Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Preparation and Characterization of Bio-Renewable Epoxy from Odal Seed Oil

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Odal seed oil (OSO) is a potential source for the preparation of green-epoxy system. The oil has nearly 57 % of unsaturation which was epoxidized using in situ generated per acetic acid in presence of an acidic ion exchange resin as catalyst. The reaction was performed at 50 oC for different time periods. It was found that the iodine value decreased substantially for EOSO-8 to a value of 42 g/100g of oil compared to OSO (92.7 g/100g of oil) indicating the reduction in unsaturation. The oxirane value increased to 2.9 g/100g for a reaction time of 8 hours (EOSO-8). FTIR spectroscopy revealed the formation of epoxy rings. NMR studies confirmed that a degree of epoxidation of around 45% was achieved for 8 hours of reaction (EOSO-8).

Keywords: Vegetable oil, epoxidation, bio-based epoxy, NMR.

1. Introduction

Epoxies belong to a class of thermosetting polymers with versatile applications such as metal coatings, adhesives, composites, electronic encapsulants etc. The widely used diglycidyl ether of bisphenol A (DGEBA) resin is derived from petroleum feedstock which is expensive and have toxic effects. A promising route to renewable epoxy prepolymer system is vegetable oils which are abundant, sustainable, inexpensive and are less toxic [1]. Vegetable oils are glyceryl esters of fatty acids and have multiple C=C bonds which can be converted to more active epoxy groups [2].

Epoxidation has been performed in various vegetable oils such as castor oil [3], cardoon seed oil [4], cotton seed oil [5], hemp oil [6], linseed oil [7], macaw palm oil [8] and sunflower oil [9]. However, there is a need to find more renewable and green oil (non- edible and non-toxic) resource to form epoxides so as to meet the demands of the industry. In this work, a novel bio-based epoxy prepolymer is synthesized using Odal seed oil. Odal plant (Sarcostigma kleinii Wight & Arn) is a woody climber largely found in Western Ghats, India. The fruit of the plant is edible and oil is extracted from the seed. The seed oil has medicinal value [10] but its application in polymer synthesis remains unexplored. In this work, the epoxidation of odal seed oil was done with peracetic acid generated in situ in presence of acidic ion exchange resin as catalyst.

2. Materials and Methods

2.1. Materials

Odal seed oil (OSO) was purchased from local market. Glacial acetic acid, and hydrogen peroxide were obtained from Merck (India) Limited. Amberlite IR 120 were supplied by Aqua purification systems, Tamil Nadu. All other chemicals used for characterization were of analytical grade.

2.2. Epoxidation of Odal seed oil

Initially, 50 g OSO, 5 g Amberlite and 5ml glacial acetic acid were taken in a 500 ml round bottom flask and stirred at 50 ^oC. Then 27 ml of 30 % H_2O_2 solution was added drop-wise to the above reaction mixture and the reaction performed for different time periods - 4, 6 and 8 hours. The crude product was subsequently washed with distilled water until free of acid and the organic layer filtered, and dried in vacuum to get epoxidized odal seed oil (EOSO).

2.3 Characterization

The fatty acid composition of OSO was carried out using a 6890N gas chromatograph coupled with 5975 MSD. Iodine value which indicates the extent of unsaturation in a substance was determined using Wijs solution as per ASTM D5768. Oxirane oxygen content or epoxy content was determined using American Oil Chemists' Society official method Cd 9-57. FTIR spectra was obtained using PerkInElmer Spectrum 400 FTIR spectrometer with a scan range of 4000-500 cm^{-1}. H-NMR analysis was performed using JEOL(JNM-ECZ400S) NMR spectrophotometer using deuterated chloroform as the solvent.

3. Results and Discussion

3.1. Fatty Acid Composition of OSO

Odal seed oil contains 35.8 % oleic acid (C18:1), 21.4 % linoleic acid (C18:2), 25.6 % palmittic acid (C16 :0) and 2.5 % stearic acid (C18:0) accounting to nearly 57 % of unsaturation. Based on the composition, its molecular weight was calculated as 860 g/mol.

3.2.Iodine value and Oxirane content

The variation of iodine value and oxirane value as a function of reaction time are shown in Fig.1a and Fig.1b, respectively. OSO is a liquid at room temperature with an iodine value of 92.7 g/100g of oil. As the reaction time increases from 4 to 8 h, the iodine value got reduced to 42 indicating that majority of the double bonds in oil has been converted to epoxy.

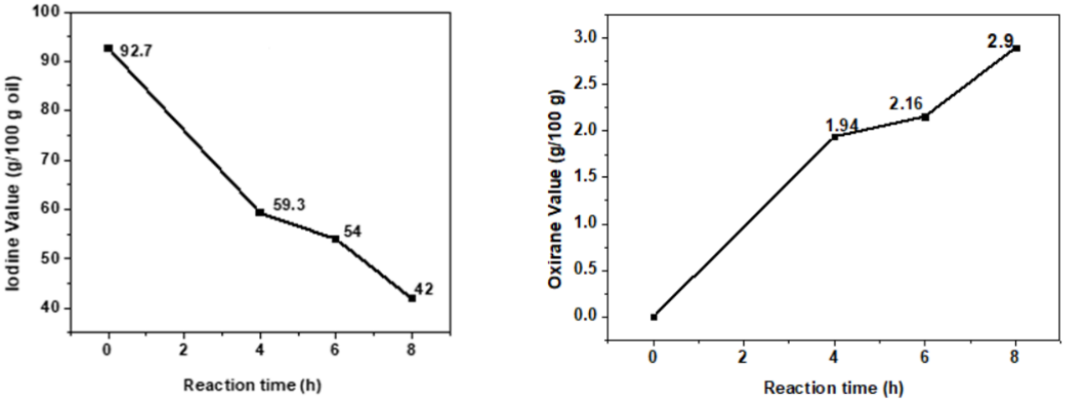


Fig.1(a) iodine value and (b) oxirane value as a function of reaction time

The oxirane content of EOSO progressively increased with time (Fig.1b) as more and more double bonds are converted to oxirane group. This is in accordance with the double bond conversion calculated from iodine values viz. 36.4%, 42.1% and 55% for 4h, 6h and 8h reaction respectively [11].

3.3. FTIR analysis

The FTIR spectra of OSO and EOSO are given in Fig.2a (4000-500 cm^{-1}) and Fig.2b (1700-700 cm^{-1}). In the FTIR spectrum of OSO, the peak at 3010 cm^{-1} corresponds to =C-H stretching vibration and a weak signal at 1651 cm^{-1} corresponds to C=C stretching of oleic and linoleic acid. The peaks at 2926 cm^{-1} and 2852 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of methylene group respectively. The peak at 1745 cm^{-1} is C=O stretching peak and peak at 1165 cm^{-1} represent C-O stretching. In the case of EOSO, the peak intensity at 3010 cm^{-1} and 1651 cm^{-1} diminishes with reaction time indicating the removal of unsaturation during epoxidation. Also, the formation of a weak signal at 823 cm^{-1} in the epoxidized oil samples (Fig.2b) confirms the conversion of double bond to epoxy ring system [12]. In the OSO spectrum, there is a broad peak at 3450-3550 cm^{-1} representing hydroxyl O-H stretching which may be due to moisture present in the sample or due to partial hydrolysis of oil. However, with EOSO samples, the peak at 3450-3550 cm^{-1} further broadened with reaction time which might be due to the spurious ring opening side reaction of the epoxy group. So, a longer reaction time is not desirable.

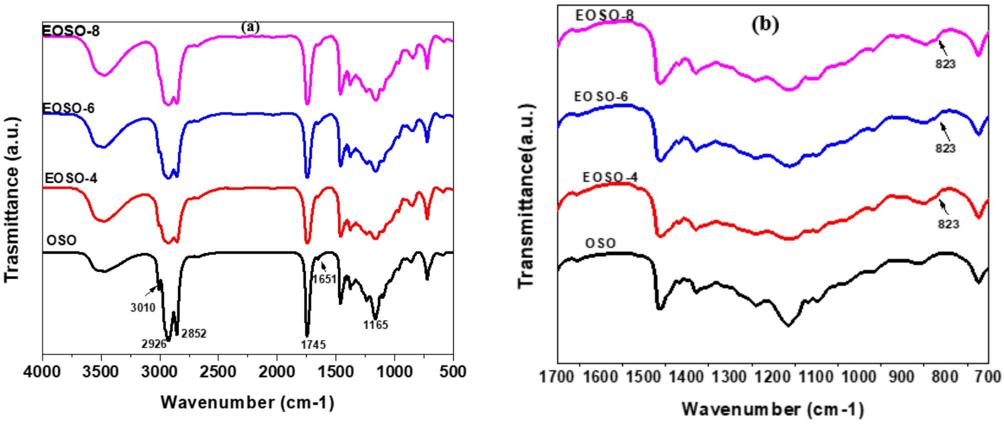


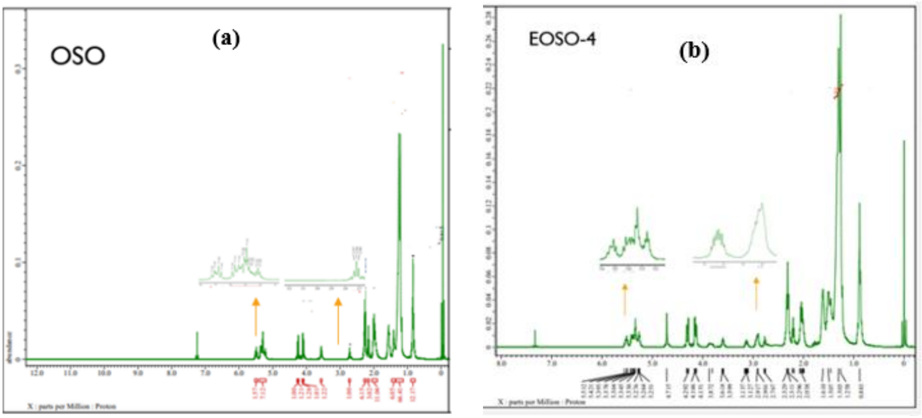
Fig.2 FTIR spectra of OSO and EOSO

3.4. Proton NMR analysis

The H-NMR spectra signals of OSO and EOSO are illustrated in Fig.3a-d. For OSO,the multiplet signal at 5.2-5.5 ppm is associated with the protons attached to the unsaturation. After epoxidation, the intensity of vinyl hydrogen signal at 5.2-5.5 ppm significantly reduced indicating the formation of epoxide group. Moreover, the presence of epoxide group in all the samples of EOSO synthesized was confirmed by the appearance of signals at 2.9-3.2 ppm [13]. The degree of epoxidation (DOE) can be calculated using eqn.

$$\mathrm{DOE} = \frac{\text{Number of epoxy group}}{\text{Number of double bonds initially present}}$$

where the number of double bonds initially present is taken as the integral area under the signal at 5.2-5.5 ppm of OSO and number of epoxy group is taken as the integral area under the signal at 2.9-3.2 ppm of EOSO [14].



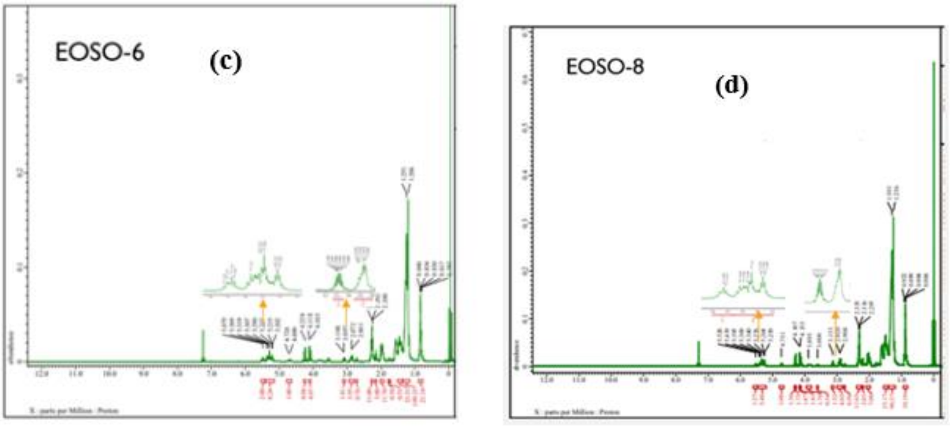


Fig.3 NMR spectrum of a) OSO b) EOSO-4 c) EOSO-6 and d) EOSO-8

The DOE for EOSO-4, EOSO-6 and EOSO-8 was found to be 33.1%, 32% and 45.4%, respectively. The extent of epoxidation got increased for a reaction time of 8 hours. The degree of epoxidation may be further increased by varying the reaction conditions which needs to be investigated.

4. Conclusion

A green epoxy system was successfully synthesized by in situ epoxidation of odal seed oil. Epoxy functionalization was confirmed by iodine value, oxirane content, FTIR and NMR spectroscopy. The degree of epoxidation increased to 45.4 % for a reaction time of 8 hours. Almost half of the double bonds present in OSO was converted to reactive epoxy group which makes it useful for a variety of industrial applications. Further studies need to be conducted for achieving a higher degree of epoxidation. The synthesized resins are being evaluated for their mechanical, thermo-mechanical and allied properties.

Acknowledgement

We gratefully acknowledge Dr. C P Regunadhan Nair, Department of Polymer Science & Rubber Technology, CUSAT, India for assistance in NMR characterization. We also acknowledge STIC, CUSAT, India for providing characterization facilities.

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