Affordable composites using renewable materials

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Abstract

Bio-based composite products are finding widespread applications due to their low cost and environmental acceptability. Development of new bio-based raw material and automated composite manufacturing is the focus of the present study. Pultrusion is the fastest and the most cost-effective composite manufacturing processes, and is well suited for high volume production for structural applications. With growing opportunities to use pultruded composites, the development of cost-effective pultrudable resin system is of great interest. A novel soy-based epoxy resin namely epoxidized allyl soyate is synthesized at the University of Missouri-Rolla. This resin forms co-polymers with the base Shell Epon epoxy resin in varied proportions to yield a family of polymeric networks. Glass fiber reinforced composite specimens are manufactured using a Durapul 6000 Labstar Pultrusion machine. The lubricity of soy-based resin significantly reduces the pull force. Mechanical tests show that pultruded composites with soy-based co-resin systems possess comparable or improved structural performance characteristics such as flexural strength, modulus and impact resistance.

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1. Introduction

Bio-based products rely upon plant-derived materials as their main ingredients. They are made from a renewable resource and generally do not contain environmentally damaging substances. By using bio-based products, the user is avoiding reliance on petroleum resources. Unsaturated triglyceride oils such as soybean, crambe, linseed and castor oil constitute one major class of renewable resources [1]. The main composition of these triglyceride oils is saturated and unsaturated fatty acids. They can be polymerized to form elastomeric network and promise alternative materials resources to petrochemical derived resin [2]. Directly using these fatty acid or their derivatives from some chemical modifications are emerging applications which include painting, coating, varnishes, cosmetics and more recently polymer and composites. Among the renewable triglyceride oils, soybean oil is attracting increased attention for industrial application because it is readily available for production in large volumes.

The largest category of industrial soybean oil use is in plastics and resins. Epoxidized soybean oil (ESO) is currently being used mainly as plasticizer or stabilizer to modify the properties of plastic resins such as PVC. ESO can be used as reactive modifier and diluents of the epoxy resin system [3]. Several researchers have investigated the curing and conversion of the soybean oil into flexible, semi-flexible and rigid cross-linked polyester using various approaches [4–7]. These studies show the potential for the synthesis of new polymers derived from renewable soybean oil. More recently, researchers began to explore the feasibility to manufacture polymer composites from epoxidized soybean oil. Crivello et al. [8] reported the fabrication and mechanical characterization of glass fiber reinforced UV-cured composites from epoxidized vegetable oils. So far, the wide structural applications of ESO are limited because of its low cross-linking density and mechanical performance. The development of soy-based resin for structural application is still a challenge for the polymer and composite industry.

The objective of this research is to develop an inexpensive but enhanced soy-based epoxy resin, namely, epoxidized allyl soyate (EAS), from unsaturated soybean oil. It is expected that these modified soy-based epoxy resins possess higher reactivity, and therefore provide more densely intermolecular cross-linking and yields materials, which are stronger than the materials obtained.
25% of EAS with amine curing agent. A temperature program from Non-isothermal process was used to investigate the reactivity on a thermal analyzer (TA Instrument with DSC model 2010). Transition properties for neat soy-based resin and EPON co-resin (DSC) is used to study the curing characteristics and thermal the polymerization process. Differential scanning calorimetry epoxidized soyate resin, the degree of epoxidation controls therefore cross-linked polymer network can be formed. For are opened and form new chemical chain with amine molecule; itity groups. When ESO reacts with the curing agent, epoxy rings also improve composite properties compared to other methods production for structural applications. Pultrusion technology also improves composite properties compared to other methods because the fibers are under tension as the resin cures and hence are tightly bonded to each other. In the pultrusion process, many uniform cross section profiles can be manufactured continuously as long as raw materials are supplied. Fiber reinforcement can take form of any one or combination of several types such as rovings, mats, fabrics and cloths. This variety of available reinforcement allows much design flexibility thus allowing a part to be customized to a specific application.

Composite specimens were manufactured using a Durapul 6000 Labstar pultrusion machine (see Fig. 2) at the University of Missouri-Rolla. The 914.4 mm length die has a cross section profile of 50.8 mm × 3.175 mm. Glass reinforced composites were obtained by DSC. Resin formulation is represented by weight content with different levels of epoxidized soy based resins from 10% to 30%. The neat resin properties such as viscosity, pot life and reactivity, were noted to be comparable to the standard resin.

Table 1 gives the comparison of cure parameters from commercially available unmodified ESO. Epoxidized allyl soyate (EAS) resin system was recently synthesized at University of Missouri-Rolla [9,10]. These materials consist of mixtures of epoxidized fatty acid esters. The epoxidized soy-based resins provide better inter-molecular cross-linking and yield materials, which are stronger than the materials obtained with commercially available epoxidized soybean oil. The curing behavior and glass transition temperature were monitored using differential scanning calorimeter. Standardized tests showed that soy-based resin has mechanical properties comparable to Shell Epon resin.

2. Characterization of soy-based resin

2.1. Preparation of co-resin system

Epon 9500/Epicure 9550 from the Shell Chemical Company were selected as base epoxy resin. Epon 9500 is a resin designed specifically for pultruding composites, which can be processed at high line speeds with low pull loads and good quality. Epoxidized allyl soyate (EAS) was synthesized through a lab scale two-step process from food grade soybean oil. Firstly, the large molecular triglycerides are transesterified to yield fatty acid methyl ester and allyl ester using methanol alcohol and allyl alcohol, respectively. In the second step, the fatty acid esters were epoxidized to yield soyate epoxy resins. The epoxidation of the carbon–carbon double bond of the unsaturated vegetable oil is known to proceed without molecular rearrangement.

The co-resin formulations were prepared by directly mixing the epoxidized soyate resins into base Epon resin and curing in one step. By weight, following ratios of Epon epoxy/epoxidized soyate resins were used: 100% Epon resin, 90%/10%, 80%/20% and 70%/30%. Then hardening agent was added in a ratio of 100/33 and mixed well, and degassed for a few minutes. For $T_g$ and mechanical testing specimens, resin mixtures were poured into a preheated mold, which was first treated with Chemlease 41 mold release compound. The cure reaction was performed in a Blue-M Laboratory oven with hot air circulation. Resin mixture was kept at 80°C for 1 h and then the temperature was ramped to 177°C and held for 1.5 h.

2.2. Curing reactivity of soy-based resin

Epoxidized soybean oil molecule contains epoxy functional- ity groups. When ESO reacts with the curing agent, epoxy rings are opened and form new chemical chain with amine molecule; therefore cross-linked polymer network can be formed. For epoxidized soyate resin, the degree of epoxidation controls the polymerization process. Differential scanning calorimetry (DSC) is used to study the curing characteristics and thermal transition properties for neat soy-based resin and EPON co-resin on a thermal analyzer (TA Instrument with DSC model 2010). Non-isothermal process was used to investigate the reactivity of EAS with amine curing agent. A temperature program from 25°C to 250°C at heating rate of 10 K/min was used. Glass transition temperatures measurement by DSC was carried out over a temperature range from −50°C to 200°C at a heating rate of 5 K/min. Table 1 gives the comparison of cure parameters obtained by DSC. Resin formulation is represented by weight content with different levels of epoxidized soy based resins from 10% to 30%. The neat resin properties such as viscosity, pot life and reactivity, were noted to be comparable to the standard resin. Fig. 1 compares the ductility behavior of EAS formulation and the base epoxy resin. These flexibility properties in the resin matrix were the result of larger molecular weight soybean oil. The increase in ductility was accompanied by corresponding decreases in the ultimate strength and modules.

3. Soy-based composites using pultrusion process

3.1. Manufacturing of composites

Pultrusion is the fastest and the most cost-effective composite manufacturing process, and is well suited to high volume production for structural applications. Pultrusion technology also improves composite properties compared to other methods because the fibers are under tension as the resin cures and hence are tightly bonded to each other. In the pultrusion process, many uniform cross section profiles can be manufactured continuously as long as raw materials are supplied. Fiber reinforcement can take form of any one or combination of several types such as rovings, mats, fabrics and cloths. This variety of available reinforcement allows much design flexibility thus allowing a part to be customized to a specific application.

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![Fig. 1. Ductility behavior of soy-based resin system.](image-url)
made with fiberglass rovings of 113 yield that provides a fiber content of 63% by volume. The Epon 9500/Epicure 9550 will cure at a die temperature ranging from 170°C to 190°C. Maximum safe processing temperature should be controlled under 200°C to prevent curing of the resin at the die entrance area. The pulling speed was 5.08 mm/s and varied slightly throughout the process. After pultrusion, all test specimens were post cured for 90 min at 160°C in an oven.

3.2. Mechanical characterization of pultruded composites

3.2.1. Tensile and flexural properties

Although the mechanical properties of a composite part is dominated by the amount and orientation of the fiber reinforcements, the resin must be strong enough to adequately transfer the load to the fibers for the structure to benefit from the presence of the fibers. The main factor that affects the resin property is the cross-linking density. The addition of flexible epoxidized soybean oil into epoxy resins would increase failure strain of the resin. The rectangular composite test specimens with dimensions of 254 mm × 12.7 mm × 3.175 mm were cut from pultruded panels with a high speed cutter and edges were polished with very fine aluminum oxide sandpaper. Tensile testing of pultruded fiberglass composites specimens was performed using an INSTRON 4204 machine. Each specimen was tested to failure following the procedure in accordance with ASTM D3039-97. Flexural strength and modulus were tested in the same INSTRON machine following ASTM D-790 standard. The specimen dimensions were 127 mm × 12.7 mm × 3.175 mm, the span was 50.8 mm, and cross head speed was 0.0423 mm/s.

The results of the mechanical testing of the pultruded composites are shown in Figs. 3 and 4. The average ultimate strength of specimens were almost the same as the neat Epon epoxy resin at 10 wt.% of soyate resins but began to decrease with the increasing content of the soyate resins. Because soy-based resins have lower reactivity and less functional epoxy group density, the cross-linking density of the soyate co-resin systems will decrease when the proportions of soyate resins increase. However, Young’s modulus of the composites using soyate co-resins did not show much change compared with the base epoxy resin when low content soyate resins less than 20% were added. Unlike tensile properties, the flexural properties of a unidirectional composite structure are much more dependent on the nature of the resin because the fibers are generally not oriented in the direction of the applied force. Therefore, the resin makes the greater contribution to the flexural properties than to the tensile properties. The movement of molecules relative to each other is a major factor in influencing the flexural strength and stiffness of the polymer.

3.2.2. Impact properties

The impact response in fiber reinforced epoxy composites reflects a failure process involving crack initiation and growth
in the resin matrix, fiber breakage, fiber pullout, delamination and debonding. The energy absorbing capability of the composites during impact is therefore strongly dependent on the tensile strain capacity of the resin and the interface between fiber and resin. The flexible resins derived from soybean oil have high strain-to-failure properties. The increased flexibility and reduced yield strength could improve impact resistance of the composites using soyate resin additives. In this study, a low velocity impact test was used to compare the effect of the different resin formulations on impact resistance of composites. A custom-built gas gun ballistic apparatus was used to fire a 9.525 mm diameter spherical steel ball on to the composite panels. In the impact testing, the damage was visually inspected. The damage included a circular area radiating out from the point of impact and cracks propagated along the unidirectional roving direction. It was found that the various resin formulations produced different crack lengths. The crack length can be used to qualitatively indicate the impact resistance of each specimen. Fig. 5 gives the crack length comparison for different resin formulations. The results showed that specimens with soy-based resin EAS had reductions in crack length of about 20% as compared to the neat Epon formulations. The flexible EAS resin system improved the impact damage resistance of composites.

3.2.3. Effect of soy-based resin on pultrusion pulling force
Pulling force provides a relative measure of resistance to pulling composite parts out of the die through pultrusion. Under normal operating conditions, overall forces can be affected by numerous factors such as the viscosity of the resin, the relative percentage of glass and resin, the coefficient of thermal expansion of the gel and solid phase of the materials, the length of the die, the cross sectional area of the cavity, and most importantly the degree of shrinkage of the resins. Typically, epoxy resin is much more difficult to pull thru than polyester and vinyl ester resins because epoxy shrinks very little upon curing and is prone to stick to the die. A high content of mold release additive is normally needed to perform the epoxy composites pultrusion successfully. In this research, an extra benefit using soyate co-resin system was found, i.e., the pulling force during pultrusion process was significantly reduced and epoxy composites pultrusion process becomes easier. The pulling force values are compared for various resin formulations as shown in Fig. 6. This benefit is due to the good lubricity properties from the oily fraction of soy-based resin.

4. Conclusions
A novel epoxidized soy-based resin (EAS) was developed from modified natural soybean oil. EAS provide better intermolecular cross-linking and yield materials, which are tougher than the materials obtained from commercially available ESO. When co-polymerization is achieved, the addition of EAS to a commercial epoxy resin yields a viable low-cost, high performance thermoset product and is ideal for pultrusion process. Mechanical tests show that the pultruded glass fiber reinforced composites with soy-based co-resin systems possess comparable or improved structural performance characteristics such as flexural strength, modulus and impact resistance. The lubricity of soybean oil significantly reduces the pull force in the pultrusion process. The epoxidized soy-based resin system holds great potential for environmentally friendly and low cost raw materials in fabrication of epoxy composites for structural applications.

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