Progress in Organic Coatings 88 (2015) 263–271

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Study of thermal stability and thermo-mechanical behavior of functionalized soybean oil modified toughened epoxy/organo clay nanocomposite

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ARTICLE INFO

Article history:
Received 19 January 2015
Received in revised form 23 June 2015
Accepted 14 July 2015
Available online 8 August 2015

Keywords:
Bio based epoxy
Nanoclay
Thermal properties
Curing behavior
Coefficient of thermal expansion

ABSTRACT

In the current study, nano-clay was incorporated in toughened epoxy modified with epoxidized soybean oil (ESO) to improve the mechanical and thermal properties. Curing behavior was studied by Fourier Transform Infrared spectroscopy and Differential Scanning Calorimetry analysis to investigate the effect of ESO bioresin and nanoclay on cross-linking reaction. The increase in enthalpy of curing reaction and decrease in peak temperature of nanocomposite corroborated the catalytic effect of clay on the curing process. The thermal stability parameters like integral procedural decomposition temperature and decomposed activation energy were determined using Horowitz and Metzger equation. Dynamic mechanical analysis demonstrated the high storage modulus, improved crosslink density and good damping behavior of nanocomposite. Thermo mechanical analyzer was used to examine the coefficient of thermal expansion (CTE) of bio-based epoxy blend and nanocomposite in both glassy and rubbery region. The CTE value is decreased after addition of clay to the modified epoxy blend which confirmed the improved dimensional stability of the nanocomposite. TEM and X-ray diffraction analysis confirmed both intercalated and exfoliated clay platelet within the epoxy blend.

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1. Introduction

Epoxy resins are extensively used for coatings, adhesives, composites, etc. due to their unique properties. However, the scarce toughness or poor elongation at break of epoxy confines its extensive applications in different fields [1]. To overcome this drawback, vegetable oils based bio-resins have been reported as successful toughening agents due to their reduced viscosity and renewability [2–4]. However the enhancement of toughness is achieved with the deterioration of their mechanical and thermal properties [3–7]. Therefore, it is essential to develop an efficient composite material with stiffness–toughness balance and better resistance to thermal degradation.

In the area of polymer nanotechnology, the addition of nanofillers into the biobased polymer system plays an important role in improving the thermal stability, glass transition temperature, and dimensional stability [8–11]. In recent years, organically modified nanoclays have received growing attention in both academic and industrial fields because of their unique property in enhancing the physical properties of polymers such as improved tensile strength and moduli, reduced gas permeability, decreased thermal expansion coefficient, enhanced thermal stability, higher flammability resistance, poor water uptake etc. when compared with the pure polymers [12–16]. Corresponding investigations have also been reported on the improved properties like mechanical, thermal, corrosion and chemical resistance of clay filled epoxy nanocomposite earlier [17–32].

Likewise, vegetable oil toughened thermoset/silicate nanocomposites with better properties have been reported in the last decade. Liu et al. investigated the thermal stability and glass transition temperature of clay filled epoxidized soybean oil nanocomposite [33]. They reported the intercalated structure of nanocomposite with higher storage modulus and glass transition temperature at 5–10 wt.% C30B clay content. Lu et al. have evaluated, the better performance in thermal, mechanical, and vapor barrier properties of conjugated soybean oil/organo clay nanocomposites [34]. Miyagawa et al. studied the effect of clay on the thermophysical properties of bioresin modified unsaturated polyester composite with higher tensile strength, improved storage modulus, reduced expansion co-efficient and poor moisture absorption at 1.5% clay

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http://dx.doi.org/10.1016/j.porgcoat.2015.07.012
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content [35]. Das and Karak examined the improved chemical resistance, reduced viscosity and flammability behavior of *Mesua ferrea* L. seed oil based epoxy blend nanocomposite with 5% clay [36]. Zhang et al. reported the effect of clay on improvement in thermal and dynamic mechanical properties of epoxidized soybean oil modified cyanate ester network [37]. Similarly, Uyama et al. analyzed the superior hardness, modulus and thermal stability of epoxidized naturally oil nanocomposite through acid catalyzed curing process [38].

We reported the maximum toughened property of modified epoxy at 20 wt.% ESO content with moderate reduction in tensile strength and modulus and thermal property in our previous work [12]. In current research, an attempt has been made to enhance its tensile, thermal and thermo mechanical property of toughened epoxy/20% ESO blend by addition of C30B clay. Here, we investigated the effect of C30B clay on tensile properties, curing behavior, thermal stability, viscoelastic property and expansion coefficient of ESO modified epoxy blend.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A-based (DGEBA) epoxy resin of grade EPOXIL-25 with an epoxy equivalent weight 196 g/mol and Ambient temperature curing agent Triethylene tetramine (TETA) of grade MH-91 were obtained from the M/s Marshal Polymers, Kolkata, India. Soybean oil (Density = 0.92 g/ml) of commercial grade was purchased from local sources and epoxidized in our laboratory to be used as reactive diluents. All other chemicals were of analytical grade and used as received.

2.2. Synthesis of bioresin and bio-epoxy blends and nanocomposite

The epoxidized soybean oil was synthesized by in-situ epoxidation process using hydrogen peroxide and acetic acid by our group reported earlier [12]. Bio-based epoxy blends were prepared by blending with ESO bioresin at different ratio with DGEBA epoxy resin at different phr ratios. Among them, 20% ESO based epoxy blend was optimized based on impact strength and used here as base matrix to prepare nanocomposite. For the development of nanocomposite, nanoclay at various weight percentage has been incorporated and subsequently stirred mechanically at 2000 rpm for 2 h for better exfoliation. Then curing agent TETA was added to the resin blends in stochiometric ratio and then poured into aluminum mold. Initial curing was done at room temperature for 24 h, followed by post curing at 80 °C for 2 h and 120 °C for 2 h. All samples were fabricated using hand layup followed by compression molding technique. Then the specimens were cut to suitable dimensions according to ASTM standards and characterized.

2.3. Characterization

2.3.1. Fourier Transform Infrared spectroscopy

Fourier Transformation Infrared (FT-IR) spectra were recorded with 4 cm^{-1} resolution on an FT-IR spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA). FT-IR software OMNIC series suite was used to acquire the data of crosslinked blend and nancomposite.

2.3.2. Mechanical properties

Rectangular specimens of epoxy blend and nanocomposite of dimensions 165 × 25 × 3 mm, were subjected to tensile testing as per ASTM-D-3039, using Universal Testing Machine, (Instron 3382, UK). The test was carried out at a crosshead speed of 1 mm/min and a gauge length of 50 mm. Notched specimens of dimensions 63.5 × 12.7 × 3 mm were prepared to determine the Izod impact strength. Notch depth of 2.54 mm and notch angle 45° were made using a notch cutter (Tinouus olesan, UK). The tests were carried in an izod impact tester (Tinouus olesan, UK) as per ASTM-D-256.

2.3.3. Thermal properties

Thermal degradation behavior of pure epoxy, epoxy/ESO blend and nanocomposite were carried out using thermogravimetric analysis (TGA) (Q 50 TA Instruments, USA). Samples of 7–10 mg weight were scanned from 40 to 750 °C at a heating rate of 10 °C/min in nitrogen atmosphere. Corresponding initial, final degradation temperature and rate of degradation peak temperature were noted. The thermal stability parameters integral procedural decomposition temperature (IPDT) and decomposed activation energy (E_t) were determined using Horowitz and Metzger equation.

The glass transition temperature of all samples was determined by Differential Scanning Calorimetry, DSC (Q20, M/s TA Instrument, USA) in a temperature range of 25–200 °C at a heating rate 10 °C/min. The curing behavior of epoxy/ESO blend and clay filled epoxy/ESO nanocomposite were analyzed employing DSC from 30 to 250 °C at a heating rate 10 °C/min under N_2 atmosphere. Curing agent TETA was mixed with resin at a stoichiometric epoxide/amine ratio at room temperature and stirred properly to form homogeneous mixture before curing process.

The dynamic mechanical study was carried out by Dynamic mechanical analyzer, DMA (Q 800, M/s TA instrument, USA) in three point bending mode and the corresponding viscoelastic properties of the materials were determined as a function of temperature. The temperature range used in the present investigation was varied from 30 °C to 200 °C, with a heating rate of 10 °C/min. The samples were scanned at a fixed frequency of 1 Hz and a strain of 0.1%.

Co-efficient of thermal expansion (CTE) of the samples was determined by using Thermo mechanical analyzer (TMA) (Perkin Elmer Diamond TMA, USA) to analyze the dimensional stability. Samples of dimensions 5 × 5 × 3 mm are tested with temperature range from ambient to 250 °C in Argon environment at a heating rate 10 °C/min.

2.3.4. Morphology study

The morphological analysis of impact fractured epoxy blend and composites was carried out using Scanning Electron Microscopy (EVO MA 15, Carl Zeiss, SMT, Germany) to study the interfacial adhesion between clay and matrix. The samples were sputtered with platinum and were dried for half an hour at 70 °C in vacuum, prior to imaging.

Diffraction spectra of wide-angle X-ray scattering (WAXS) were obtained with a Rigaku diffraction system (Cu Ka radiation with $\lambda = 0.15418$ nm) having a monochrometer operating at 45 kV at room temperature. The diffractogram step size was $2\theta = 0.0248$, a count time of 2.88 s and a 2θ range from 1 to 10°.

The intercalated or exfoliated clay layers in the amine-cured epoxymatrix were observed with transmission electronmicroscopy (TEM). A JEOL 1400 TEM with field emission filament in 120 kV accelerating voltage was used to collect bright field TEM images of the ESO based epoxy/clay nanocomposites.

3. Results and discussion

3.1. Mechanical properties

The tensile and impact properties of bio-based epoxy blend and nanocomposite are presented in Table 1. In earlier reports, it was reported that the tensile strength and tensile modulus decreased gradually with the increase in ESO content due to its ductile aliphatic long chain structure and low crosslink density

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