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Electrically conductive green composites based on epoxidized linseed oil and polyaniline: An insight into electrical, thermal and mechanical properties

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ABSTRACT

Renewable resource based electrically conductive composites were prepared using polyaniline (PANI) as a conductive filler and epoxidized linseed oil (ELO) as the matrix. Linseed oil (LO) was epoxidized to form ELO and characterized through ^{1}H NMR and IR spectra. Bio-based ELO/PANI conducting composites were prepared by varying the PANI concentration with an aim of attaining the electrical conductivity in the antistatic range (10^{-8} to 10^{-3} S/cm) to replace its petro-based counterpart. Conductivity increased with PANI upto the order of 10^{-6} S/cm with percolation threshold at around 7% of PANI. The shear stress and viscosity of the uncured ELO resin and ELO/PANI resin mixture were studied as a function of shear rate. Differential scanning calorimetry (DSC) studies showed that addition of PANI had a minimal effect on ELO curing at all concentrations. Dynamic mechanical analysis indicated that PANI as a filler provided mechanical fortification in the rubbery region and increased glass transition temperature (T_g) significantly. Thermal stability of ELO remained almost unaffected with the PANI incorporation. Microscopic observation revealed good distribution of PANI in ELO matrix even at higher loading. Interestingly, tensile strength and Young's modulus increased by ~8 and ~27 folds, respectively, at 15% PANI content.

1. Introduction

Electrically conductive polymer composites are prospective materials for several engineering applications such as electrically conductive adhesives, electromagnetic interference shielding materials, antistatic formulations, sensors, fuel cell, rechargeable batteries and electronic devices, etc. [1–5]. These composites are made up of host matrix that provides the mechanical strength and conductive fillers particles that offer electrical conduction [6]. Intrinsically conducting polymers (ICP) are an important class of conductive fillers that are environmentally stable and cost effective alternate to the traditional expensive metallic fillers which are prone to corrosion with the passage of time [4]. Among ICPs, Polyaniline (PANI) is one of the most studied polymers both by academicians and industries by virtue of its versatile nature like the ease of synthesis, good polymerization yield, low cost, adjustable conductivity and good environmental stability [5,7]. Despite possessing such advantages, researchers have not been able to exploit its properties because of its infusibility and insolubility [8]. A better way is the compounding of PANI with inherently insulating polymer matrices to develop conducting composites for various engineering applications. Epoxy is one of the commonly used thermosetting matrices for such composites because of its outstanding thermal and mechanical properties, minimal curing shrinkage, and ability to withstand harsh chemical environments. This has increased its suitability for numerous applications like structural materials and adhesives, coatings, aeronautical materials, electronic packaging and composites, etc. [9–18].

PANI doped with organic acids like camphorsulfonic acid (CSA) [19,20], dodecylbezenesulfonic acid (DBSA) [21,22] and *p*-toluenesulfonic acid (PTSA) [23,24] has been used earlier as preferable filler by various researchers. Peltola et al. [19] prepared PANI-CSA based epoxy adhesives having the conductivity in the range of 10^{-8}-10^{-3} S/cm, (applicable for antistatic application) at less than 2% of PANI loading. Later, Tsotra et al. [21] formulated epoxy/PANI-DBSA composites, and obtained the conductivity of 2×10^{-7} S/cm at 10% PANI content which qualifies for electrostatic discharge (ESD) application. Soares et al. [25] reported the conductivity of epoxy/PANI-DBSA (7%) and epoxy/PANI-DBSA (18%) adhesives of the order of 10^{-8} and 10^{-5} S/cm, respectively, through physical mixing method. Mir et al. [26] developed electrically conductive adhesives with inorganic acid (HCl) doped PANI and established the conductivity of the order of 10^{-6} S/cm

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at 10% PANI content. The selection of curing agent plays a crucial role in attaining the desired conductivity level. Basic amines, commonly used as cross-linking agents, tend to deprotonate PANI because of their basic nature, and thereby, reduce its conductivity [25]. Acid anhydrides such as hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, etc. are widely used as cross-linkers for epoxy resin along with an accelerator to reduce the curing temperatures. Since BF_3-complex is a Lewis acid and does not affect the conductivity of PANI, it is mostly used as curing agent as well as an accelerator in cross-linking of epoxy resin [27].

The rapidly depleting fossil resources and increasing environmental sustainability concerns have motivated the researchers to explore renewable and/or bio-based feedstock as an alternative to petro-based materials [28,29]. In this context, vegetable oils are receiving overwhelming attention worldwide due to their ability to form pre-polymers, a plethora of availability, non-hazardous nature, environmental friendliness and biodegradability [30]. Vegetable oils are chemically composed of mainly triglycerides with long aliphatic carbon chain and multiple unsaturation contents which serve as active sites for direct polymerization or after modification [31]. Various modifications that may be carried out at the unsaturation of the fatty acid chain are acrylation, maleination, halogenation, ozonolysis, dimerization, metathesis, epoxidation and hydroxylation, etc. [32]. Among several modifications possible for plant oils, epoxidation is the most common, straight forward and inexpensive method. In situ method of epoxidation is widely used by researchers as it is solvent free and epoxy content of the epoxidized oil can be appropriately controlled by varying the reaction time [33–35]. Epoxidized oils are considered as renewable raw materials for the preparation of bio-based thermoset products for numerous engineering applications because of their relatively lower viscosity and better processability [35]. They are widely used as reactive diluents for epoxy thermosets for their strong viscosity reducing ability, and also as preferable pre-polymers for the synthesis of polyols used in the manufacturing of polyurethanes with superior thermal and mechanical performance [36,37]. Among all oils, Linseed oil (LO) is the most suitable oil due to its high unsaturation content (53% linolenic acid and 6.6 number of double bonds/molecule) that can be easily epoxidized and can yield higher epoxy values closer to that of commercial epoxy. Being a drying oil, it is frequently used as paint binder and wood finish. Additionally, it has also found applications in enamels, linoleum, oilcloth, printer's ink, and as waterproofing for raincoats [31,38]. Epoxidized linseed oil (ELO) is commonly used as plasticizers for PVC and epoxy resins to provide flexibility, and also for coatings and adhesive applications [39,40]. Many researchers have developed ELO based composites with interesting properties using various reinforcements [41,42]. Another instance of its use previously as a greener substitute involve development of polyhedral oligomeric silsesquioxane based bionanocomposite to reduce dependence on petro-based epoxy resin [43].

In the present study, we report the preparation of bio-based conducting composite taking ELO as bio-renewable matrix and PANI as conducting filler. LO was epoxidized via in situ method, and subsequently, the effect of PANI on the electrical, thermal and thermo-mechanical properties of ELO network cured with hexahydrophthalic anhydride (HHPA) and BF_3-complex was investigated. To the best of our knowledge, no such system of bio-based epoxy resin/PANI has been studied previously. The work was undertaken with the aim of developing ELO/PANI composites with the target values of conductivity in the range (10^{-8} to 10^{-6} S/cm) applicable for antistatic coating/ESD application.

2. Experimental

2.1. Materials

Aniline and Ammonium peroxydisulfate (APS) were purchased from Merck, India. *p*-toluenesulfonic acid (PTSA) was obtained from Vetec Sigma, India. LO was procured from Himedia, India. Seralite (SRC-120), an acidic ion exchange resin, and magnesium sulfate ($MgSO_4$) were purchased from SRL Pvt. Ltd, India. Glacial Acetic acid (CH_3COOH), Hydrogen peroxide (H_2O_2) (30 wt%), and sodium carbonate (Na_2CO_3) were procured from Rankem, India. HHPA for curing was obtained from Sigma-Aldrich, USA. BF_3-ethylamine complex was supplied by TCI, India.

2.2. Synthesis of PTSA doped PANI

PANI doped with PTSA was prepared via the conventional one phase polymerization technique in aqueous phase as reported in our earlier publication [44]. In a typical procedure, aniline (5 gm) and PTSA (10.22 gm) were mixed in distilled water (250 ml) and stirred for 1 h to make homogenous solution keeping the temperature between 0 and 5 °C. Subsequently, APS (12.25 gm) was added slowly to this mixture maintaining the molar ratio of PANI: PTSA: APS at 1:1:1. Stirring was continued for 5 h and followed by the addition of acetone (25 ml) to seize the polymerization. Solution was filtered, washed with distilled water and acetone and dried in oven at 65 °C for 24 h.

2.3. Epoxidation of LO

Epoxidation of LO was performed in the presence of glacial CH_3COOH and H_2O_2 in a three-necked round bottom flask equipped with magnetic stirrer, a dropping funnel and a thermometer as reported by Kim et al. [35]. Linseed oil (79 gm) and CH_3COOH (30 gm) were added in the molar ratio of 1:1 (1 mol unsaturation in oil) to the round bottom flask along with 25% seralite SRC-120 (19.75 gm) (acidic ion exchange resin) and stirred for 30 min. To this solution, H_2O_2 (113 gm) was added dropwise in the ratio of 2:1 of H_2O_2 and oil unsaturation and the mixture was stirred for 5 h with the temperature maintained at 60 °C throughout the reaction (Fig. 1). After the completion of reaction, mixture was filtered with cheese cloth to remove seralite catalyst. Subsequently, ELO layer was separated and washed with 2% Na_2CO_3 solution and filtered using $MgSO_4$ to remove moisture and dried overnight in vacuum oven at 60 °C.

2.4. Preparation of ELO/PANI composites

The calculated amount of PANI and ELO were dispersed in acetone using ultrasonic bath (Labmann, LMUC-4) for 1 h. Mixture was stirred at 55–60 °C for 5 h to improve the dispersion quality and to remove the acetone completely from mixture. Curing agent along with the accelerator was added in the ratio of 44:5 per 100 parts of ELO as reported earlier [27]. The mixture obtained was poured in steel molds applied with silicon spray. The samples were then cured at 120 °C in a thermostatic oven for 5 h.

Composites with 0, 3, 5, 7, 10, 15% PANI concentration are abbreviated as ELO, ELO/PANI-3, ELO/PANI-5, ELO/PANI-7, ELO/PANI-10, ELO/PANI-15, respectively.

2.5. Characterization

2.5.1. LO/ELO characterization

Epoxy equivalent weight (EEW) was determined by titration with 0.1 N HBr in glacial acetic acid as per the ASTM D 1652. Iodine value was obtained according to ASTM D 5768-02 using Wijs solution [45].

FT-IR spectra of LO and ELO were recorded with FT-IR spectrophotometer (Perkin Elmer FT-IR C91158, UK) within the range from 4000 cm^{-1} to 400 cm^{-1} with a 4 cm^{-1} resolution. ^1H NMR spectra was obtained from JEOL resonance spectrometer (JNM-ECX-400II) using deuterated chloroform ($CDCl_3$) as a solvent. Degree of epoxidation (DOE) was calculated using equation (1) as reported by Jebrane et al. [34].