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Research paper

Reinforcing ability and co-catalytic effects of organo-montmorillonite clay on the epoxidized soybean oil bio-thermoset

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ABSTRACT

Epoxidized soybean oil (ESO) containing octadecyl trimethyl ammonium functionalized montmorillonite (OMMT, 1–5 wt.%) were thermally cured using methylhexahydropthalic anhydride in the presence of 2-ethyl-4-methylimidazole catalyst. The mechanical properties of ESO nanocomposites were studied through the tensile and fracture toughness tests. The thermal properties were characterized by means of dynamic mechanical analyzer, thermogravimetric analyzer and differential scanning calorimeter. The addition of OMMT into ESO significantly improved the modulus, tensile strength, glass transition temperature, crosslink density, gel content and thermal stability of ESO/OMMT bio-thermoset. These are mainly attributed to the well-exfoliated OMMT and the co-catalytic effect of octadecyl trimethyl ammonium.

1. Introduction

Biopolymers produced from the renewable natural resources are of scientific interest in the polymer industries since they are more environmental friendly and sustainable driven (Kevadiya et al., 2011). Vegetable oils can be a promising resource for the synthesis and preparation of bio-polymers. Approximately 10% of the total global market share of vegetable oils was utilized as the oleo-chemical to produce bio-polymers nowadays. Soybean oil is one of the renewable natural resources which can be epoxidized and used for several applications, such as plasticizers for the poly(vinyl chloride), starting materials for polyols, and bioresins for bio-thermosets.

Though epoxidized soybean oil (ESO) resin can be crosslinked to produce bio-thermosets (Crivello and Carlson, 1996; Gerbase et al., 2002; Gupta et al., 2010; Jin and Park, 2007; Kim and Sharma, 2012; Ortiz et al., 2005; Tan and Chow, 2011a), the poor mechanical and thermal properties of ESO have remained a challenge. It has been reported that the tensile strength, tensile modulus and glass transition temperature of ESO thermosets were in the range of 5–10 MPa, 50–65 MPa and 25–50 °C respectively (Pan et al., 2011; Park et al., 2004; Shibata et al., 2011). Some strategies have been implemented to improve the mechanical and thermal properties of ESO thermosets, for example, addition of fibers (Retegi et al., 2012; Shibata et al., 2009; Takahashi et al., 2008), addition of clay (Liu et al., 2005; Tanrattanakul and Saithai, 2009; Uyama et al., 2003), hybridization with maleated soybean oil and maleated methyl soyate (Tran et al., 2006), modification with silane coupling agent (Tsujimoto et al., 2010) and blending with petrochemical-based epoxy resins (Altuna et al., 2011; Gupta et al., 2011; Jin and Park, 2008; Ratna, 2001).

In this study, ESO bio-thermoset were synthesized and prepared in the presence of methylhexahydropthalic anhydride (curing agent), 2-ethyl-4-methylimidazole (catalyst) and octadecyl trimethyl ammonium functionalized montmorillonite (OMMT layered silicates). We hypothesized that the mechanical and thermal properties of ESO thermosets can be increased by the addition of OMMT. It is believed that the property enhancement can be achieved when the clay is well-exfoliated in the ESO matrix. We also attempted to check the potential of organic intercalant of OMMT (i.e., octadecyl trimethyl ammonium, OTA) in facilitating the curing reaction of ESO through co-catalytic mechanism.

2. Experimental

2.1. Materials

Epoxidized soybean oil (ESO) resin with 6.1 wt.% of epoxy content and molecular weight of about 950 g/mol was supplied by Shangdong Longkou Longda Chemical Industry (China). Methylhexahydropthalic anhydride (MHHPA, CAPE Technology, Malaysia) and the 2-ethyl-4-methylimidazole (EMI, Sigma–Aldrich, Malaysia) were selected as the curing agent and catalyst, respectively. Organo-montmorillonite clay (OMMT, Nanomer I.28E) was purchased from Nanocor, Inc., (USA). Table 1 shows the material designations and compositions of the ESO/OMMT nanocomposites.

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Table 1
Material designations and compositions of ESO/OMMT nanocomposites.

Material designation	ESO/MHHPA mixing ratio	Composition	
		EMI loading (phr)	OMMT clay (wt.%)
ESO	1.0	1.0	0
ESO/OMMT_1	1.0	1.0	1.0
ESO/OMMT_2	1.0	1.0	2.0
ESO/OMMT_3	1.0	1.0	3.0
ESO/OMMT_4	1.0	1.0	4.0
ESO/OMMT_5	1.0	1.0	5.0

2.2. Preparation of ESO/OMMT nanocomposites

ESO resin was first premixed with the OMMT clay at a mixing ratio as shown in Table 1, followed by sonication at room temperature for 1 h. Next, the ESO/OMMT and MHHPA/EMI mixtures were mixed and stirred mechanically at 300 rpm for 5 min. The ESO mixture was then poured into the mould and subjected to the thermal curing process in an oven at 140 °C for 3 h. The cure temperature and time have been optimized based on our previous study (Tan et al., 2013).

2.3. Characterization of ESO/OMMT nanocomposites

2.3.1. Mechanical characterization

Tensile test was conducted according to ASTM D 638 using Instron 3366 machine, UK at a crosshead speed of 5 mm/min. The fracture toughness measurement was carried out according to the principles of linear elastic fracture mechanics on single-edge notched tensile samples at a testing speed of 10 mm/min. The dimension of the sample is 60 mm × 20 mm × 3 mm (length × width × thickness) with the crack length-to-width ratio (a/W ratio) of 0.4. Further details have been reported elsewhere (Tan and Chow, 2012).

2.3.2. Thermal characterization

The viscoelastic properties of the ESO/OMMT nanocomposites were studied using the dynamic mechanical analyzer (SDTA861e, Mettler Toledo, USA). The specimen with the dimension of 25 mm × 10 mm × 2 mm (length × width × thickness) was scanned from 15 to 200 °C at a heating rate of 5 °C/min, in N_2 atmosphere, under the single-cantilever mode. The frequency and displacement were set at 1 Hz and 0.05 mm, respectively. The crosslink density (v_c) was calculated using Eq. (1).

$$v_c = \frac{E'}{3RT} \quad (1)$$

where v_c is the crosslink density of the ESO/OMMT network, E' is the storage modulus measured in the rubbery plateau at $T_g + 40$ °C, R is the gas constant, and T is the absolute temperature.

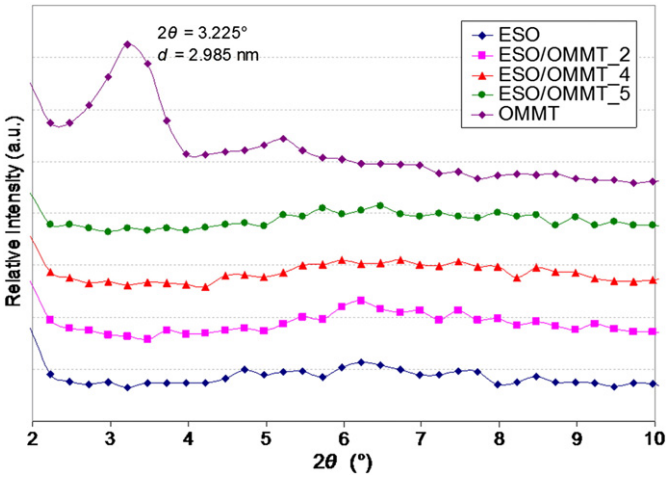

Fig. 1. XRD spectra of ESO and ESO/OMMT nanocomposites.

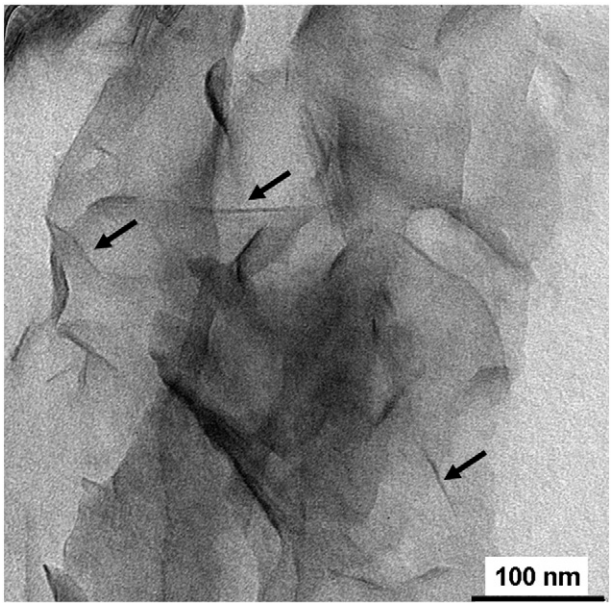

Fig. 2. TEM micrographs of ESO/OMMT nanocomposites at 63,000× magnification.

The thermal decomposition of the ESO/OMMT nanocomposites was determined using thermogravimetric analyzer (TGA, Perkin Elmer, USA). 10 mg of the sample was heated from room temperature to 600 °C at a heating rate of 10 °C/min, under the N_2 atmosphere.

Differential scanning calorimetry (DSC) was performed on the cured ESO/OMMT sample using DSC (Perkin Elmer, USA). The DSC

Table 2
Mechanical and physical properties of ESO and ESO/OMMT nanocomposites.

Materials	Tensile properties			K_{IC} (MPa $m^{1/2}$)	v_c [a] (10^{-3} mol/cm^3)	Gel content [b] (%)
	Modulus (MPa)	Strength (MPa)	Elongation at break (%)			
ESO	319.6 ± 17.2	13.7 ± 0.6	10.9 ± 1.2	2.03 ± 0.30	0.190	87.0 ± 0.2
ESO/OMMT_1	406.5 ± 07.2	17.3 ± 0.9	10.1 ± 0.9	1.86 ± 0.20	0.196	88.0 ± 0.3
ESO/OMMT_2	463.8 ± 11.3	19.3 ± 1.3	9.9 ± 0.7	1.28 ± 0.10	0.267	89.2 ± 0.2
ESO/OMMT_3	541.7 ± 14.7	26.7 ± 1.3	9.0 ± 0.6	0.79 ± 0.11	0.278	90.0 ± 0.1
ESO/OMMT_4	572.9 ± 08.7	29.1 ± 1.1	7.5 ± 0.8	0.70 ± 0.03	0.287	90.4 ± 0.2
ESO/OMMT_5	672.6 ± 08.8	24.9 ± 0.8	6.5 ± 1.0	0.67 ± 0.08	0.303	91.3 ± 0.1

[Note: [a] Determined from dynamic mechanical analyzer; [b] Determined from gel content analysis].