensate the loss of mechanical performance over aromatic PU resins. The cure kinetics of polyurethanes will be studied by differential scanning calorimetry (DSC) and the reaction rates of the aliphatic and aromatic polyurethanes will be compared. Mechanical performance will be evaluated by conducting tensile, flexure and impact tests. The economics of aromatic system and aliphatic systems will be assessed.

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PHASE I - REPORT
MISSOURI S&T – NATIONAL UNIVERSITY TRANSPORTATION CENTER
ADVANCED MATERIALS AND NON-DESTRUCTIVE TESTING TECHNOLOGIES

Sequential #: R255 - 00027343

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: 09/01/2009 – 08/31/2010

Project Summary:

Glass fiber reinforced polyurethane composites were manufactured with aliphatic and aromatic PU/Soy-PU resin systems using the pultrusion process. The PU/Soy-PU resin systems were obtained from Bayer MaterialScience. The conventional pultrusion set-up at Missouri S&T was modified for PU pultrusion using a metering unit and an injection box. The pultruded panels were 2 in. wide 0.125 in. thick. Tension and impact tests were conducted on the pultruded PU composites. Results indicate that aliphatic PU composites are more flexible and have better impact properties at lower energy levels than their aromatic counterparts. Also, neat resin dog-bone samples were manufactured using aromatic PU/Soy-PU resin systems. Soy-based neat resin coupons showed comparable properties to that of the base PU resin systems. Future work in the next phase of the project will include synthesizing and mechanical characterization of PU nanocomposites.

Summary of Results:
Glass fiber reinforced composites are finding various applications in automotive, housing and transportation sectors due to their low weight, high corrosion resistance and moisture/chemical stability. These advantages make composites an alternative to the conventionally used materials. Pultrusion is one of the economical composite manufacturing processes due to its high manufacturing speeds and low labor costs. Pultrusion involves the fiber reinforcements mixed with resin system pulled through a heated die resulting in a solid composite part. Reinforcements which can be used during pultrusion include carbon, graphite, glass and natural fibers while, epoxy, polyester, vinyl ester and phenolics are used as resin matrix. Polyurethane (PU) resin system has been in use for a long time due to its better mechanical properties and chemical resistance. PUs were not used until recently in the pultrusion process due to their low pot life and high viscosity.

PUs are generally characterized as aromatic and aliphatic resin systems. Aromatic PUs generally have higher mechanical properties when compared to the aliphatic resin systems due to their chemical structure, but exhibit poor UV resistance. Bayer MaterialScience has developed a thermoset bio-based PU resin system which can be used in the pultrusion process. Due to the low pot life of PU, a metering unit is used for mixing the PU resin system during the pultrusion process to ensure proper mixing and avoid inclusion of air/moisture during the mixing process. In the present work, pultruded soy-PU composites were manufactured and characterized.

Manufacturing of Aromatic PU Neat Resin Samples:

Raw materials required for manufacturing neat-resin polyurethane samples are highly susceptible to moisture. Care has to be taken not to induce moisture in the raw materials during the mixing process. Polyol and Isocyanate components were mixed thoroughly and poured into metal molds. These samples were then heated in an oven at 50°C for one hour and post cured at 110°C for one hour. Neat resin samples were tested for their tensile properties. Tension tests were conducted according to ASTM D638 "Standard Test Method for Tensile Properties of Plastics". Tensile modulus, tensile strength and failure strain are listed in Table 1. Results suggest that the properties of soy-based PU are comparable to that of the base PU resin system.

Table 1: Neat resin tension test results for Base PU and Soy-PU

	Tensile Modulus (GPa)	Tensile Strength (MPa)	Failure Strain (%)
Base PU	2.60 ± 0.08	64.45 ± 1.38	11.00 ± 1.64
Soy-based PU	2.70 ± 0.14	67.17 ± 2.43	11.76 ± 1.05

Manufacturing of Pultruded Aromatic PU Composites:

Pultruded PU composite parts were manufactured using the metering unit, injection box and the modified pultrusion process. Two types of aromatic PU resins namely base PU and soy-based PU were used. 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. wide and 0.125 in 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 and an initial pull speed of 6 in/min was maintained. The pull speed was then increased to 30 in/min. The pull speed and the die temperature were kept constant while pultruding base PU and soy-based PU resin systems. Figure 1 shows the pultruded parts.

Pultruded samples were 2 in. wide and 0.125 in. thick and were tested for their tensile properties in accordance with ASTM 3039 "Standard Test Method for

Tensile Properties of Polymer Matrix Composite Materials". The tensile test specimens were 6 in. x 0.5 in. x 0.125 in. in size and tested at a crosshead speed of 0.05 in/min. Figure 2 shows the tensile test setup. Figure 3 shows the tensile stress vs. strain for base PU and soy-based PU composites. Tensile properties are listed in Table 2. Results show that the soy-PU and base PU composites have comparable properties.

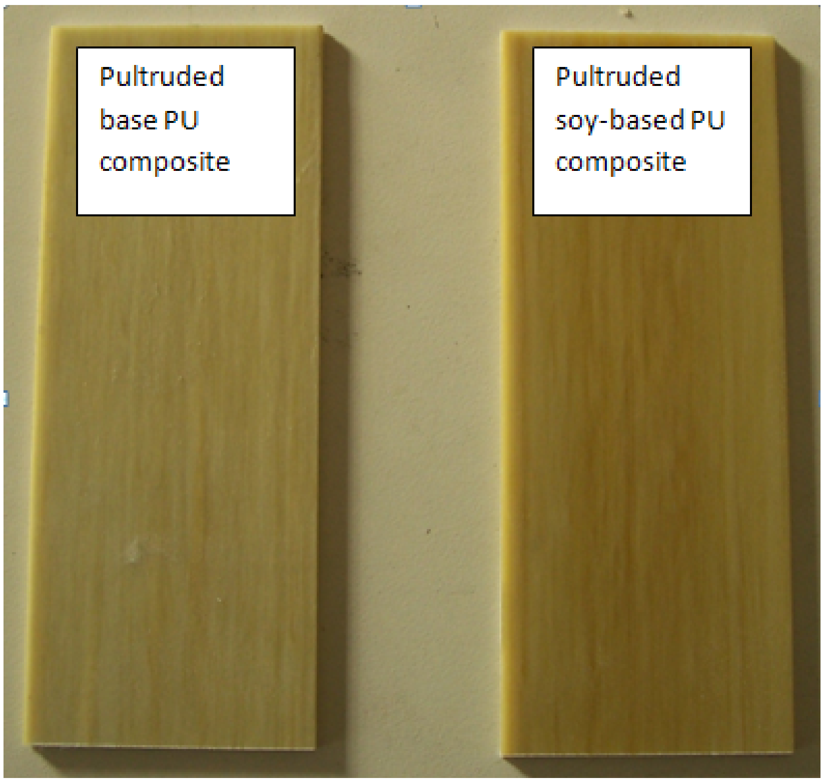

Figure 1. Pultruded parts manufactured at Missouri S&T

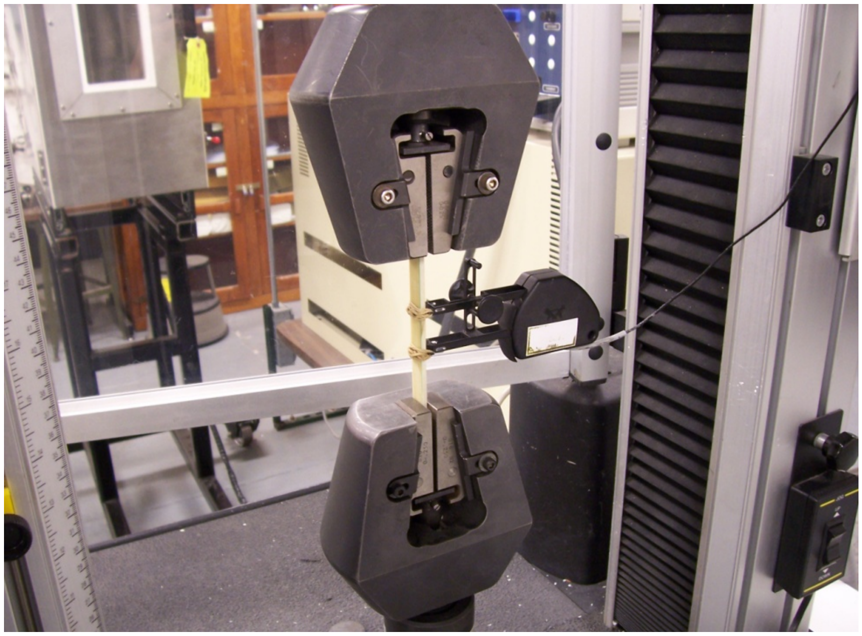

Figure 2. Tensile test setup at Missouri S&T

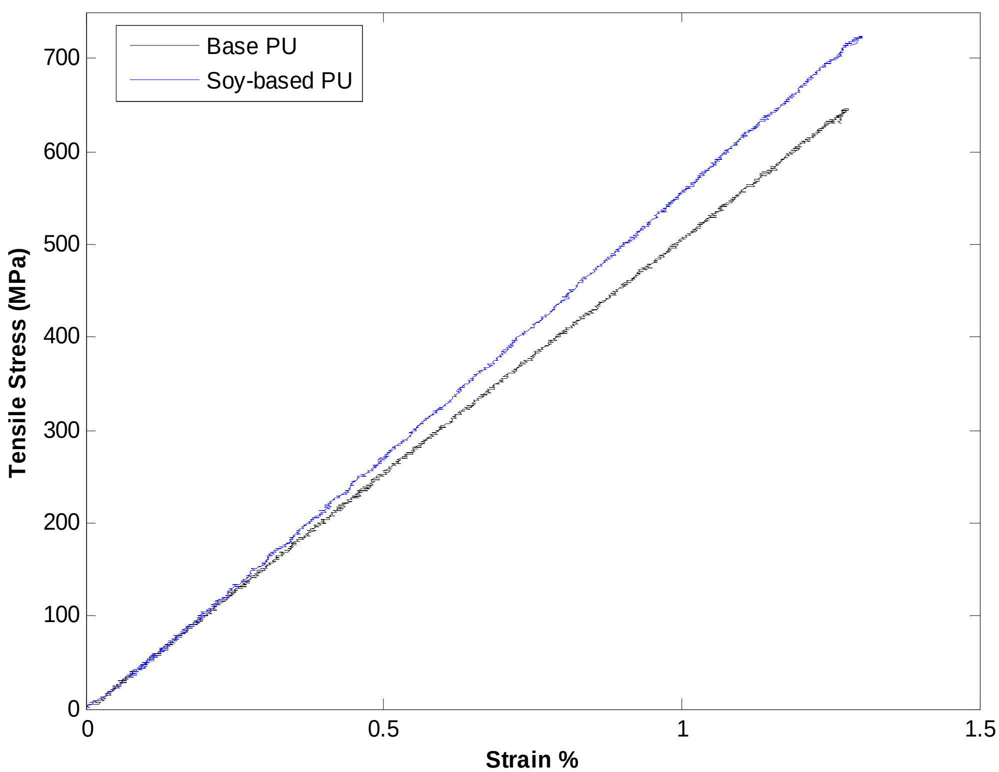

Figure 3. Tensile stress vs strain for pultruded PU composites

Table 2. Tension test results for Base PU and Soy-PU pultruded aromatic composites

	Tensile Modulus (GPa)	Tensile Strength (MPa)	Failure Strain (%)
Base PU composite	52.80 ± 3.43	630.35 ± 24.06	1.21 ± 0.065
Soy-PU composite	56.15 ± 2.6	700.10 ± 72.17	1.26 ± 0.099

Manufacturing of Aliphatic pultruded PU Composites:

Glass fiber reinforced PU composites were manufactured with an aliphatic PU resin system. Polyol was mixed to maintain homogeneity before and during the pultrusion process. Metering unit was set to mix the raw materials in the required ratio (polyol: isocyanate = 1:1.56 by weight). The pultrusion die was heated to the suggested temperature range and the line speed was maintained at 30 in/ minute. Figure 4 shows the cured aliphatic PU composite pulled through the pultrusion die.

Pultruded aliphatic and 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. wide, a fixture with an opening of 1.75 in. x 1.75 in. was used for the impact tests. The impactor had a mass of 6.48 kg. and a diameter of 0.5 in. Two energy levels of 2 J and 15 J were considered to induce barely visible damage and clearly visible damage on the specimens. Five specimens were tested for each resin formulation at each energy level.

Figure 4. Pultruded aliphatic PU composite manufactured at Missouri S&T

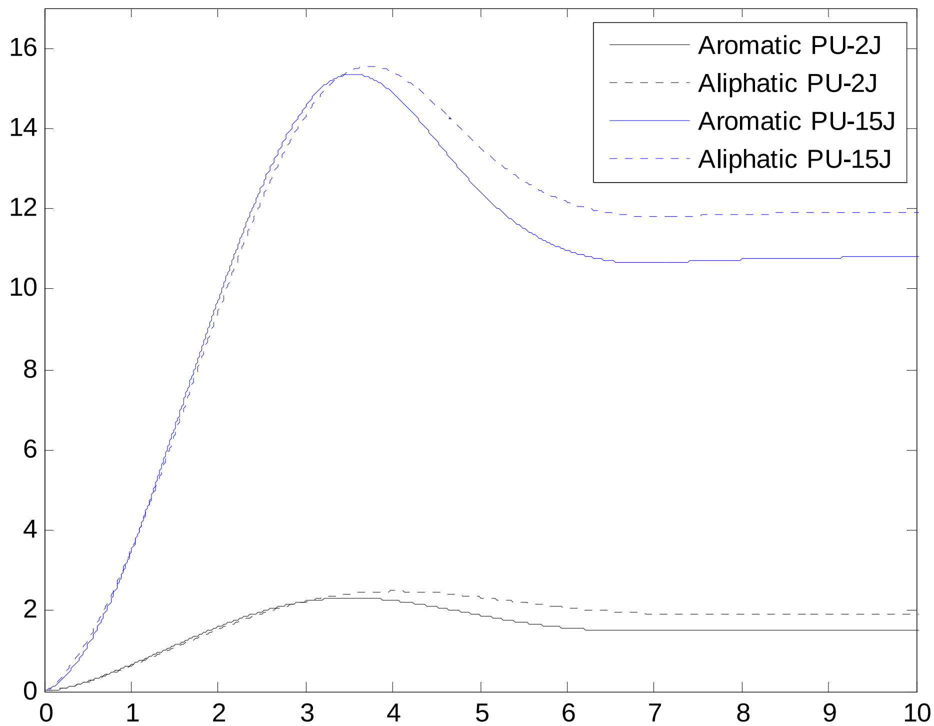

Figure 5. Energy vs time plot for glass reinforced PU composites

Figure 5 plots the net energy absorbed by the aromatic and aliphatic PU composites after the impact. 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. Aliphatic PU composites absorbed more energy due to their elastic nature. Figure 6 shows the variation of velocity of the impactor as a function of time. Rebound velocity was higher in the case of aromatic PU composites confirming that they are stiffer than the aliphatic PU composites. Figure 7 shows the load vs displacement curve during the impact test. It was observed that aromatic PU composites had higher slope during the loading phase. The slope of the force-indentation curve during the loading phase (also known as the contact stiffness), is higher for aromatic composites indicating that the aromatic composites are stiffer than their aliphatic counterparts.

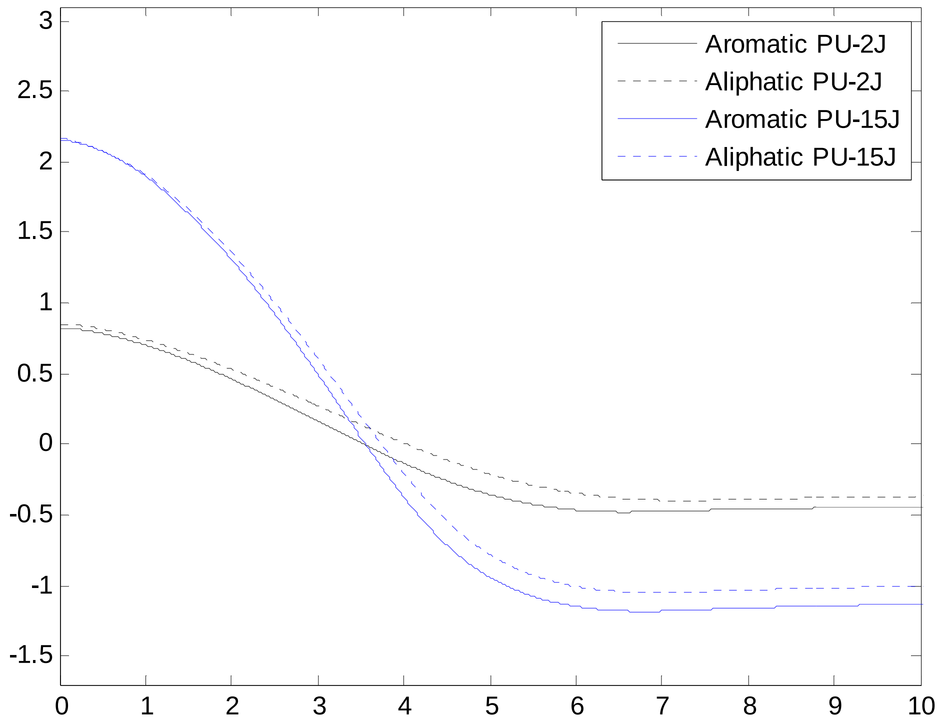

Figure 6. Velocity vs time

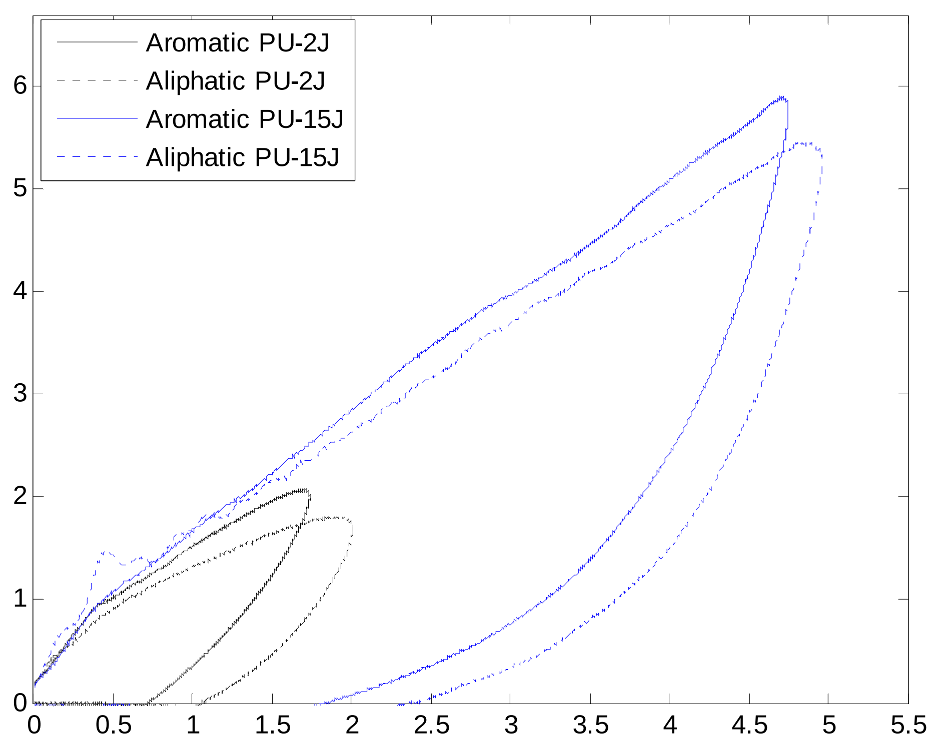

Figure 7. Load vs displacement curve