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A study on effect of organo modified clay on curing behavior and thermo-physical properties of epoxy methyl ester based epoxy nanocomposite

Sushanta K Sahoo, Smita Mohanty*, Sanjay K Nayak

Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering & Technology (CIPET), B/25, CNI complex, Patia, Bhubaneswar 751024, Odisha, India

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ABSTRACT

Non-isothermal curing kinetics was studied using differential scanning calorimetry (DSC) analysis to investigate the effect of nanoclay (C30B) on crosslinking reaction of epoxidized methyl soyate bioresin modified epoxy blend curing with triethylenetetramine. The kinetic parameters were determined by using Kissinger–Akahira–Sunose method and autocatalytic model. Addition of bioresin lowered the activation energy of epoxy on account of reduced viscosity allowing better contact of resin with curing agent. On the other hand incorporation of clay within the epoxy blend increased the activation energy (E_a) of curing due to the steric effect of clay and increased viscosity. The overall order of the reaction $m+n$ was found to be increased on addition of bioresin and decreased on incorporation of C30B clay within blend. Dynamic mechanical analysis revealed higher glass transition temperature and crosslink density of the nanocomposite. Thermal stability of epoxy blend is enhanced by addition of clay which restricted the mobility of chain and hindered the decomposition process.

1. Introduction

Sustainable polymers from plant oils have drawn significant attention by the researchers in recent years [1–2]. Triglyceride oil based bio-resins are reported as the most successful modifier for thermoset resin as it reduces the viscosity of the resin system, overcomes the brittleness and most importantly biological origin [3–4]. However, this improvement in toughness of epoxy matrix is usually achieved by sacrificing the thermophysical properties which limits the wide use of plant oil modified epoxy blend in structural applications [5–13]. Various nanoparticles have been used to modify the properties of polymer like stiffness, strength, thermophysical property etc. [14].

Addition of modified nanoscopic layered silicates into thermoset matrix has received increasing attention on account of the presence of organophilic layers which allow the polymer to polymerize within the galleries and enhances the performance [15–17].

The properties of thermoset nanocomposites mostly depend on the chemical structure of polymer resin, properties of nanofillers, curing agent, chemical interaction between fillers and polymer matrix and polymerization methods [14–20].

It is important to understand the curing mechanism of the clay filled polymer system to control the curing reaction and obtain better physical properties of the nanocomposite [18–20]. Differential scanning calorimetry (DSC) is one of the extensively used techniques to study the curing kinetics of epoxy in isothermal or dynamic mode using various kinetic models. ICTAC Kinetics Committee recommendations were followed for collection of kinetic data and performing kinetic computations [21–22].

Various authors have studied on effect of clay on curing behavior and thermal properties of epoxy in last decade [17–20,23–28]. Research on plant oil based thermoset nanocomposite is growing significantly by the academia and industries because of their unique properties. In recent years, it is reported that clay enhances the thermal stability and thermomechanical performance of the biobased thermoset nanocomposite [29–35]. However, curing kinetics study on plant oil modified epoxy nanocomposite is limited. In our previous work, we have studied the effective toughening of epoxy by modifying epoxidized methyl soyate (EMS) bioresin sacrificing the thermal and thermophysical properties [13]. Current investigation is based on the effect of C30B organo clay on the thermal properties and curing behavior of EMS toughened epoxy blend cured with triethylenetetramine.

* Corresponding author.
E-mail address: papers.journal@gmail.com (S. Mohanty).

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2. Experimental

2.1. Materials and methods

Diglycidyl ether of bisphenol A-based (DGEBA) epoxy resin of grade with an epoxy equivalent weight 190–195 g/mol and ambient temperature curing agent triethylenetetramine (TETA) were obtained from the M/s Marshal Polymers, Kolkata, India. Epoxidized methyl soyate was synthesized in our laboratory by our group. C30B clay was procured from Southern Clay Pvt. Ltd., USA. All required chemicals were of analytical grade and procured from M/s Merck Chemicals, India.

2.2. Preparation of resin blend and nanocomposite

The epoxidized soybean oil was transesterified to form epoxidized methyl soyate by our group as reported in our previous work [13]. Toughened bio-based epoxy blend was prepared by blending EMS bioresin with DGEBA epoxy resin at ratio 20:80. The resin mixture was prepared by mechanical stirring and ultrasonicated and subsequently kept in vacuum oven to eliminate air bubbles. 5 wt% of nano clay C30B was incorporated within epoxy/20% EMS resin blend and then mechanically stirred at 2500 rpm for 1 h to achieve better exfoliation of clay in nanocomposite. Then curing agent TETA was added to the resin blends in the stoichiometric ratio. For TGA and DMA testing, samples are initially cured at room temperature for 24 h followed by post curing at 80 °C for 2 h and 120 °C for 1 h.

2.3. Characterization

2.3.1. Non isothermal curing kinetics

Non-isothermal curing of all epoxy systems were carried out by differential scanning calorimetry DSC (Q20, M/s TA Instrument, USA) in temperature range of 25–250 °C at heating rate of 5, 10 and 15 °C/min under N_2 atmosphere. The instrument was calibrated for temperature and enthalpy using indium prior to the experiment. Curing agent triethylenetetramine (TETA) was mixed with epoxy resin system at stoichiometric epoxide/amine ratio at room temperature and subsequently stirred properly to form homogeneous mixture. Samples of about 5–7 mg were placed in covered sealed aluminium pans for curing. Kissinger–Akahira–Sunose method and autocatalytic model were applied in this study to determine the kinetic parameters.

2.3.2. Thermogravimetric analysis

Thermal degradation behavior of epoxy/EMS blend and nanocomposite were studied using thermogravimetric analysis, (TGA) (Q 50 TA Instruments, USA). Samples of 7–10 mg weight were scanned from 40 to 600 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The thermal parameters like T_{onset} -the temperature at which the degradation starts; T_p -the temperature at which degradation rate is maximum: T_{endset} -the temperature at ending process; T_5,T_{10} -the temperatures corresponding to 5 wt% and 10 wt% weight losses are determined.

2.3.3. Dynamic mechanical analysis

The DMA measurements were carried out in the three point bending mode of the equipment (Q 800, M/s TA instrument, USA)

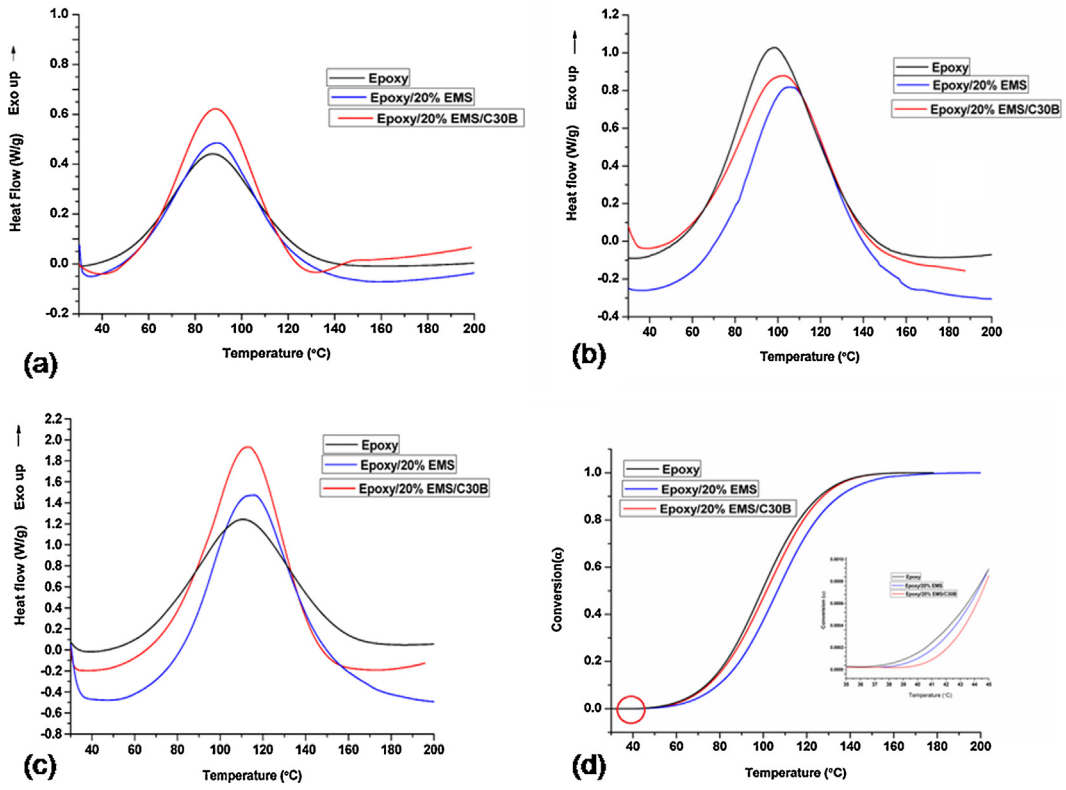

Fig. 1. DSC curing curve of (a) epoxy (b) epoxy/20% EMS blend and (c) epoxy/20% EMS/C30B at different heating rate (d) Degree of conversion vs. temperature plot of modifying epoxy systems at heating rate of 10 °C/min.