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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF EPOXY RESIN MODIFIED WITH VEGETABLE OIL AND ORGANICALLY MODIFIED CLAY

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ABSTRACT

A new class of green nanocomposites has been developed by reinforcing clay into the triglyceride based epoxy resins. Epoxidised biopolymer nanocomposites were synthesized from epoxidized palm oil and organomontmorillonite (OMMT) clay using an *in situ* polymerization reaction. OMMT was prepared using Cetyl trimethyl ammonium bromide. A stoichiometric amount of epoxidised palm oil was mixed with diglycidyl ether of bisphenol A, diaminodiphenylmethane and organo montmorillonite(OMMT) in proper proportions. The resultant biopolymer nanocomposites were characterized using FT-IR, UV, TG/ DTA, SEM and TEM analysis. It was found that the desired properties polymer nanocomposites were achieved when the OMMT loading was 3 wt% and 7 wt%. All the nanocomposites were found to have improved in thermal properties as compared with ordinary polymer.

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INTRODUCTION

Vegetable oil is one of the cheapest and most abundant biological feedstock available in large quantities and its use as starting material offers numerous advantages such as low toxicity and inherent biodegradability [Wang, 2005]. The traditional non-biodegradable polymers, which are produced from fossil fuels, have considerably disturbed and damaged the ecosystem of nature. For this reason there is an urgent need to develop renewable source-based biopolymer materials that would not involve the use of toxic or noxious components in their manufacture and could allow degradation via a natural composting process. Although much attention has been paid to biopolymer/clay nanocomposites. Thus the economic value of the vegetable oil could be increased by converting the vegetable oil into epoxidized vegetable oil. The double bonds in the vegetable oil are used as reactive sites in the coatings and they can also be functionalized by epoxidation. Epoxidation of fatty acid derived from the palm oil is the one of the chemical modification of oil. Epoxidation is a simple and efficient method for introducing a new reactive group and widely used in various applications. A new class of green nanocomposites has been developed by reinforcing clay into the triglyceride based epoxy resins.

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MATERIALS

Commercial grade palm oil was purchased from local market. Diglycidyl ether of Bis-phenol A (DGEBA) and (1-hexadecyl)trimethyl ammonium bromide was obtained from Alfa Aesar (Great Britain). Montmorillonite clay (K 10 powder) and 4,4'-diaminodiphenylmethane from SIGMA – ALDRICH. Hydrogen peroxide was purchased from EMPARATA Company. Sodium bicarbonate and sodium chloride were purchased from MERCK Company and formic acid from Nice chemicals Pvt. Ltd Cochin.

METHODS

Preparation of Na-Montmorillonite clay

About 2.5g of Montmorillonite crude was suspended in 1M NaCl (200 ml) and kept on overnight with magnetic stirrer (24 hours). The resulting clay slurry was then left to stand for 2 hours to allow sedimentation of silica and other heavy impurities and the montmorillonite was decanted off. The suspension was filtered and the filtrate was discarded. The clay slurry was then transferred to dialysis tubing and chloride ions were removed by repeated dialysis with deionised water until no precipitate was observed on the addition of 0.1 N AgNO₃ solution to a sample of the wash water. The strained sample was air dried.

Preparation of Organo-Montmorillonite clay

About 1.8 g of cetyltrimethyl ammonium bromide was made upto 100 ml in a 100 ml standard measuring flask. 2g of the purified Na- MMT was added with 100 ml of cetyltrimethylammoniumbromide solution and stirred well vigorously for 24 hours. A white precipitate formed was isolated by filtration and washed several times with ethanol, until no bromide was detected in the filtrate by one drop of 0.1N silvernitrate solution. The cetylammunium ion exchanged montmorillonite (OMMT) was then dried.

Epoxidation of Palm oil

Epoxidized Palm Oil (EPO) was prepared by using generated *in situ* peroxy acid with a constant molar ratio of PO:HCOOH/CH₃COOH:H₂O₂ (1:5:4 mole/mole) under continuous magnetic stirring at constant temperature (45°C). The reaction was carried out in a three necked ground bottom (250 ml capacity) flask equipped with thermometer and reflux condenser. Generated *in situ* peroxy acid is produced by mixing formic acid (HCOOH) or acetic acid (CH₃COOH) with H₂O₂ simultaneously. Hydrogen peroxide was slowly added drop wise into the acidic media.

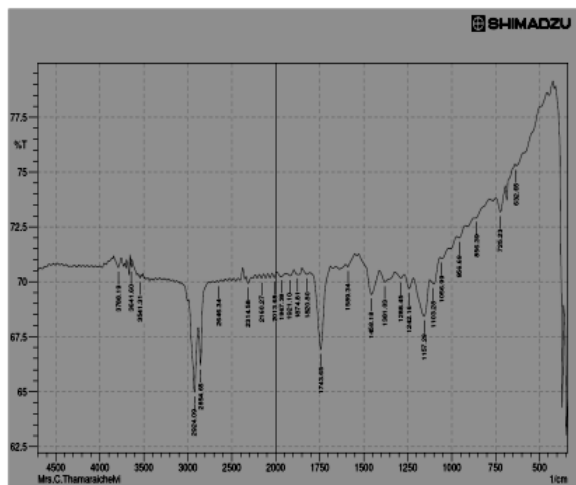
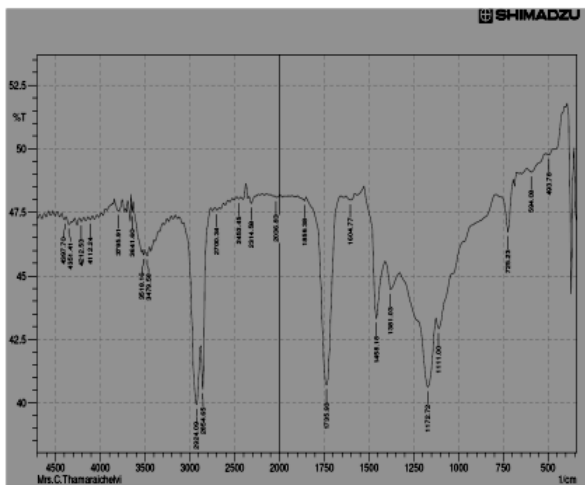


Fig.1. FT-IR spectrum for a) Palm oil (PO) b) Epoxidised Palm Oil (EPO)

Table 1. Vibrations observed in the Palm Oil (PO) and Epoxidised Palm Oil (EPO)

S.NO	ASSIGNMENT	BAND(cm ⁻¹)	
		PO	EPO
1	CH ₂ ,CH ₃ asymmetric stretching	2854.65	2854.65
2	CH ₂ asymmetric stretching	2924.09	2924.09
3	Alkyl acids(C=O)	1735.93	-
4	Oxirane	-	856.39
5	C=C	1604.77	-
6	Overtone and combination of -OH and stretching vibrations	2700.34	-
7	-CH ₃ asymmetric bending	1458.18	1458.18
8	Epoxide symmetric stretching	-	1242.16
9	Peroxides C-O-O-C stretching	-	856.39

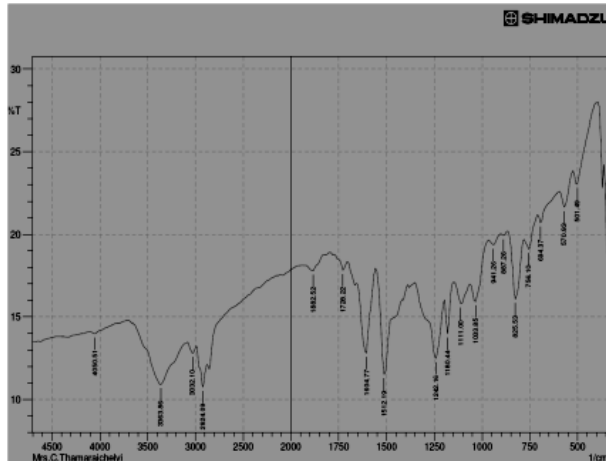
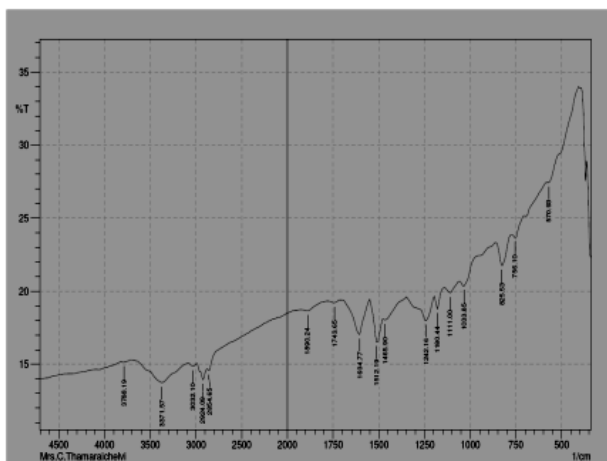
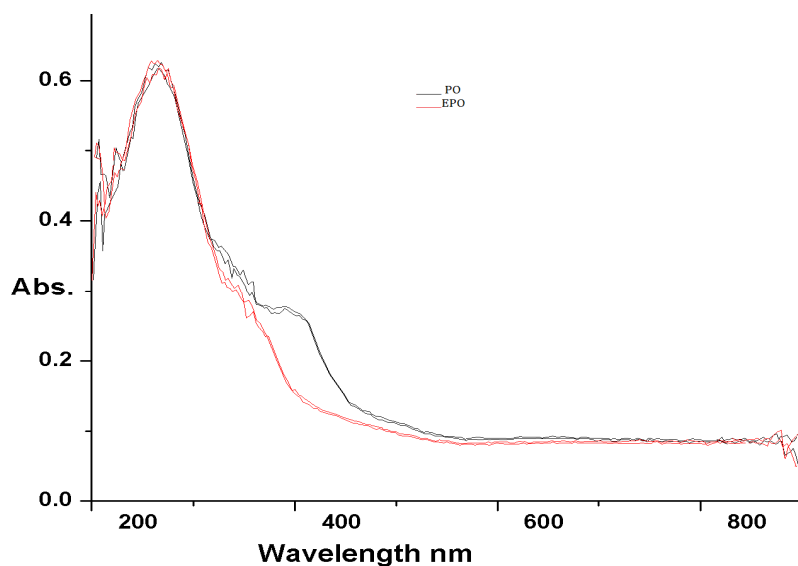
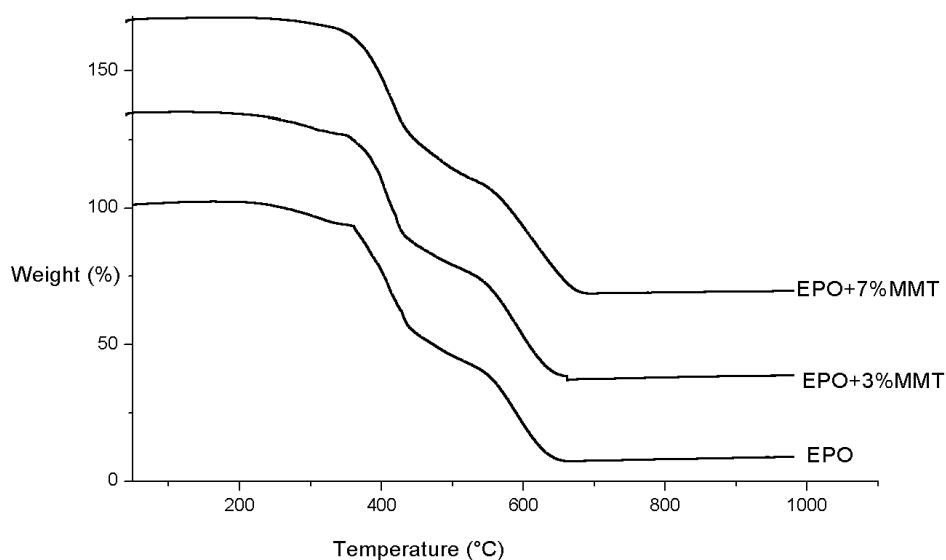


Fig. 2. The FT-IR spectrum of a) Epoxidised biopolymer b) Epoxidised biopolymer with 3% OMMT

Table 2. Vibrations observed in the Epoxidised biopolymer (EBP) and Epoxidised biopolymer with 3%

S.NO	ASSIGNMENT	BAND	
		Epoxidised biopolymer(EBP)	Epoxidised biopolymer(EBP +3% OMMT)
	C-O-C linkage	825.53	825.53
2	Phenolic OH	3371.57	3363.86
3	N-H Stretching (overtones and combination bands)	2854.65	2924.09
4.	N-H Stretching (Bending vibration- Assymmetric bending)	1604.77	1604.77
5	N-H Stretching (Bending vibration- Symmetric bending)	1512.19	1512.19
6	C-N Stretching	1180.44	1180.44
7	Si-O bending	-	501
8	Si-O stretching	-	941

**Fig. 3. UV Spectrum of PO and EPO****Fig.4 TGA graph for Epoxidised biopolymer (EBP), Epoxidised biopolymer with 3% OMMT and Epoxidised biopolymer with 7% OMMT**

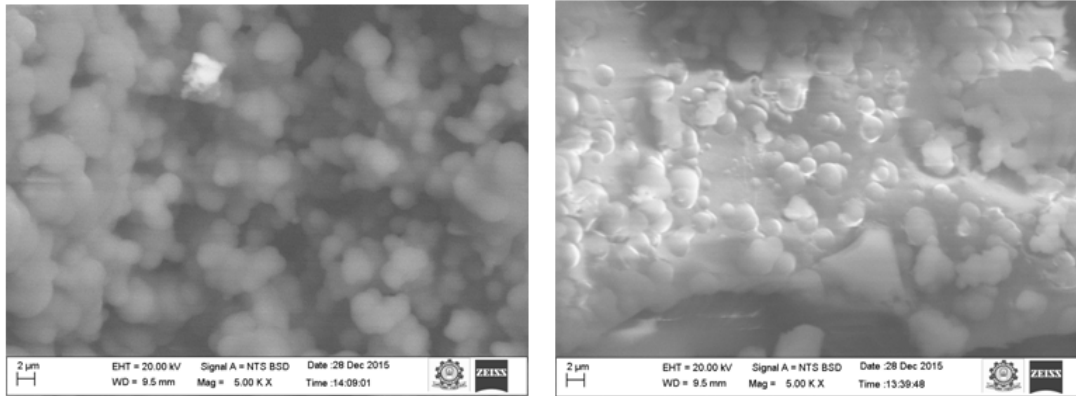
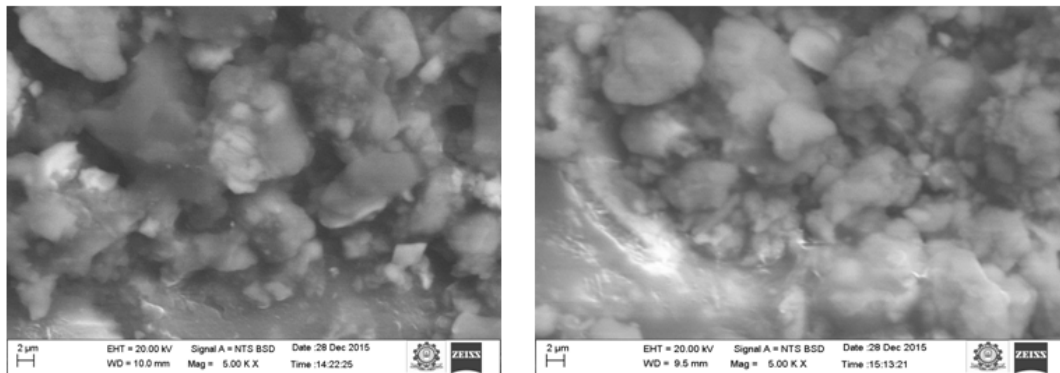
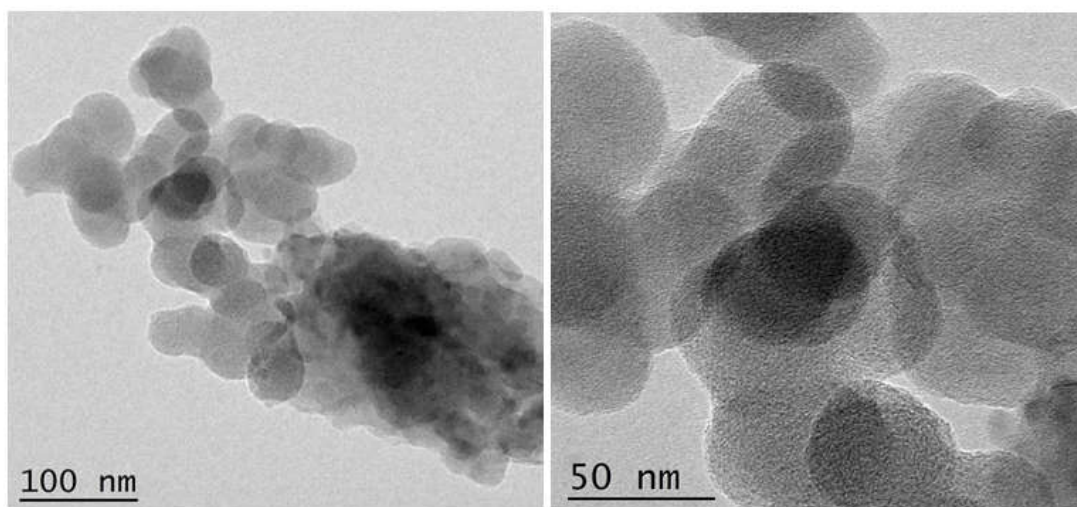
Fast introduction to this reagent will cause an excessive development of oxygen due to the decomposition of H_2O_2 at high temperature. After the reaction finished, samples of reaction mixture were taken out and thoroughly washed with sodium bicarbonate (5 wt%), distilled water and sodium chloride (5 wt%) to separate the organic layer from the mixture.

Synthesis of Epoxidised biopolymer Nanocomposites

Palm oil based epoxy matrix was prepared by mixing palm epoxy resin with base DGEBA resin at 30/70wt% at 60°C with vigorous stirring. The homogeneous solution thus obtained was mixed with stoichiometric amount of DDM at 90°C. The mixture was degassed to remove the trapped air bubbles and poured into a preheated mould.

Table 3. Thermal behaviour of cured resins samples

Resin	T _i °C	T _{max} °C	Y _c %
Epoxidised biopolymer	380	570	40
Epoxidised biopolymer + 3% OMMT	385	590	50
Epoxidised biopolymer+7% OMMT	385	595	55

**Fig. 5. SEM images of epoxidised biopolymer matrix****Fig. 6. SEM images of OMMT loaded epoxidised biopolymer nanocomposites****Fig. 7. TEM images of OMMT loaded epoxidised biopolymer nanocomposites**

The casting was cured at 120°C for 3 hours and post cured at 180°C for 2 hours and finally removed from the mould and characterized.

Development of OMMT loaded- Epoxidised biopolymer Nanocomposites

Palm-based resin (30/70-wt%) mixed with different organophilic montmorillonite clay concentrations (3wt%, and 7wt%) based on the total weight of the resin mixture at 60°C for 24 hours using a mechanical stirrer. A stoichiometric amount of the amine curing agent corresponding to the epoxy equivalents was added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 hours. The castings were then post cured at 180°C for 2 hours and finally removed from the mould and characterized.

4. Results and Discussion

FT-IR Analysis

The FT-IR spectra of palm oil (PO) and epoxidised palm oil (EPO) are shown in Fig.1. It showed the characteristic absorption bands of C-H asymmetric stretching is observed at 2854.65 cm⁻¹ and 2924 cm⁻¹ for CH₂ and CH₃ groups respectively. The sharp peak at 1735.93 cm⁻¹ indicates the presence of C=O for alkyl acids in PO. This peak is absent in EPO, confirms that the C=O is disappear due to epoxidation. The presence of small peak at 856.39 cm⁻¹ in the EPO is due to oxirane ring. The epoxide symmetric stretching band is centred at 1242.16 cm⁻¹ in EPO. During the epoxidation process, 10% of palm oil is converted to peroxides, as a side product. This is indicated by the presence of C-O-O-C stretching at 856.39 cm⁻¹. Overtones and combination of OH stretching vibration is observed at 2700.34 cm⁻¹ in PO. Si-O groups of OMMT absorbing near 3625 cm⁻¹ and 1035 cm⁻¹. 3% MMT and 7% MMT shows the 3300-2700 cm⁻¹ and 1700-1300 cm⁻¹ regions of the IR spectra of six aliphatic alkyl ammonium derivatives of MMT. The band positions and their assignments are provided in the Table 2. The C-O deformation band is centered at 825 cm⁻¹ in DGEBA. C-H stretching of terminal oxirane group is observed at 3032 cm⁻¹. There are also bands corresponding to the ether linkage located at 1000-1100 cm⁻¹. Among all the curing agents used to obtain epoxy thermosets, this chapter will be focused on one specific type diamines. Their high reactivity is attributed to the high nucleophilicity of the nitrogen atom of the aminogroup although it is conditioned by its chemical structure. The amino group shows well defined absorptions both in the mid and in the near infrared ranges. The main absorption in the mid range are stretching and deformation of N-H bonds. Although the N-H stretching the N-H stretching is located between 3500 and 3300 cm⁻¹. The N-H deformation is located at 1650-1500 cm⁻¹. The band at 501 cm⁻¹ indicates the presence of Si-O bending in 3% MMT. The bands corresponding to the Si-O group at 1035 cm⁻¹ is due to OMMT. The combination band of second overtone of the epoxy ring stretching with the fundamental C-H stretching is centered at 4531 cm⁻¹ in DGEBA.

Ultraviolet Visible Spectrophotometer (UV-DRS)

The UV-DRS spectrum was recorded in Shimadzu UV-Visible spectrophotometer 2450 in the wavelength range 200-900 nm. Epoxidation process was confirmed by the absence π^*

π^* transition at the wavelength range between 380-480 nm in EPO.

Thermogravimetric Analysis (TG/DTA)

The effects of EPO and OMMT contents on the thermal stabilities of the DGEBA/EPO, DGEBA/EPO/OMMT system were studied by TGA at a heating rate of 20°C/min under nitrogen atmosphere. Thermogravimetric analysis of cured resin samples was done to evaluate relative thermal stability. Typical TG trace is shown in Fig.3. The initial decomposition temperature (T_i) and temperature of maximum rate of weight loss (T_{max}) were noted down from these traces and the results are summarized in Table 1, char yield at 980°C was also determined. The highest char yield was observed in 7% MMT loaded biopolymer matrix and lowest value was in biopolymer matrix which is not having OMMT clay. The presence of silica particles in biopolymer may be responsible for this behavior. However the initial decomposition temperature were same for all these three polymer matrices.

Morphology and Structural analysis of Epoxidised biopolymer Nanocomposites

SEM Analysis

The SEM micrographs indicate that there is no phase separation between silicate layers and the epoxidised biopolymer matrix. The SEM analysis of the composites exhibits relatively uniform dispersion of MMT layers in addition to the good interface of the material.

TEM Analysis

TEM analysis was then performed to learn more about the epoxidised biopolymer nanocomposites and MMT loaded epoxidised biopolymer nanocomposites. Both TEM images clearly show that the MMT were individualized and the uniformly dispersed within the epoxidised biopolymer nanocomposites. The structure of the nanocomposites are spherical in shape. The degree or uniformity of dispersion of the MMT within the polymer plays an important role on its mechanical properties.

Conclusion

Epoxidised biopolymer and OMMT loaded epoxidised biopolymer nanocomposites were prepared using epoxidised palm oil, DDM, DGEBA and OMMT clay. The polar group containing triglyceride based matrix favoured in the formation of an exfoliated structure for the nanocomposites. The rigid bio-based nanocomposites prepared exhibited remarkable improvement in the material properties, such as thermal stability. The FT-IR, XRD, TG/DTA analysis of the composites exhibits relatively uniform dispersion of MMT layers in addition to the good interface of the material.

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