DEVELOPMENT AND THERMO-PHYSICAL PROPERTIES OF BIO-BASED POLYMER/CLAY NANOCOMPOSITES

Mahmoodul Haq[1], Rigoberto Burgueño[1†], Amar K. Mohanty[2], and Manjusri Misra[3]

[1] Dept. of Civil and Env. Eng., [2] School of Packaging, [3] Composite Mats. and Struct. Ctr. Michigan State University, East Lansing, Michigan 48824, USA

Abstract

Bio-based resin systems obtained as blends of functionalized vegetable oils and petroleum based resins have been found to increase toughness of petroleum based resins and improve their environmental friendliness. Nevertheless, this improvement in toughness generally compromises the stiffness of the resin system. Nano-scale layered silicate (nano-clay) polymer nanocomposites exhibit enhanced mechanical and physical properties at relatively low weight fractions of inclusions. The reported study shows that proper stiffness – toughness balance along with enhancement in many other physical properties can be obtained by incorporating nano-scale layered silicates in bio-blended polymers. Polymer nanocomposites with varying clay contents and varying bio-blend (epoxidized soya bean oil) in unsaturated polyester resins were manufactured. Tensile properties and moisture absorption properties were studied. Fracture surface morphologies and characterization of nanocomposites were performed using electron microscopy. The resulting bio-blended polymer nanocomposites exhibit promising results for use in structural applications.

Background

Increasing environmental concerns such as biodegradability, recycling issues and dependability on non-renewable petroleum reserves have limited the wide spread use of synthetic fiber-reinforced-polymer (FRP) composites and propelled the development of alternatives for synthetic fibers and petroleum resins [7][10] for the development of bio-based composites, or biocomposites. The use of all natural bio-resins has been limited due to performance based concerns such as low mechanical and thermophysical properties [5][6]. As a result, bio-based resins obtained from partial replacement of non-renewable synthetic resins (in this case, petroleum based unsaturated polyester) with renewable resins, or bio-resins such as functionalized vegetable oils has been proposed and studied in the literature [1][4]. Soybean oil is available abundantly across the United States, and varieties of epoxidized soybean oils are already commercially available. Such functionalized vegetable oils (FVO) are used in coatings and plasticizer additives. More value-added applications of such epoxidized vegetable oil can further benefit the agriculture industry while reducing the burden of petroleum-based products.

Bio-based resins obtained by replacement of a part of unsaturated polyester with soybean oil, specifically epoxidized methyl soyate (EMS), can enhance toughness but compromise many other mechanical, thermal, physical and barrier properties of the

† Corresponding Author: Rigoberto Burgueño, 3574 Engineering Building, Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824-1226; burgueno@msu.edu

resulting resin system. However, these concerns, caused by the blending of EMS can be overcome by introduction of nanoclay. Moreover, stiffness and toughness are opposing performance parameters and a proper balance is required to develop an efficient biocomposite.

Polymers reinforced with layered silicates or nanoclays have shown to exhibit enhancements in mechanical, thermal and barrier properties at low concentrations. The enhancement of mechanical and barrier properties in polymers with addition of small concentrations of nanoclays is well established in the literature [3][5]. Le Baron et al. [3] provide a good review on polymer clay hybrid nanocomposites. Apart from the increase in mechanical properties (e.g., stiffness, strength), the inclusion of nanoclay particles introduces multifunctionality to the resulting nanocomposite resin system by enhancing barrier properties, flame retardancy and ablation resistance.

Similarly, among thermoset resins, petroleum based unsaturated polyesters (UPEs) have gained importance and are commonly used due to their low cost, ease of handling, and good balance of mechanical, electrical chemical properties and fire resistance properties [1][5]. However, UPE is inherently brittle. In addition, the stiffness of UPE is lower than the matrix systems used for structural FRP composites. Regarding these limitations, research has shown the increase in modulus both below and above glass transition temperature of UPE resins reinforced with functionalized nanoclay, or organoclay. However, Nair et al. [9] show that the increase in stiffness is generally obtained by compromising toughness. They also report that the toughness of layered silicate composites is dependent on the morphology and concentration of the clay content [9].

The increase in stiffness due to the addition of nanoclay inclusions will thus increase the stiffness of the resin system and decrease toughness. Addition of EMS enhances toughness but compromises stiffness. It follows that the result of a blended resin system could have better stiffness-toughness balance than the original unsaturated polyester resin. Similarly, the increase in moisture absorption in the bio-based resin due to addition of EMS can be circumvented with the enhancement of barrier properties obtained from nanoclay reinforcement. Hence, the combination of nanoclay platelets with blends of EMS and UPE resins can result in novel multifunctional composites with superior properties than the original resin systems incorporating the beneficial effects of both nanoclay reinforcement and EMS.

The impact properties and dynamic mechanical analysis of UPE-EMS blends with 2.5 wt% organoclay (Nanomer I.44PA) has been reported by our group [8]. This paper reports on further efforts to evaluate the effect of clay loading on varying UPE-EMS blends and expanding the set of measured thermophysical properties. Experimental evaluation of tensile properties, toughness, storage modulus, glass transition temperature (T_g), linear coefficient of thermal expansion and moisture absorption properties were studied. In this communication, the processing methods for the bio based nanocomposites and their tensile modulus and moisture absorption properties are provided. The degree of dispersion and exfoliation of nanoclay in the resin systems was characterized using transmission electron microscopy. The fracture surfaces were characterized using scanning electron microscopy. Full results from the study are provided in reference [2].

Experimental Methods

The main component of the engineered resin system was ortho unsaturated polyester resin (UPE, Polylite® 32570-00, Reichhold Inc., NC), which contains 33.5 wt.% styrene. A bio-based resin, epoxidized methyl soyate (EMS, Vikoflex® 7010, Arkema Inc, PA) replaced up to 10 wt.% of UPE. The organoclay used in this work was Cloisite 30B® (Southern Clay Products, Inc. TX). The resin system (blend of UPE, EMS and organoclay) 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 total 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 hours, followed by 160˚C for 2 hours.

Bio-based resin systems with substitution up to 10% EMS in UPE were possible, as higher amounts caused processing problems. Clay loading of 0 wt.%, 0.5 wt.%, 1.0 wt.% and 1.5 wt.% were processed for each resin system. For nanoclay reinforced resin systems, the clay was sonicated in acetone for two hours using a solution concentration of 50 liters of acetone to 1 kilogram of clay, while it was constantly stirred by a magnetic stirrer. The energy spent on sonication was approximately 30 kJ. The UPE and EMS were then blended and mixed with a magnetic stirrer at approximately 55^{o}C until the majority of acetone was removed. Residual acetone was then removed by vacuum extraction at approximately 55^{o}C for 24 hours. At higher concentrations of EMS and clay, the resin hardened during the acetone removal process. This issue was not observed at clay content of less than 1.5 wt.% and EMS contents of less than 10%. The styrene present in the UPE also evaporated with the acetone. Thus, after the acetone removal process, the lost styrene was replaced. The addition of bio-resin reduces the styrene content in the total resin system compared with the amount in neat UPE. It was thus suspected that the premature curing of bio-based resin blends during acetone removal was due to reduction in styrene content. Hence, additional styrene was added to the bio-based resin systems to maintain the total resin system styrene content at 33.5 wt.%. For the specific case of the resin system with 10% EMS and 1.5 wt% clay, the mixing of UPE and EMS before acetone extraction process yielded premature curing of the resin. As a result, only for this resin system (10% EMS, 1.5 wt.% clay), acetone extraction was performed with only UPE, and EMS was added later along with the lost styrene. After acetone removal and addition of the lost styrene, the promoter and initiator were blended into the solution. Following proper mixing of all components, the nanocomposites were cured at 100^{o}C for 2 hours followed by 160^{o}C for 2 hours.

The morphology of the processed nanocomposites was evaluated with transmission electron microscopy (TEM). Ultramicrotomy at room temperature was carried using a diamond knife with an included angle of 4˚ to produce sections of approximately 70nm thick. A JEOL 2200FS TEM with 10kV acceleration was used to obtain bright field images. Tensile tests were performed according to ASTM D638 standards. From the same test, Poisson's ratio was measured using a biaxial extensometer. Six coupons were tested per nanocomposite type. The failure surfaces from the tensile coupons were observed with a JEOL 6300 field emission scanning electron microscope (SEM) at 10kV acceleration voltage. Moisture absorption testing was performed by storing samples in an environmental chamber at 30^{o}C and 90% relative humidity and measuring the increase in weight of the samples. After initial measurements, increase in weights of the samples was monitored at regular intervals until steady state was achieved. The dimensions of test specimens were approximately 12.7 mm by 75 mm. The edges of samples were coated a with two-part impervious epoxy to eliminate edge effects. Two

specimens were monitored for each resin system in the study. Moisture absorption was evaluated as the percent weight gain at steady state.

Results and Discussion

Results of the thermo-physical characterization validated the concept of achieving multifunctional properties for the resulting bio-based polymer nanocomposites. Tensile modulus results for unmodified and bio-based resin systems with varying clay contents are provided in Figure 1. Direct tensile tests revealed an elastic modulus decrease of about 28% with addition of 10% EMS in neat UPE (no clay). At the same time, the elastic modulus increased by approximately 15% to 20% with the addition of 1.5 wt.% nano-clay inclusions. The resin system that had the largest amount of EMS (10%) and nano-clay inclusion (1.5 wt.%) was found to have a tensile modulus approximately 13% lower than the neat UPE without any EMS or clay inclusions. Although, the stiffness lost due to addition of EMS was not completely recovered by addition of nano-clay in this experimental matrix, the authors have confidence that this is possible with higher clay contents and better processing. Nevertheless, the lower modulus of about 13% for 10%EMS bio-blends with 1.5wt.% clay is not surprising since it is a noticeable improvement from the approximately 28% decrease in elastic modulus observed with the 10% EMS neat resin system with no clay.

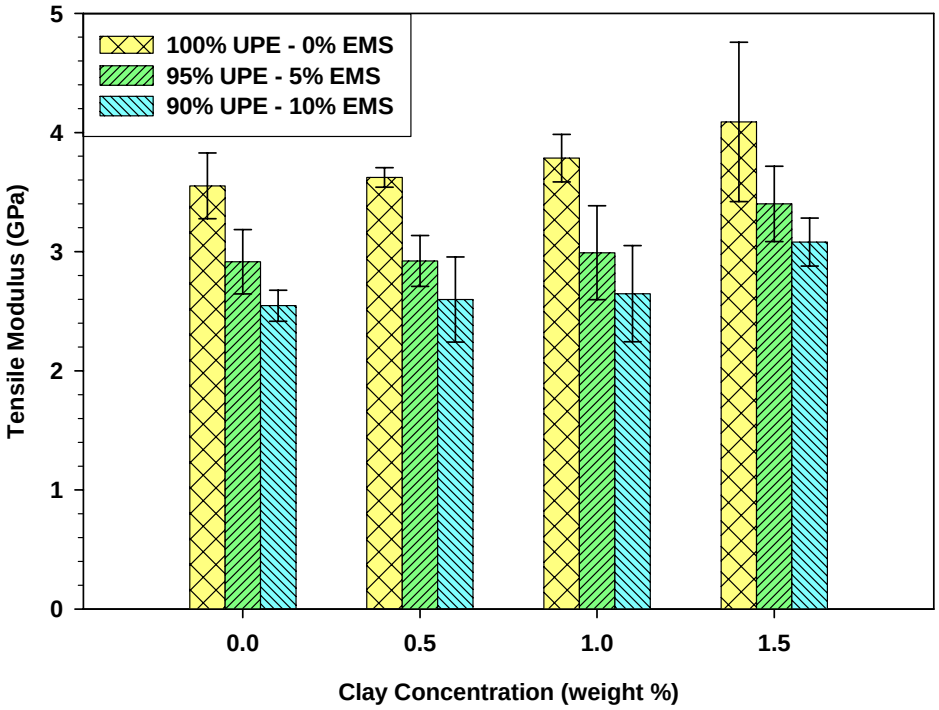

Figure 1. Experimental tensile modulus of bio-blend resin systems with varying clay contents

The reduction in stiffness due to addition of EMS was accompanied by an improvement in toughness of the resulting bio-based resin. With increasing EMS

content, failure strains increased while the tensile strengths reduced. Similarly, it was observed that the addition of nanoclay increased the brittleness of the nanocomposite leading to lower failure strains. Hence, the increase in brittleness due to the addition of nanoclay inclusions is balanced by an increase in ductility and toughness due to the addition of the EMS bio-resin.

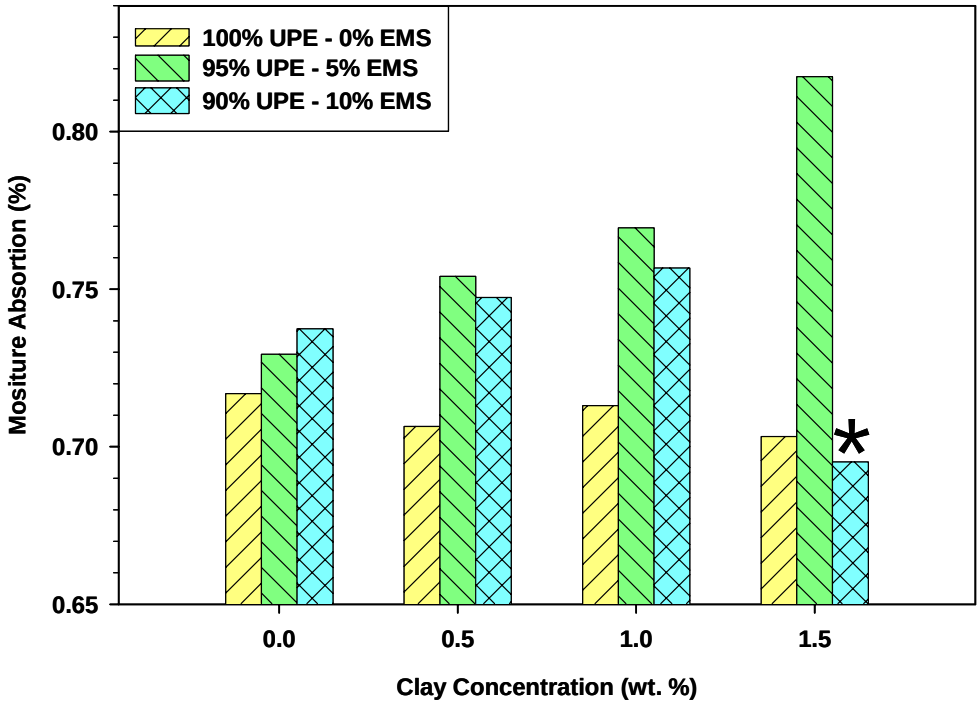

Figure 2. Moisture absorption of bio-blend resin systems with varying clay contents

Moisture properties of the resin systems in the study showed trends similar to the elastic modulus values obtained from tensile tests. The addition of EMS increased the moisture absorption of the resulting bio-based resin. However, results indicate that the adverse effects of EMS blends on moisture absorption can be decreased through the barrier properties provided by the nanoclay inclusions. The moisture absorbed by the polymer resin systems was measured over a period of 50 days in an environmental chamber. Moisture absorption of all nanocomposites stabilized after approximately 35 days (800 hours). The representative moisture absorption value for a resin system was determined after steady state was achieved. The moisture absorption results are provided in *Figure 2*. For neat UPE resin systems (no EMS), it was observed that increase in clay content enhanced the moisture barrier properties. A similar trend was not observed for the UPE/EMS blend resin systems. The effect of EMS in increasing moisture absorption seems to be larger than the barrier enhancement gained from the addition of clay. However, this effect was observed to be dependent on the processing technique. As discussed earlier, the resin system with 10% EMS and 1.5 wt.% clay was processed with a slightly different technique (data point denoted by ***** in *Figure 2*), in which the EMS bio-resin was added *after* acetone removal. For this bio-based resin system, the loss in barrier properties due to addition of EMS content was recovered by nanoclay inclusions and even had better barrier properties than neat UPE.

Figure 3 shows the bright field TEM micrographs of clay platelets distributed in a

UPE matrix. It was observed that the clay platelets were well dispersed but partially exfoliated and partially intercalated in the resin matrix. Similar micrographs were observed for the nanoclay reinforced bio-based blends. It is expected that higher sonication energies will provide better exfoliation of the clay platelets. At the same time, excessive sonication energy/time may lead to breaking of clay platelets, thus reducing their aspect ratio and leading to inferior nanocomposite properties. Processing techniques with varying sonication energies and mixing procedures should be studied to better understand the resulting morphology and their thermo-physical properties of composites. Such a study is in progress by the authors and outcomes will be provided in future communications.

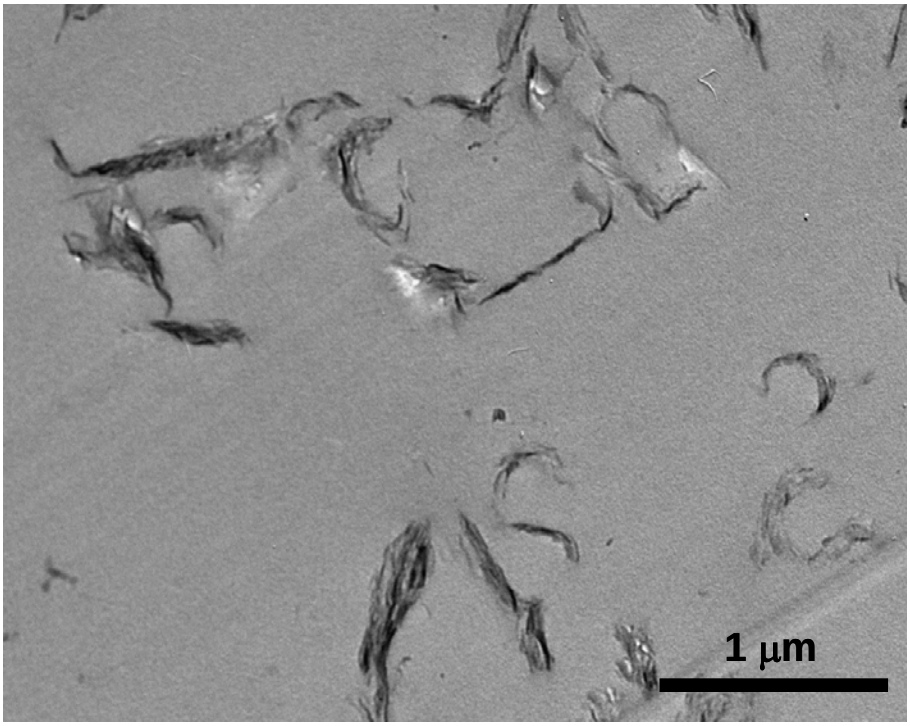

Figure 3 Bright-field TEM micrographs revealing homogenous dispersion with partially exfoliated and intercalated clay particles in UPE matrix.

Tensile fracture surfaces of the bio-based resin systems with and without nanoclay reinforcement were evaluated through a scanning electron microscope. Figure 4(a) and Figure 4(b) show the SEM micrographs of tensile fracture surfaces of neat UPE and a 10% EMS bio-based resin blend with 1.5wt.% clay inclusions, respectively. The roughness of the fracture surface has generally been associated to fracture properties and critical strain energy release rates [11]. Smooth featureless fracture surfaces are attributed to brittle failures and rougher fracture surfaces are attributed to tougher nanocomposites [11]. Neat UPE had the most smooth and featureless surface (Figure 4(a)). However, it was observed that the roughness of fracture surface increased with increasing EMS content. Similar increase in surface roughness was observed with increasing clay content (Figure 4(b)). The fracture surface morphology observations suggests that the combination of EMS and clay composites provide a tougher material.

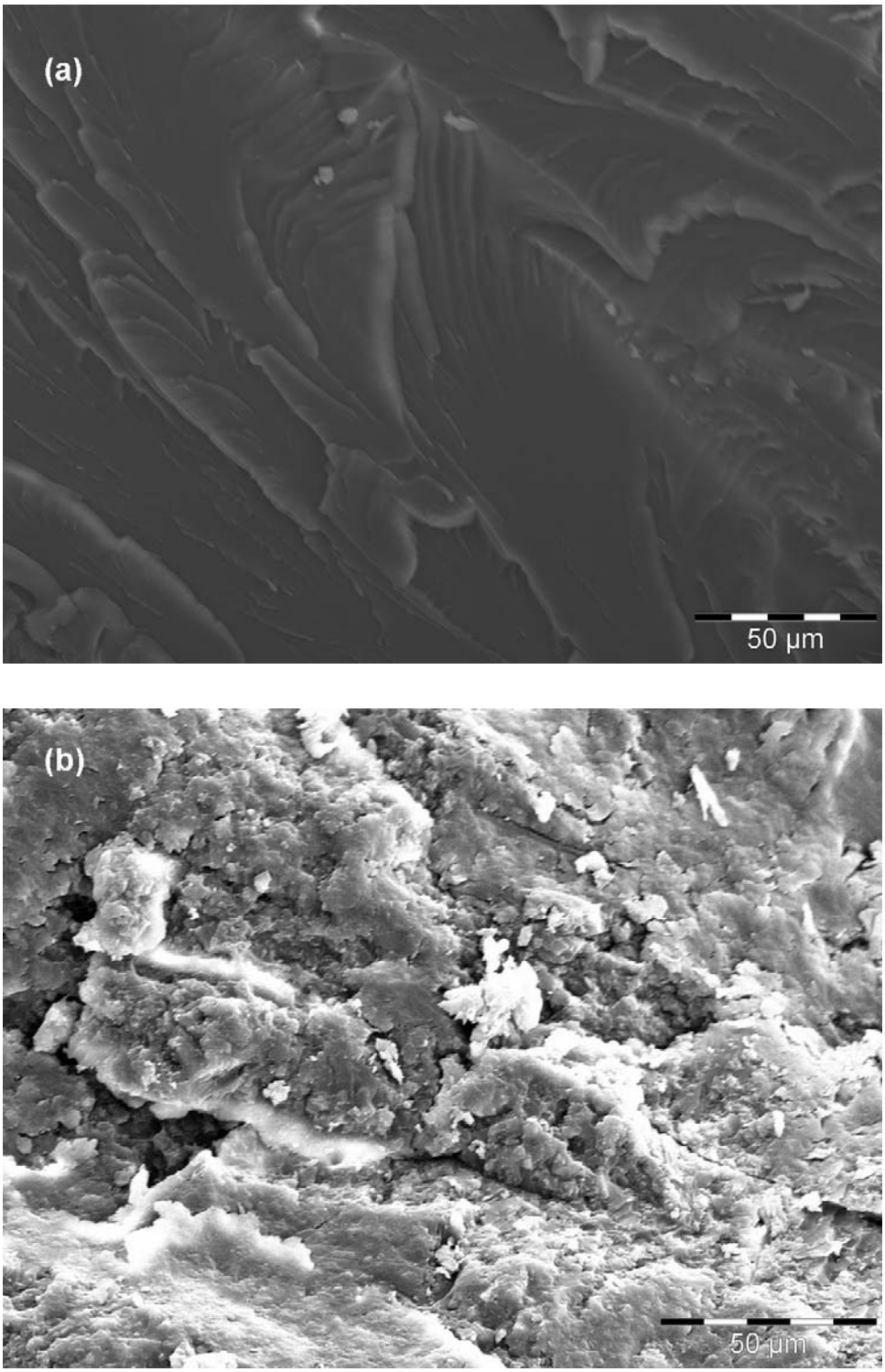

Figure 4 SEM micrographs of tensile failure surfaces, a) Neat UPE without inclusions, scale bar = 50 μm, b) Bio-blend of 10% EMS and 90% UPE with 1.5 wt%. clay inclusions, scale bar = 50 μm.

Conclusions

The development of bio-based resin systems from the blends of synthetic and natural polymers has many benefits including environmental friendliness, cost effectiveness and improved toughness of the resulting composites. Tensile modulus, moisture absorption and microscopy characterization of nano-clay reinforced bio-based nanocomposites were performed on UPE/EMS blends with varying contents of EMS and nanoclay reinforcement. It was observed that the decrease in modulus due to addition of EMS was partially recovered through nanoclay reinforcement. On the other hand, addition of EMS improved toughness of the bio-based resin system. As a result, the nanoclay reinforced UPE/EMS nanocomposites showed a balanced improvement in stiffness and toughness. Similarly, the barrier properties lost due to the addition of EMS blends were recovered with nanoclay reinforcement. Also, fracture surface morphologies suggest tougher composites can be achieved with the combination of EMS and nanoclay. Thus, the synergistic combination of nanoclay reinforced EMS/UPE blends produces multifunctional nanocomposites with enhanced, or similar, properties than the neat petroleum-based resin. The resulting bio-based resin system holds great promise for use in wide applications. At the same time, more work needs to be done in improving processing techniques such that higher amounts of bio-resin content and nanoclay reinforcement can be incorporated to maximize the multifunctionality that these bio-based nanocomposites can offer.

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