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Modification of cottonseed oil for amine cured epoxy resin: Studies on thermo-mechanical, physico-chemical, morphological and antimicrobial properties

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ABSTRACT

Cottonseed oil (CSO) has been transformed into useful polymerizable oxygenated monomers (epoxies) by Prilezhaev epoxidation. The epoxidized cottonseed oil (ECSO) has been used as an internal plasticizer and toughening agent for commercially available diglycidyl ether of bisphenol-A (DGEBA). Development of toughening system described in this work involved two steps: (i) reaction of ECSO with triethylenetetramine (TETA) to form amine terminated prepolymer (PPECSO) and (ii) blending PPECSO with DGEBA in different ratios to give crosslinked epoxy networks. Curing of the fully reacted DGEBA/ECSO/TETA blend has been studied by differential scanning calorimetry. Thermal and mechanical properties of modified epoxy resins have been studied to evaluate the plasticizing effect of the vegetable oil derivative. Chemical/solvent resistance, degree of swelling, water vapor transmission, anti-corrosive and antimicrobial properties as well as effect of ECSO content on these properties has also been investigated.

1. Introduction

Renewable resources such as natural oil can provide sustainable platform to substitute the petroleum feedstock partially or to some extent totally by chemical modification. Bio-based polymers have found much more attention in recent years, especially in the polymer and coating industries, as they are biodegradable, eco-friendly, non-noxious, low cost and the raw materials are also abundantly available [1–8].

Epoxy resins are a class of versatile and most interesting polymeric materials which form network on curing. Epoxy resins are widely used as structural adhesives and in paint and coatings. They contribute to good thermal stability, mechanical properties and chemical/corrosion resistance, attributed to use in ambient and thermal cure applications [9–12]. The main drawback of epoxy thermosets is its brittleness due to high crosslinking, which results in lowering the impact strength, fracture energy and poor peeling, therefore limiting its application. Toughness in brittle epoxy resins can be achieved by, (i) chemically modifying the backbone with flexible spacers; (ii) increasing molecular weight of the epoxy backbone; (iii) decreasing the crosslink density of the matrix; and (iv) homogenizing the toughener phase in epoxy matrix. Modification of epoxy resin has been done with polystyrene, poly(methyl methacrylate), poly(etherimide), poly(benzimidazole), poly(ether ether ketone), carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN), polysiloxane, polyurethanes either by blending or chemical reaction between modifier and epoxy resin [10,12–15].

Recently, epoxidized vegetable oil (EVO) has been reported to be effective modifier and can be used as toughening agent to modify epoxy resin. Some investigators have reported that the toughness of the matrix can be enhanced either by incorporating flexible linkage or by reducing the crosslink density [12,14–18]. Many researchers have investigated the use of epoxidized soybean oil (ESO) [4,14,15,17,19–28,33], epoxidized linseed oil (ELO) [12,29], epoxidized palm oil (EPO) [16], epoxidized castor oil (ECO) [18,26,30], epoxidized crambe oil (ECMO) [10], tung oil [25], epoxidized rapeseed oil (ERO) [27] as reactive modifiers, toughening agent, internal plasticizer and reactive diluent for the commercial epoxy resin for polymer and coating applications.

Ratna [14] and Kar et al. [21] studied the toughening of DGEBA based epoxy resin using pre-polymerized ESO cured with an ambient temperature hardener. Modified epoxy films were studied for impact behaviour, surface morphology and adhesion properties and optimum properties were observed at 20% ESO concentration. Parzuchowski et al. [22] and Sarwono et al. [16] investigated

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epoxy resins modified with ESO and EPO, respectively and studied the thermo-mechanical properties and surface morphology of resulting epoxy networks and compared them with the parent epoxy network. Incorporation of EVO to epoxy resin reduces the glass transition temperature (T_g) as well as alters the mechanical properties; reduction in crosslinking density and plasticizing effect is responsible for this behaviour. ESO modified epoxy resin with anhydride and amine crosslinkers was investigated by Shabeer et al. [31]. Storage modulus (E') and T_g increases with anhydride cured while it decreases with amine cured resin. Czub [32] studied low to high ESO content modified epoxy resin and found that lower oil content modified epoxy resin shows very good mechanical properties, low water absorption and good chemical resistance while higher oil content shows excellent impact strength, elasticity and flexibility. Wang et al. [4] and Gerbase et al. [33] reported the influence of oxirane content, oxirane type, pendent saturated chain content on thermal and mechanical properties of ESO modified epoxy resins; similar results were reported by Park et al. [18] with castor oil. Mondrzyk et al. [34] investigated the effect of quaternary ammonium compound and alkyl chain length on structure–bioactivity relationship of epoxy-amine resins against Gram-positive and Gram-negative bacterial strain.

India is an agrarian country and is the 2nd largest producer of cottonseed oil in the world with production estimated for the year of 2014 is 1.39×10^6 MT [35]. CSO has a 2:1 ratio of polyunsaturated (65–70%) to saturated fatty acids (26–35%), unsaturated fatty acids consists of 18–24% oleic, 42–52% linoleic and linolenic [36]. Considering the availability of CSO in India and its ability to provide desired functionalities, it may be a more potential, vital and cheap source for the production of plant oil-based resin for coating applications.

The main objective of this work is to toughen DGEBA based epoxy resins by incorporating modified amine terminated CSO (PPECSO) as internal plasticizer. Effect of the modified oil content on the curing behaviour of DGEBA/ECSO/TETA composition and thermo-mechanical, physico-chemical and antimicrobial properties of the resulting epoxy networks has also been studied and discussed.

2. Experimental

2.1. Materials

Cottonseed oil (CSO, Jayajothi Industries, Hyderabad, India), hydrogen peroxide (30% W/V), 98% sulphuric acid, sodium sulphate, sodium bi-carbonate, hydrochloric acid, sodium chloride, sodium hydroxide, xylene, glacial acetic acid (s.d. fine Chemicals, Mumbai, India), diglycidyl ether of bisphenol-A (DGEBA, Atul Ltd., Valsad, India) (EEW = 200 g/equivalent), triethylenetetramine (TETA, Alpha Acer) (amine value = 1428 mg KOH/g), 85% formic acid (Finar Chemicals, Hyderabad, India), etc. were used without further purification.

2.2. Characterization

Fourier transform-infrared (FT-IR) spectra of the oil, epoxidized oil, reaction aliquots, and products were recorded on Perkin Elmer Spectrum 100 (USA). Neat liquid samples were done by using KBr disc and free film samples were done by using Universal Attenuated Total Reflectance (UATR) Polarization Accessory. Each sample was scanned 8 times within a range 450–4000 cm^{-1} with resolution of 4 cm^{-1}. The ^1H NMR of ECSO was done using Bruker-500 MHz spectrometer taking tetramethylsilane (TMS) as the standard at ambient temperature in $CDCl_3$ solvent.

Curing behaviour of films was done by differential scanning calorimetry (DSC) (DSC-7020, Hitachi Tokyo, Japan) under nitrogen environment and heating rate of 5 °C/min. The temperature range used was from 0 °C to 250 °C. Standard aluminium crucible/lid was used for sampling the material, weight of sample taken about 5 mg. The visco-elastic behaviour of the epoxy films in nitrogen atmosphere was analyzed with dynamic thermal mechanical analyzer (DMTA) (model: DMA-Q-800, TA Instruments, USA) in a tensile mode at a frequency of 1 Hz and a heating rate of 5 °C/min. The sample dimension was 15 mm × 10 mm × 0.15 mm and the temperature range used was from −100 °C to 150 °C. Thermogravimetric analysis (TGA) was carried out with TGA-Q-500 (TA Instruments, USA) under nitrogen environment and heating rate of 10 °C/min up to a temperature of 500 °C. The film resistance and solubility against water and solvent (xylene) is measured by swelling ratio (Q) as per ASTM D2765-11. Morphological study of unmodified and modified epoxy films were carried out with Scanning Electron Microscopy (SEM), Hitachi-S520 (Oxford Link ISIS-SEM model) Japan.

The tensile strength and % elongation of free epoxy films were done with Universal Testing Machine (UTM) model AGS-10k NG (Shimadzu, Japan) at room temperature. The system was connected with autograph controller/measurement unit. The dumbbell shaped test specimens having length 100 mm, breadth 10 mm and thickness 0.10–0.15 mm were used, according to ASTM D638-10. The gauge length was 50 mm and crosshead speed of 10 mm/min. The data reported are average of three experimental values. Test for adhesion on metal surface (cast iron) was done by self-aligning adhesion tester (automatic) type-V on metal surface according to the ASTM D4541-09. The stress applied by detaching assembly (U) is in MPa. The abrasion test for all fully cured epoxy resin was done on Taber instrument (Model-5131, USA) as per the ASTM D4060-10. The coated mild steel panel was weighed first and then fixed on the base facing upward in the trough with the help of hinges at the corners of instrument. The abrader wheels (*H-10*) having a load of 500 g on each arm were attached, their heads placed over the coated surface of the panel and driven mechanically to rotate while the panel was kept rotating. The panels were weighed after 1000 cycles. Abrasion resistance was expressed in terms of wear index (I) (mg/1000cycles) and calculated by Eq. (1).

$$I = \frac{(A - B) \times 1000}{C} \quad (1)$$

where A and B—weight of test specimen before and after abrasion (mg), C—number of cycles of abrasion recorded (here, C = 1000).

Impact resistance test for epoxy coatings were performed on 24-gauge steel panels of 150 mm length and 100 mm breadth by Aggregate impact tester (Sheen Instruments Ltd., England) as per the ASTM D2794-93 standard. Test panel of 0.2 mm coating thickness was placed on aperture which is at the base of instrument. Weight of 10.5 lbs (including indenter) released from the height of 70 cm. Test was done on both site (direct and reverse to coated surface). Flexural test were performed as per the ASTM D522-93a standard by 180° conical mandrel tester (Sheen Instruments Ltd., England) of 200 mm length with a diameter of 3 mm at one end and 38 mm at the other end. The specimen size was 150 mm × 100 mm × 0.8 mm. Results are mentioned in terms of pass/fail by taking average of tree experiments.

Unmodified and modified epoxy free films were subjected to exposure in various chemical media to study their behaviour viz. change of weight, overall appearance, loss of gloss, solubility, etc. Test was performed as per the ASTM D543-06 (immersion test) standard for 7 days. Water vapour transmission (WVT) test was performed as per the ASTM D1653-03 (wet-cup method) to study the rate of moisture permeation through the coating free film. During the test, cups were kept under very low relative humidity (~0) condition at room temperature in a desiccator. Noted the weight