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Biodegradable bioepoxy resins based on epoxidized natural oil (cottonseed & algae) cured with citric and tartaric acids through solution polymerization: A renewable approach

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ABSTRACT

Biodegradable bioepoxy resins were prepared from epoxidized cottonseed oil (ECO) and algae oil (EAO). CO and AO were epoxidized using the environmentally benign reagent hydrogen peroxide in quantitative yield. The bioepoxy resins were obtained on reaction of ECO and EAO with citric acid (COCA/AOCA) and tartaric acid (COTA/AOTA) respectively. Bioepoxy resins were characterized for their solution viscosity, molecular weight distribution, thermal behaviour, tensile strength and resistance to the chemical factors test. Bioepoxy resins were soluble in alkali solution (1 M) and resistant to most of the organic solvents. The thermal properties were determined by thermogravimetric analysis and differential scanning calorimetry. Thermal stability and chemical resistivity tests of bioepoxy resins were compared with the petroleum-based epoxy resin (P-epoxy and P-epoxy 1). The results indicated higher thermal stability of bioepoxy resins compared to both P-epoxy and P-epoxy 1. The biodegradation tests of COCA, COTA, AOCA and AOTA were conducted under identical conditions and the results demonstrated that COCA was degraded up to 92% in 24 days and COTA was 87% degraded in 56 days similarly AOCA decomposed completely in 90 days and AOTA decomposed in almost 240 days by bacterial consortium. The larvicidal property of bioepoxy resins was studied against mosquito larvae. Assays revealed that the average toxicity of COCA was 68% in 48 h while the COTA was less toxic and causes 46% mortality in 48 h. Similarly AOCA was found to be toxic against larvae and causes 20% mortality in 48 h while the AOTA was not found to be effective against larvae whereas P-epoxy has 100% mortality in 24 h. Seed germination was tested in bioepoxy resins using black eyed pea. Bioepoxy resins supported seed germination.

1. Introduction

Biopolymers are constantly grabbing increasing attention as these materials can be used to replace the traditional thermo-stable petrochemical polymers and have been considered for different applications including coatings, adhesives, engineering composites; electrical laminates etc., (Kumar et al., 2010; Teng and Soucek, 2000) due to their low toxicity, intrinsic biodegradability and low processing cost (Biermann et al., 2000). The reason for this interest in natural oils is their particular structure which is characterized by the presence of different fatty acids in a triglyceride structure. Some of the natural oils have been directly polymerized into cross-linked polymers in literature, (Hong et al., 2012) however polymerization of most of the oils often requires their conversion into reactive monomers which solves the drawback of the low reactivity of natural triglycerides. This can be attained through an introduction of new reactive groups in the fatty acid chains through functionalization of olefinic moiety e.g. epoxidation, hydroformylation, ring-opening of epoxidized oils with hydrogen active compounds (Pan et al., 2011; Pawar et al., 2016; Petrovic et al., 2002).

Epoxy resins are a class of thermosetting resins routinely used as encapsulates, casting materials, potting compounds, coatings, adhesives, binders, inks, plasticizers, abrasives, automotive and electrical components etc (Lee and Neville, 1967). Epoxy resins

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possess properties such as low shrinkage, high strength, excellent adhesion to several substrates, effective electrical insulation and greater thermal and chemical resistance (May, 1988). Commercially epoxy resins are synthesized from bisphenol A (BPA). The diglycidyl ether of bisphenol A (DGEBA) is used extensively as an epoxy component of thermosetting polymers. The rigid aromatic structure of BPA brings overall high performance to the cured resins. Unfortunately the BPA, an endocrine disrupter can mimic the body's own hormones and may lead to several negative impacts on human health. The bisphenol A based resins are sensitive to hydrolysis and leaching of BPA leading to widespread human exposure revealed by various studies (Cao et al., 2009; Joskow et al., 2006). Numerous developed countries have recently restricted its use in food contact materials, mainly baby bottles (Ma et al., 2016). In addition, most of the common curing agents of epoxy resins such as aliphatic and aromatic amines and anhydrides are fossil fuel based and toxic.

Recent awareness on BPA toxicity and high cost of fossil resources promting researchers to substitute partially or fully with other biobased materials in industrial applications and attempts to move toward sustainability, it will be significant to find all the components of epoxy resin formulation to be biobased, such as bio-based curing agents to substitute for the nonrenewable-based curing agents. There are several poly(carboxylic acid)s produced by biological processes that can be used as curing agents for epoxidized natural oil (Sauer et al., 2008). Citric acid (CA) is produced commercially through fermentation. Tartaric acid (TA) is economical derived from natural sources such as grapes or produced naturally. These low cost polyfunctional monomers are important to obtain fully cured biobased networks. Several researchers described the utilization of citric acid to crosslink starch, cellulose fibres (Wing, 1996), more recently, Gogoi et al. (2015) described the blends of epoxidized alkyd resins from jatropha oil and epoxidized oil cured with aqueous citric acid solution. The biodegradation of chain-coupled polyesters based on tartaric acid have recently been reported by Dhamaniya et al. (2014). In the field of green chemistry development now-a-days researchers are actively engaged in synthesizing biodegradable bioepoxy resins, which are not only derived from natural resources, such as vegetable oils and fats, corn-starch, pea-starch or microbes, but also are easily decomposed than other available synthetic polymers (Leja and Lewandowicz, 2010). Shogren et al. (2004) showed the preparation and mineralization of epoxy resins prepared from epoxidized soybean oil with aliphatic dicarboxylic acid.

The Maharashtra state of India is significant producer of cotton. Cotton seeds are used as fodder food for animals and the cottonseed oil has demand as cooking oil and lubricating agent (Bailey, 1948). The byproducts of cotton have been used for the preparation of biopolymers (Cheng et al., 2012). It is amongst second best potential sources for plant proteins after soybean and the ninth finest oil-producing crop (Ahmad et al., 2007). The production of cottonseed oil in India during 2010–2011 was 11.99 lakh tones and by 2025 and 2050 the production is projected to increase to 28.53 and 35.55 lakh tones (Hegde, 2012). The cottonseed oil with required amount of unsaturated fatty acids enhances its value as raw material for the preparation of biopolymers.

Algal oil has now been touted as a new and interesting field with sufficient unsaturation as an excellent source for biopolymer preparation. This has many advantages like high oil yield, ability to grow in robust environment as, no costly nutrients like glucose or peptones are required necessarily (Trentacoste et al., 2014). Additionally, algae oil has been foreseen converting solar energy and carbon dioxide into renewable and ecological energy (Pawar et al., 2015). These advantages of algae oils are repeatedly and increasingly emphasized (Kerton et al., 2013), confirmed efficient use of epoxidized algae oil (EAO) as a viable raw material for polymer preparation. The applications of algae oil to date is mainly constrained to the extraction of the naturally occurring ingredients and their utilization as biofuels, pigments, vitamins or for human and animal nutrition, beside these some recent reports available on use of algae oil are, Petrovic et al. (2013) reported the polyols and polyurethanes from crude algae oil, Roesle et al. (2014) prepared the synthetic polyesters from algae oil and we (Pawar et al., 2015) have reported the rigid polyurethane foams from algae oil using biobased chain extenders.

In view of above points in the present research work bioepoxy resins based on cottonseed oil (CO) and algae oil (AO) has been synthesized and characterized by different techniques and reports its biodegradation, larvicidal activity and seed germination. The prepared bioepoxy resins are completely biodegradable bioepoxy resins. The bacterial granules (consortia) were used for biodegradation of bioepoxy resins made from natural oil (AO and CO). The larvicidal activity against mosquito larvae of COCA, COTA, AOCA and AOTA bioepoxy resins was examined and compared with petroleum epoxy resin. The seed germination was tested in bioepoxy resin and petroleum epoxy resin using black eyed pea (*Vigna unguiculata*) and results were compared with the soil. The bioepoxy COCA, COTA and AOCA, AOTA obtained by the reaction of epoxidized cottonseed oil (ECO) and epoxidized algae oil (EAO) with citric and tartaric acid respectively developed by us may be alternative choice to the synthetic polymers produced from petrochemical industry. Present research work is the continuation to our ongoing research activities of synthesis of biodegradable bioepoxy resins (Kadam et al., 2015; Yemul et al., 2013) where mahua oil and karanja oil has been used for the synthesis of bioepoxy resins. Furthermore, the bioepoxy resin was used for manufacturing fancy, non-toxic, eco-friendly cast-resin articles as represented in Fig. S1 (supporting information).

2. Materials and methods

2.1. Materials

Algae oil (IV) 120, and acid value 0.2 mg KOH/g obtained from *chlorella* microalgae was gift sample from Soley Institute Turkey. Cottonseed oil was procured from local market and used as received. The oils were characterized by refractive index, saponification value, acid value and iodine value. Trimethylolpropane triglycidyl ether (equivalent weight 138 g/mol) and bisphenol A diglycidyl ether (equivalent weight 176 g/mol) was purchased from Sigma Aldrich, Canada. Other chemicals such as hydrogen peroxide (30%), acetic acid (85%), anhydrous Na_2SO_4, amberlyst 15-WET (strongly acidic polymeric catalyst), citric acid and tartaric acid (AR, SD. Finechem, India) were used as received without any further purification.

2.2. Methods

2.2.1. Titrimetric methods (OH value, acid value, iodine value)

Algae oil and cottonseed oil was characterized for specific gravity (ASTM D5355 – 95), refractive index (ASTM D1747 – 09), saponification (ASTM D464 – 05), acid (ASTM D5768-02), hydroxyl (ASTMD1957-86) and iodine values (ASTM D5768-02).

2.2.2. GC-Analysis

The fatty acid composition, of AO and CO was determined from the methyl ester derivatives by gas chromatography-mass spectrometry (GC–MS). AO and CO methyl esters were prepared by refluxing these oils in a dry methanol in presence sodium methoxide (Mahapatra and Karak, 2004). Analysis was carried out using Perkin Elmer Auto System XL GC Turbomass. GC–MS equipped with DB-5MS column (30 m × 0.25 mm × 0.25 μm). Carrier gas was