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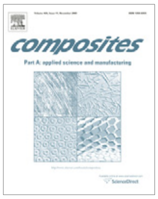

Bio-based polymer nanocomposites from UPE/EML blends and nanoclay: Development, experimental characterization and limits to synergistic performance

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ABSTRACT

Bio-based nanocomposites, defined as blends of petroleum and vegetable oil resins reinforced with nanoparticles, can lead to synergistic material property enhancement; and evaluation of their performance and limits can allow for their optimal design. An array of 12 nanocomposite designs with up to 30% epoxidized methyl linseedate (EML) and up to 5.0 wt.% nanoclay in unsaturated polyester were manufactured using a solvent-based technique. Mechanical, thermal and diffusion properties of resulting composites were experimentally characterized. Reduction of mechanical and transient properties due to bio-resin blending were recovered by the addition of nanoclay for EML contents of up to 20%, while 30% EML composites showed little improvement. Systems with 2.5 wt.% nanoclay and up to 20% EML showed optimal performance with balanced properties and processing ease. The developed eco-friendly bio-based nanocomposites exhibit good stiffness–toughness balance along with improvements in other mechanical and transient properties, thereby showing potential for use in structural applications.

1. Introduction

Environmentally friendly polymers with properties suitable for use in load-bearing applications can be obtained by reinforcing blends of petroleum and vegetable oil based resins with nanoclay. Such hybrid combinations have been found to produce composites that exhibit synergistic behavior with improvements to multiple properties that are superior or similar to the base petroleum polymer.

Bio-based polymer systems, defined as a combination of petroleum-based resins as the primary constituent and natural bio-resins as the secondary constituent, can be reinforced with nanoclay to obtain novel, value added applications for natural polymers [1]. The blending of epoxidized vegetable oils, or bio-resins, with petroleum-based resin has been shown to improve the toughness of the resulting polymer system [2–5]. However, this increase in toughness seriously affects the stiffness [3–5], thermal [4,5] and barrier [4] properties of the resulting polymer. Stiffness and toughness are opposing performance parameters and a proper balance is required to develop an efficient biocomposite. Hence, the aim of the work presented here was to obtain bio-based nanocomposites wherein the reduction in properties due to bio-resin addition could be recovered by the addition of nanoclay, with the synergistic behavior not limited only to stiffness–toughness balance but also to transient (thermal and moisture diffusion) properties.

The initial attempt to the aforementioned goal was performed by blending petroleum-based unsaturated polyester (UPE) with epoxidized methyl soyate (EMS) as the bio-resin [4]. The resulting bio-based resins were reinforced with nanoclay (Cloisite 30B®). The processing technique used allowed only a limited incorporation of bio-resin (10%) and nanoclay (1.5 wt.%). In spite of the low amounts of nanoclay and bio-resin, the results showed promise in the synergistic behavior of these materials with improvements in toughness due to addition of bio-resin and enhancements in stiffness, thermal and moisture barrier properties due to nanoclay addition. Nanoclay addition resulted in complete recovery of moisture barrier properties but only partial recovery of stiffness and other properties. This study [4] led to the following recommendations: (a) to improve the processing technique such that the incorporation of relatively higher amounts of bio-resin (>10%) and nanoclay (>1.5 wt.%) were possible, (b) to perform a detailed characterization of an array of nano-reinforced bio-based polymer systems to study the effects of constituents on their complimentary behavior, and (c) to find optimized material combinations that have ease of processing along with enhanced synergistic behavior.

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The development of alternatives for petroleum-derived materials with plant-based renewable materials has been propelled from an environmental viewpoint [1,2,6,7]. Mohanty et al. [2] provide a good overview on bio-polymers, bio-fibers and bio-based composites, or biocomposites. Improvements in toughness have been reported for blends of petroleum-based resins and bio-resins [2–5]. This increase in toughness has been attributed to the reduction in cross-link density in the system, leading to increased plastic deformations [5]. Additionally, research has shown that use of plant-oil based polymeric materials do not show adequate properties of rigidity and strength for load-bearing applications by themselves and require modification [1]. On the other hand, reinforcement of petroleum-based polymers with layered silicates, or nanoclays, has been shown to enhance stiffness along with improvements in thermal, barrier, flammability and ablation resistance properties [8]. Nanoclay reinforcement has also been used with natural bio-resins like soy- [1,9,10] and corn-based [11] resins with similar enhancements. Polymer/clay nanocomposites are well understood and considerable literature and review articles exist on this topic [8,12–14]. In spite of the noted enhancements, stiffness improvement due to addition of nanoclay also increases the brittleness of the resulting polymer nanocomposites [4]. Moreover, petroleum-based polymers such as unsaturated polyesters (UPEs), which are commonly used due to their low cost, ease of handling, and good balance of mechanical, electrical, chemical and fire resistance properties, are inherently brittle [15,16]. Thus, combination of bio-resin and nanoclay should result in a hybrid material that inherits enhanced toughness from the bio-resin and enhanced stiffness from the nanoclay. The substitution of non-renewable synthetic polymers with renewable polymers has been thus proposed and studied considerably [3,16–24]. Nevertheless, in order to fully exploit the benefits offered by hybrid bio-based nanocomposites, higher amounts of bio-resin and nanoclay need to be incorporated through an efficient processing technique [25] and limits to their synergistic behavior should be evaluated.

In this work, the shortcomings and recommendations from the above-mentioned UPE/EMS nanocomposites study [4] were taken into consideration and improvements were made. First, the choice of bio-resin was changed from EMS to EML (epoxidized methyl linseedate). This choice followed from studies on neat resin (no clay) properties of blends from UPE with EMS [3] and EML [17], which revealed higher loss in stiffness properties due to bio-resin addition in EMS-based resin systems. This suggested better performance of UPE/EML blends than UPE/EMS blends. Secondly, an improved manufacturing method identified from a detailed processing study by the authors was used [25]. The method allowed incorporation of up to 30 wt.% EML and 5.0 wt.% nanoclay. Thirdly, since it was possible to incorporate relatively larger amounts of nanoclay and EML contents, this study was also aimed at finding performance limits on the effects of EML and nanoclay on the resulting nanocomposites, thereby allowing the identification of optimized combinations that would result in a balance of properties along with ease of processing. The following sections summarize an experimental evaluation of the noted hybrid materials with details on the processing method, thermo-mechanical testing, characterization of nanoclay morphology and distribution, and the identification of synergistic behavior.

2. Experimental methods

Experimental determination of thermo-physical properties and material characterization were performed on an array of bio-based clay nanocomposites. Details on materials, processing, parameters studied, and testing are provided in the following.

2.1. Materials

The main component of the bio-based polymer systems was ortho-unsaturated polyester resin (UPE, Polylite® 32570-00, Reichhold Inc., NC), which contains 33.5 wt.% styrene. A bio-based modifier, epoxidized methyl linseedate (EML, Vikoflex® 9010, Arkema Inc., PA) replaced up to 30 wt.% of the UPE. EML is a mixture of methyl esters of fatty acid compositions that construct the linseed oil. The detailed composition is 40–50 wt.% methyl linolenate epoxy, 24–26 wt.% methyl oleate epoxy, 17–22 wt.% methyl linoleate epoxy, 4–7 wt.% methyl palmitate, and 2–5 wt.% methyl stearate. The nanoclay used in this work was Cloisite 30B® (Southern Clay Products, Inc., TX). The resin system (mixture of UPE, EML and nanoclay) was processed with cobalt naphthenate (Sigma–Aldrich, MO) as a promoter and 2-butanone peroxide (Sigma–Aldrich) as an initiator. A constant ratio by weight of the resin system to the promoter and initiator was utilized to cure all samples. The mixing ratio was 100 parts by weight of the resin system to 0.03 parts promoter and 1.50 parts initiator. Samples were cured at 100 °C for 2 h, followed by 160 °C for 2 h.

2.2. Experimental matrix and nomenclature

The amount of bio-resin (epoxidized methyl linseedate, EML) that replaced the primary resin component (UPE), was varied from 0% to 30% in increments of 10%. A total of four neat resin (no clay) systems were obtained. Each of these resin systems were then reinforced with nanoclay inclusions at a loading of 2.5 wt.% and 5.0 wt.%. Twelve polymer systems were thus evaluated by varying clay and EML contents as summarized in Table 1. The nomenclature used to describe the polymer systems is: “A/B/C”, where “A” refers to the amount of UPE, “B” represents the amount of EML, and “C” refers to the weight fraction of nanoclay inclusions. For example, Specimen ID 7 in Table 1 is referred to as 80/20/2.5, indicating that a 100 g of resin system has 80 g of UPE, 20 g of EML and is reinforced with 2.5 wt.% of nanoclay platelets. The actual amount of nanoclay required per 100 g of resin blend to maintain 2.5 wt.% and 5.0 wt.% is 2.564 g and 5.263 g, respectively. For brevity and simplicity, the following text will use 2.5 wt.% and 5.0 wt.% instead of the actual nanoclay weights.

2.3. Polymer nanocomposite processing

The technique used for processing the nanoclay reinforced bio-based resin systems follows the findings from our group’s study on solvent-based processing for bio-based clay/polymer nanocomposites [25]. The technique found to be most efficient consists of sonicating the nanoclay in acetone to an energy level of 300 kJ using a solution concentration of approximately 50 l of acetone to 1 kg of clay while it is constantly stirred. After sonication only the UPE solution is added. The acetone + nanoclay + UPE solution is mixed continuously on a hot plate at approximately 55 °C to remove a majority of the acetone. The remaining acetone is removed by vacuum extraction at 55 °C for 24 h. During the acetone removal process the styrene present in the UPE is also removed. With the amounts of constituents known, the amount of styrene lost is determined from the difference in weights of the resin system before and after the acetone removal step. Thus, after acetone removal the bio-resin (EML) is added along with an amount of styrene equal to that lost during the vacuum extraction process. The processed solution is cooled to room temperature and then blended with the initiator and promoter. Test samples were prepared by pouring the processed solution into silicone molds followed by curing. A flow chart depicting the process is shown in Fig. 1.