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In situ synthesis of green bionanocomposites based on aqueous citric acid cured epoxidized soybean oil-carboxylic acid functionalized multiwalled carbon nanotubes

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ABSTRACT

A new class of green bionanocomposites was prepared by an *in situ* solvent and catalyst free method. The composite structure was decorated by the incorporation of various wt% (0–3%) of carboxylic acid functionalized multiwalled carbon nanotubes (c-MWCNTs) into an aqueous citric acid cured epoxidized soybean oil polymer networks. The formation of the epoxidized soybean oil/citric acid/c-MWCNTs bionanocomposites is evident from the Fourier transform infrared (FT-IR) spectroscopic analysis. The c-MWCNTs remarkably accelerated the curing rate of the bionanocomposites. Transmission electron microscopy (TEM) study revealed the homogeneous distribution of c-MWCNTs within the polymer networks. The anchoring of the polymer layers on the surface of the c-MWCNTs resulted in increased diameter (35–40 nm) of the c-MWCNTs in the bionanocomposites. The strong H-bonding and covalent interactions between c-MWCNTs and epoxidized soybean oil-citric acid polymer networks resulted significant improvement in thermal and mechanical properties of the bionanocomposites. The thermal stability and tensile strength of the bionanocomposites increased by 38 °C and 2.09 MPa (~4 fold) respectively with 3 wt% c-MWCNTs loading. The bionanocomposites also exhibited excellent chemical resistance.

1. Introduction

Environmental concerns and high rate of diminution of the petroleum resources have triggered great interest in the development of materials based on renewable resources. Among the various sources of renewable raw materials, vegetable oils attracted much more attention due to their social, environmental, and economic advantages (Meier et al., 2007; Lligadas et al., 2010; Espinosa and Meier, 2011; Biermann et al., 2011). In addition, assorted chemical modifications can be done on vegetable oils to obtain functionalized vegetable oils which can be used to obtain industrially important diverse products (Gogoi et al., 2015a,b). Sun and Wool reported a detailed depiction of plausible chemical modifications that can be performed on vegetable oils to obtain diverse functionalized vegetable oils, many of which are very useful in industrial applications (Sun and Wool, 2005). Epoxidation of vegetable oils is one of the most important chemical modifications which can be achieved by the acid-catalyzed (Okieimen et al., 2002) or the enzymatic processes (Hilker et al., 2001; Klaas and Warwel, 1999). The basic difference in the chemical structures of triglyceride obtained from various oilseeds is the fatty acid composition and the amount of double bonds. Soybean oil is an important vegetable oil offering a wide range of advantages. Soybean oil contains a large number of double bonds (oleic acid ~23%, linoleic acid ~53%, and alpha-linolenic acid ~9% with 1, 2, and 3 number of unsaturations respectively), giving an average of about 4.6 double bonds per triglyceride, and accordingly produces an epoxidised oil with high functionality (Altuna et al., 2013).

Due to the worldwide availability of soybean oil in large scale, it provides advantages as potential raw material for a variety of industrial applications. Presently, the US is the top producer of soybean oil in the world (Zhang et al., 2013). Nowadays, epoxidized soybean oil, which is obtained easily from soybean oil is produced industrially at large scale and commercial availability is brought forward to synthesize polymers by using its epoxy groups. Polymer networks can be obtained by ring opening polymerization of epoxidized soybean oil with polyamine, polyacid or anhydride. Wang et al. reported the synthesis of a series of soybean-oil-based elastomers poly(epoxidized soybean oil-co-decamethylene diamine) (PESD) by ring-opening polymerization from epoxidized soybean

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oil and decamethylene diamine (DDA) in different molar ratios. The elastomers exhibited a wide range of applications with favorable processability and tunable properties (Wang et al., 2012a,b). Recently, Altuna et al. has reported the preparation of a class of "green" polymeric materials based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution. The self-healing ability of the polymer networks giving higher added value to the material with high biomass content (Altuna et al., 2013). This study revealed a class of smart materials which is capable of stress relaxation and self-healing without the addition of any extrinsic catalyst. The use polycarboxylic acid i.e., citric acid, produced in large scale from citrus fruits, blessed the material as self-healable and recyclable. The —COOH groups take part in thermally activated transesterification reaction with β-hydroxyester links generated by the epoxy-acid reaction at elevated temperature without the addition of any extrinsic catalyst.

However, there is still need for the improvement of performance characteristics of these materials for their practical uses. In this regard, multiwalled carbon nanotubes (MWCNTs) can play an important role in the improvement of performance characteristics of these polymeric materials. Due to the excellent electronic properties, thermal conductivity, and mechanical strength of MWCNTs attracted great deal of interest as advanced materials and created a high level of activity in materials research for its potential application in various industries (Kim et al., 2009; Kim, 2009). MWCNTs also possess outstanding properties, like high aspect ratio, excellent chemical and environmental stability, which makes them ideal candidates as nano reinforcing filler for the polymer based nanocomposites. Inspired from these features of MWCNTs, a number of efforts had been devoted to fabricate MWCNT/polymer nanocomposites in the development of high-performance composite materials (Kar and Choudhury, 2013; Kwon and Kim, 2005; Sahoo et al., 2010). The properties of the polymer composites, including tensile strength (Kanagaraj et al., 2007), tensile modulus (Jin et al., 2007), ductility and toughness (Yang et al., 2007), glass transition temperature (Pham et al., 2003), thermal conductivity (Singh et al., 2007), electrical conductivity (Grossiord et al., 2007), solvent resistance (Guo et al., 2005) *etc*., improved significantly due to the incorporation of MWCNTs. However, due to the high cost and limited availability of the MWCNTs, only a few practical applications in industrial fields (electronic and electric appliances) have been recognized till date. The nanocomposites with very low loading of MWCNTs and polymer materials which are derived from sustainable resources can compensate the cost effectiveness of MWCNTs. It is obvious that the improved performances of the nanocomposites will have a role.

It is worth knowing that for the effective nano reinforcement of multiwalled carbon nanotubes (MWCNTs), homogeneous dispersion of MWCNTs within the polymer matrix and good interfacial adhesion between MWCNTs and polymer matrix is obligatory. In general, MWCNTs agglomerate due to van der Waals attraction and become extremely difficult to disperse and align within polymer matrix. These affect the efficient load transfer to the polymer matrix and the reinforcement of MWCNTs in the nanocomposites. The functionalization of MWCNTs can be regarded as an effective way to achieve better dispersion and strong interfacial interactions, which lead to improve the load transfer across the MWCNTs-polymer matrix interface. Thus, the functionalization of MWCNTs imparts compatibility with the polymer matrix and thereby improves the overall properties of the polymer/MWCNTs nanocomposites (Sahoo et al., 2010). There are several ways for functionalization of MWCNTs including defect functionalization, covalent functionalization, and non-covalent functionalization (Hirsch, 2002).

Inspired from these studies, we have used carboxylic acid functionalized multiwalled carbon nanotubes (c-MWCNTs) to improve the overall performances of epoxidized soybean oil-citric acid polymer networks. Thus, in this work we have prepared a series of epoxidized soybean oil/citric acid/c-MWCNTs bionanocomposites with different wt% of c-MWCNTs in aqueous solution *via* sonication treatment. The performance characteristics like gloss, thermal stability, tensile strength, scratch hardness, and chemical resistance of the epoxidized soybean oil/citric acid/c-MWCNTs bionanocomposites were investigated as a function of c-MWCNTs content. The *in vitro* biodegradation of the bionanocomposite films were studied.

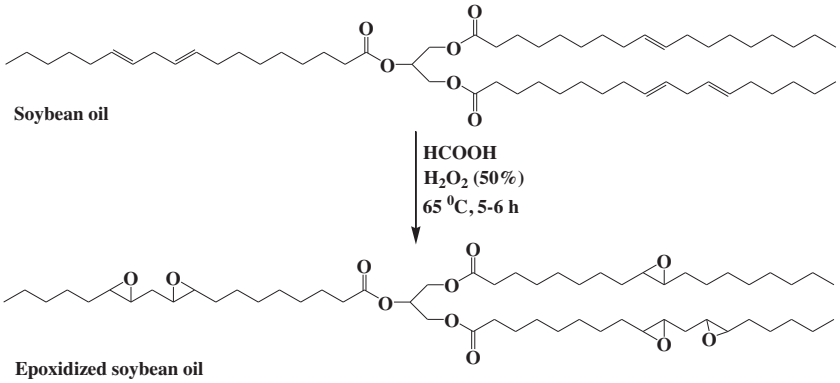
2. Experimental

2.1. Materials

Refined soybean oil was purchased from Adani Wilmer Ltd., India. Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O \geq 99.5\%$), formic acid (85%), hydrogen peroxide (50%), and nitric acid (HNO_3) were purchased from Merck, India. Multiwalled carbon nanotubes (purity > 97%, diameter = 10–15 nm, length = 0.1–10 μm, density = 1.7–2.1 g/cm^3) were purchased from Redex Technologies Pvt., Ltd., Ghaziabad, UP, India. All the chemicals were used as received.

2.2. Preparation of epoxidized soybean oil

Epoxidation of soybean oil was done with a mixture of hydrogen peroxide and formic acid (Scheme 1). The molar ratio of hydrogen peroxide: double bond: formic acid was maintained as 1.5: 1.0: 0.5. In a typical method 23.74 g of formic acid was added to 100 g of soybean oil in a three necked round bottom flask with continuous stirring. Then, the reaction temperature was raised to 65 °C and 105.28 g of hydrogen peroxide was added dropwise over a period of 3–4 h. Proper precaution was taken to avoid overheating the



Scheme 1. Schematic for the preparation of epoxidized soybean oil.