



# SYNTHESIS AND CHARACTERISATION OF COIR FIBER REINFORCED EPOXY COMPOSITES FROM PUNNAL OIL

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## Abstract

Vegetable oil is readily available and inexpensive, can be used to synthesise various types of polymers. In our present study, epoxidised punnal oil has been synthesised from punnal oil via peroxy acetic acid generated 'insitu' by treating acetic acid with hydrogen peroxide as oxygen donor. The epoxidation is catalysed by using sulphuric acid. The epoxidation is confirmed by iodine value, oxirane oxygen analysis, fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) and thin layer chromatography (TLC) analysis. Natural fibers such as jute, sisal, banana, rice husk etc are locally available in abundance and have excellent physical and mechanical properties and can be used more effectively in the development of composite materials for various applications. Epoxy composite samples are prepared from the natural fiber with different ratios using triethylamine hardener and pthaleic anhydride. The mechanical properties viz. tensile strength and the physical properties observed are discussed in detail.

**Keywords:** Punnal oil, Epoxidised punnal oil, Epoxy composites, Coir fiber, Chemical resistance

## INTRODUCTION

Epoxidised vegetable oils can be used as plasticisers, stabilisers and lubricants in the polymer industry. As energy demands increase, there is utilization of renewable resources instead of petroleum based polymers. Vegetable oils are quite abundant in nature. Soybean oil, castor oil, rape seed oil, palm oil etc are different examples of vegetable oils. Vegetable oils are triglycerides which contain different fatty acids such as oleic acid, linolenic acid, linolic acid, stearic acid and palmitic acid. These oils are readily available and inexpensive, can be used to synthesise various types of polymers [1]. Punnal oil which are obtained from punnal tree is rich in unsaturated fatty acids which are used for the conversion to polymeric material.



**Figure 1: Punnal seeds**

Epoxidation of fatty acids is a reaction of a carbon – carbon double bond with active oxygen, which results in the addition of an oxygen atom, converting the original double bond into a three membered epoxide (oxirane) ring. A composite material is made by combining two or more materials to give a unique combination of properties, one of which is made up of stiff, long fibers and the other, a binder or 'matrix' which holds the fibers in place.

Coir fibers are found between the hard, internal shell and the outer coat of a coconut. The individual fiber cells are narrow and hollow, with thick walls made of cellulose. They are pale when immature but later become hardened and yellowed as a layer of lignin is deposited on their walls. The coir fiber is relatively waterproof and is one of the few natural fibers resistant to damage by salt water. The increase of treated fiber content resulted in a significant increase in tensile strength of composites. Alkali treatment increased the strength of natural fiber composites. A strong sodium hydroxide treatment removed lignin, hemicellulose and other alkali soluble compounds from the surface of the fibers to increase the numbers of reactive hydroxyl groups on the fiber surface available for chemical bonding. The removal of these substances enhanced the surface roughness. Therefore, mechanical interlocking at the interface could be improved. Keeping this in view, the present work has been under taken to develop a polymer epoxy composites using treated coir fiber as reinforcement.



## EXPERIMENTAL

### *Materials*

The punnal oil used in this study is obtained from the local company. Glacial acetic acid, hydrogen peroxide (30wt %), sulphuric acid, 95 – 98wt% were obtained from merck. The coir fiber is collected locally. The hardener triethylamine is obtained from Merck, phthaleic anhydride and anhydrous isopropyl alcohol from the Sigma-Aldrich.

### *Epoxidation of punnal oil*

A calculated amount of punnal oil (1M) is placed in a 500ml three neck flask equipped with reflux condenser containing the required amount of acetic acid (0.5M). Then a calculated amount of 30% hydrogen peroxide is added dropwise with continuous stirring for about 1hr. Thereafter, the temperature of the reaction mixture is raised to 60°C and maintained at this temperature for a period of 8hrs. Two different molar ratios of C=C bonds to hydrogen peroxide are used. (1:1.3 and 1:1.5). The product is cooled and decanted to effect a separation of the epoxidised oil from water soluble ones. The epoxidised oil is then washed with warm water to remove residual contaminants. The product (EPO) is then analysed to determine its iodine value and oxirane oxygen.

### *Alkali treatment*

The coir fibers are cleaned and dried in atmosphere for one day and then kept in oven at 50°C to remove the moisture. The coir fibers are soaked in 4% NaOH solution for 2 hrs to remove any unwanted material and hemicelluloses, washed thoroughly in distilled water and dried under the sun for one week. Then it are weighted according to the percentage needed (5, 10, and 15wt. %).

### *Preparation of composites*

The mould cavity is coated with a thin layer of silicone grease. A calculated amount of epoxidised punnal oil (EPO), phthaleic anhydride and isopropyl alcohol are dissolved in minimum amount of acetone. The mixture is heated in an oil bath to 120°C for 2hrs. The hardener triethylamine was added. Different amounts of treated coir fiber (5, 10 and 15% wt) is added separately in the above mix and stirred. The final resultant mixture is poured into moulds. The sample is cured in an oven at 150°C for 14 hours.

## CHARACTERISATION

### *Physico-chemical properties*

Fatty acids of oil are obtained by using a Varian star 1gas chromatography - mass spectrometry (GC-MS) instrument. Fourier transform infrared spectroscopy (FTIR) spectra of virgin oils and epoxidised oils are recorded by a Thermo Nicolet AVATAR 320 FTIR spectrometer coupled with Ezomonic software. A thin layer of sample is applied over a NaCl plate and the spectrum was recorded in the range 400-4000 cm<sup>-1</sup>. Nuclear magnetic resonance (NMR) spectra are recorded using BRUCKER AVANCE 500 NMR spectrophotometer. For NMR experiment frequencies of 500 MHz is used to record 1H spectra. The solutions used are prepared in deuteriochloroform using tetramethylsilane (TMS) as the reference. Iodine value and oxirane oxygen content of oils and their derivatives are determined using standard methods [2]. A standard procedure is used to evaluate saponification values of oils.[3]

### *Thin layer chromatographic analysis*

Silica coated aluminium TLC plates are used for TLC analysis. The solvent used is a mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> in 3:7 ratio are added. Plates are visualized in an iodine chamber.

### *Chemical resistance of composites*

A chemical resistance of the composites is studied as per ASTM D 543.87 method. For chemical resistance test, the acids namely conc.HCl (1N), conc.HNO<sub>3</sub> (1N) and H<sub>2</sub>SO<sub>4</sub> (1N), the alkalis namely aqueous solution of NaOH (10%), ammonium hydroxide (10%) and sodium carbonate (20%) and the solvents diethyl ether, dimethyl acetamide, chloroform, toluene and water are selected. In each case, weighed samples are dipped in the respective chemicals under study for 60days, removed and immediately washed thoroughly with distilled water and dried by pressing them on both sides by filter papers. The % of weight loss /gain is determined.

### Moisture content test

Initially each specimen are weighed and then the specimen is dried in ventilated oven at a temperature of 80°C until the mass became constant to  $\pm 0.2\%$  between two successive weighing made at an interval of 1hrs.

$$\text{Moisture content} = \frac{m_o - m_f}{m_o} \times 100$$

Where  $m_o$  and  $m_f$  are initial and final mass respectively.

### Soil burial degradation

Specimens of each composite are placed in a series of boxes containing moisturised soil. The specimens (30 X 10 mm) are buried 100 mm beneath the surface of soil which is regularly moistened with distilled water. At predetermined time points the samples are removed, carefully washed with distilled water in order to ensure the stop of the degradation, dried at room temperature to a constant weight and then are stored in darkness.

$$\text{Weight loss} = \frac{W_o - W_t}{W_o} \times 100$$

Where  $W_o$  is the initial mass and  $W_t$  is the remaining mass at any given time, t.

### Tensile test

Tensile strength, Young's Modulus and Elongation at break are measured according to the ASTM D638 standard using universal testing at a crosshead speed of 5mm/min. 5 Specimens of each sample are tested and tensile strength, youngs modulus and elongation at break are expressed as,

$$\text{Tensile strength (MPa)} = \frac{P}{bh}$$

$$\text{Young's Modulus (MPa)} = \frac{\sigma}{\varepsilon}$$

Where, P = pulling force (N), B= Specimen width (m), H= Specimen thickness (m),  $\sigma$  = stress (N/m<sup>2</sup>),  $\varepsilon$  = strain

## RESULTS AND DISCUSSION

### Physico - chemical properties of the punnal oil

**Table 1: Physico-chemical properties of oil and EPO**

Properties	Punnal oil	EPO (1:0.5:1.3)	EPO (1:0.5:1.5)
Colour	Dark green	Pale yellow	Pale yellow
Specific gravity	0.91	0.99	1.19
Acid value	35		
Saponification value	182	-	-
Iodine value	71	52	48
Oxirane Oxygen	-	2.5	2.8
Moisture content	-	0.3%	0.56%

The iodine value and the oxirane oxygen content are important properties in the characterization of epoxidised vegetable oils. While the iodine value indicates the remaining unsaturation after the epoxidation reaction, the oxirane oxygen content indicates the epoxy groups present in the products. In the preparation of polymers, epoxy resin with a lower iodine value and higher oxirane oxygen content are desired. In the present study, the reduction in iodine value indicates the consumption of unsaturation during epoxidation.

### Thin layer chromatography

**Table 2: TLC for oil and EPO**

Solvent used = Benzene : chloroform (7 : 3)	
Rf value for oil	0.56
Rf value for EPO (1:0.5:1.3)	0.68
Rf value for EPO (1:0.5:1.5)	0.72

Thin layer chromatographic study of the resin showed a distinct single spot, indicating the purity of the sample. Rf value for resin is different from that of oil indicating the formation of the product. (see table 2)

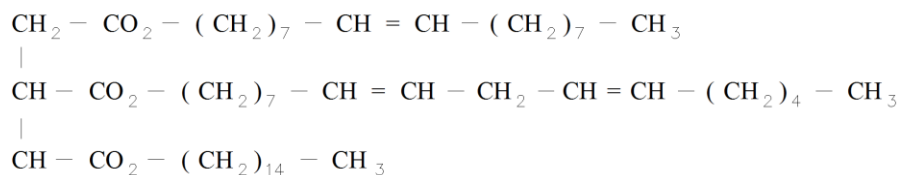
### Fatty acid composition of punnal oil

The unsaturated fatty acids present in punnal oil are oleic acid and linoleic acid containing one and two double bonds between two carbon atoms respectively. The functionality present in punnal oil is in terms of double bonds thus the C=C acts as a reaction site for chemical modification in punnal oil.

**Table 3: Fatty acid composition of punnal oil**

Fatty Acid	Composition	%
Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	14.5
Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	12.9
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	41.4
Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	29.7
Linolenic acid	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	0.2

The possible triglyceride is,



**Figure 2: Triglyceride structure of punnal oil**

Generally, oil consists basically of triacylglycerols with different degrees of unsaturation and different distribution and properties of fatty acid acyl chains. The high content of unsaturated fatty acids of about 72% in punnal oil gave rise to the high iodine value of 71g I<sub>2</sub>/100g. These properties show that punnal oil is a suitable starting material for epoxidation.

### FT-IR analysis

The IR spectrum of punnal oil also supports the presence of both saturated and unsaturated acyl groups. The conversion of double bonds to epoxy is confirmed by the FT-IR spectra. The epoxidised oil reveals that disappearance of 3009cm<sup>-1</sup> band shows C=C has been used up and appearance of the band around 910cm<sup>-1</sup> which is not in oils, is characteristic of the epoxide and it can be assigned to ring vibrations of the epoxy ring in cis-epoxides.[4]

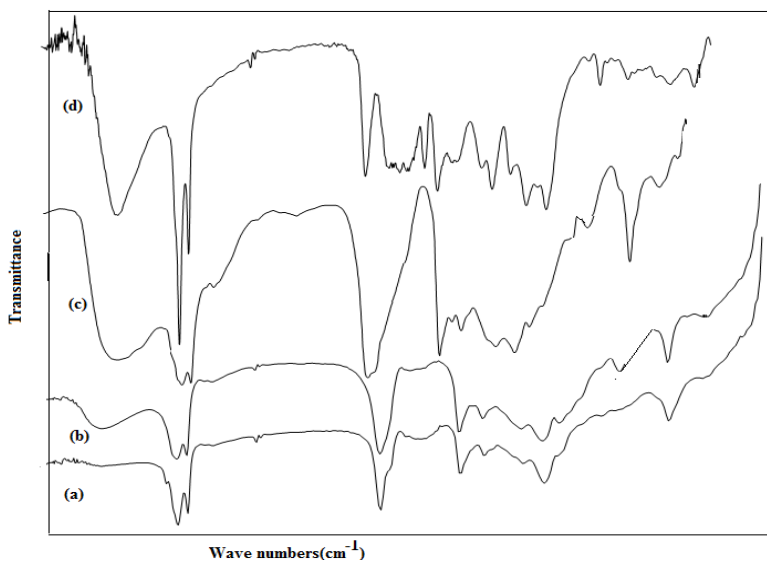


Figure 3: FT-IR spectrum of (a) Punnal oil; (b) EPO (1:0.5:1.3), (c) EPO (1:0.5:1.5), (d) Epoxy composite

*NMR analysis*

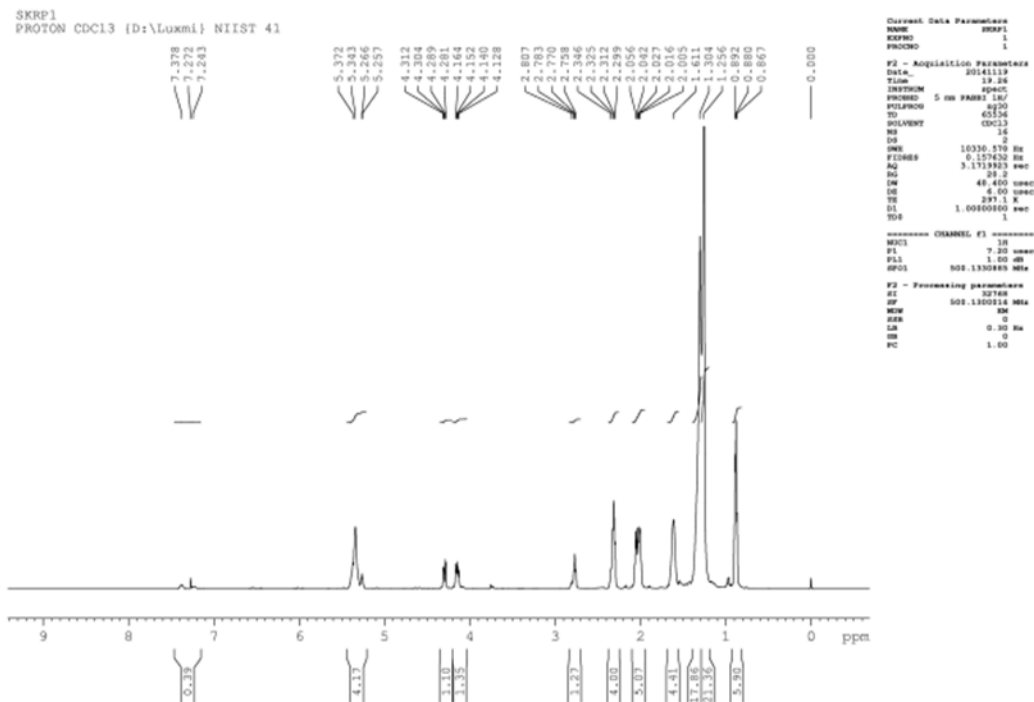


Figure 4: Proton NMR spectra of oil

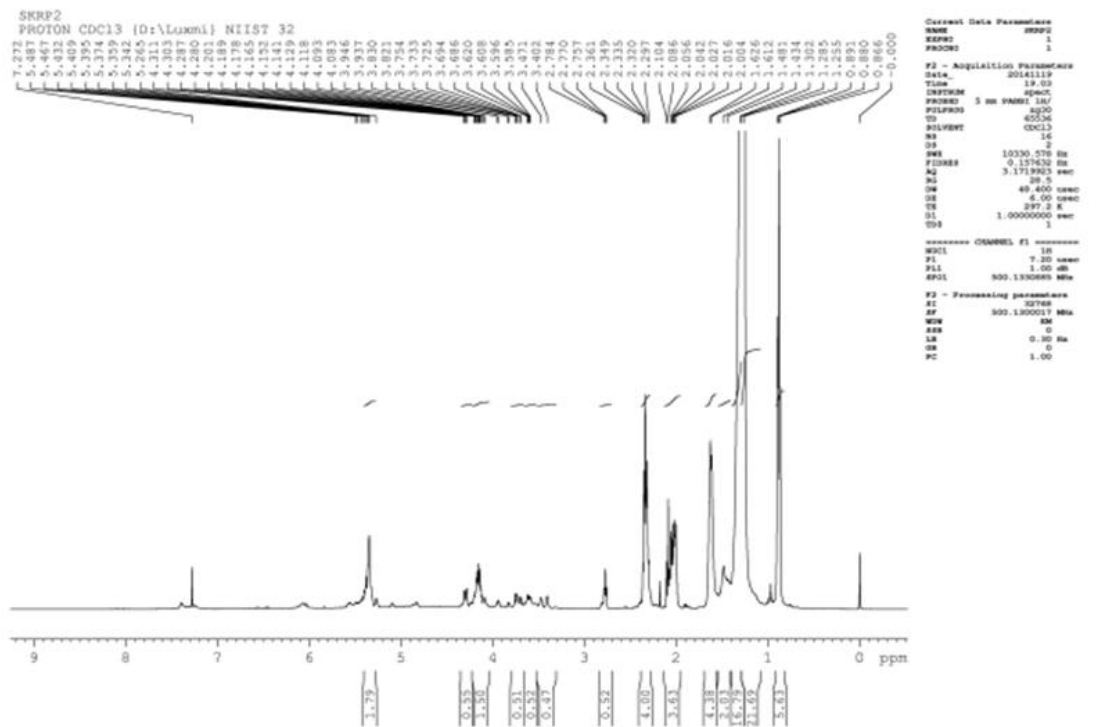


Figure 5: Proton NMR spectra of EPO(1:0.5:1.3)

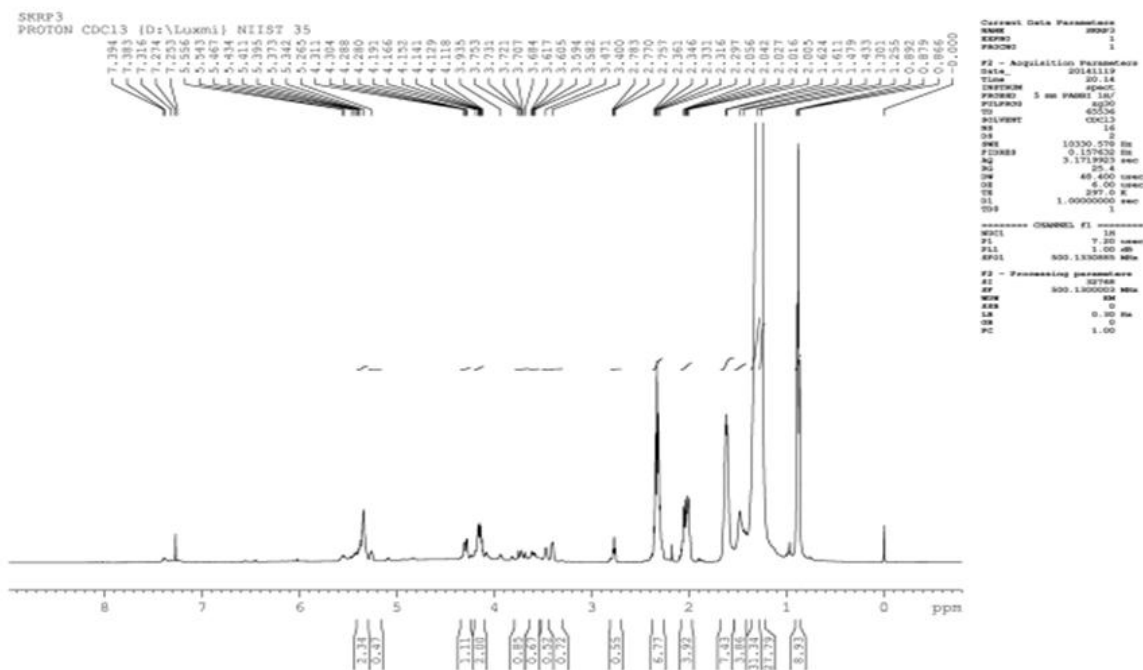
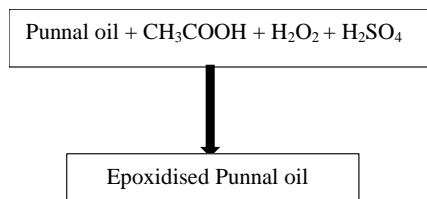


Figure 6: Proton NMR spectra of EPO (1:0.5:1.5)

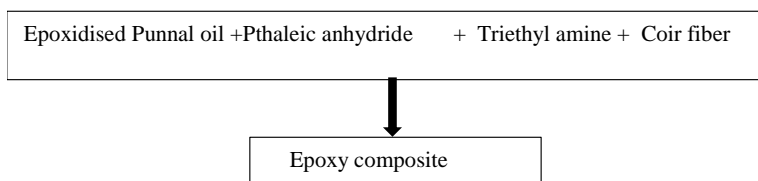
The conversion of olefinic group to epoxy group is clearly indicated by the spectra. The spectra of oil, the olefinic proton is observed in 5.3 – 5.5 ppm. In the spectra for epoxidised oil, the peak has almost disappeared. This fact suggest that the C=C undergoes complete epoxidation.

### Scheme of epoxidation

#### Scheme: I



#### Scheme: II



**Figure 7: Scheme of epoxidation**

### Chemical resistance of composites

The coir reinforced composites seem to exhibit higher weight loss than the neat epoxy composites. Furthermore, the weight loss slightly increases with increasing time of exposure to the environment for all the specimens.

**Table 4: Stability of composites to the acidic environment**

Specimen	Weight loss(%)		
	Conc.HCl (1N)	Conc.HNO <sub>3</sub> (1N)	Conc.H <sub>2</sub> SO <sub>4</sub> (1N)
Neat Epoxy(EC) (1:0.5:1.3)	0	0	0
EC + 5% coir	-0.2	-0.2	0.14
EC +10% coir	-0.2	-0.2	-0.7
EC +15% coir	-0.2	-0.2	-0.7
Neat Epoxy(EC) (1:0.5:1.5)	-0.2	0	0
EC +5% coir	-0.2	0	-0.5
EC +10% coir	-0.2	-0.2	-0.3
EC +15% coir	-0.2	-0.2	0

**Table 5: Stability of composites to the basic environment**

Specimen	Weight loss(%)		
	NaOH (10%)	NH <sub>4</sub> OH (10%)	Na <sub>2</sub> CO <sub>3</sub> (20%)
Neat Epoxy(EC) (1:0.5:1.3)	1.4	0	0
EC + 5% coir	1.4	0	-0.1
EC +10% coir	0.9	-0.1	-0.5
EC +15% coir	0.5	0.5	-0.5
Neat Epoxy(EC) (1:0.5:1.5)	-0.5	-0.5	0
EC +5% coir	-0.1	-0.29	-0.5
EC +10% coir	-0.5	-0.5	-0.29
EC +15% coir	-0.29	-0.29	-0.29

**Table 6: Stability of composites to the solvent**

Specimen	Weight loss (%)				
	Ethanol	DMA	CHCl <sub>3</sub>	Toluene	Water
Neat Epoxy(EC) (1:0.5:1.3)	0	0	-0.4	0	0
EC + 5% coir	-0.2	0	-1.7	0.3	-0.3
EC +10% coir	0.3	0	-1.7	0.33	-0.3
EC +15% coir	0.14	0	-1.7	0.14	0.6
Neat Epoxy(EC) (1:0.5:1.5)	0	0	-2.3	0	0
EC +5% coir	0	0	-2.2	0	0.3
EC +10% coir	0.13	0	-2.2	0.14	0.3
EC +15% coir	-0.2	0	-3	0	0.3

In the present study, all epoxy composites showed excellent acid, alkali and solvent resistance and no significant change in the physical appearance of epoxy samples is seen except CHCl<sub>3</sub>. In chloroform, the samples became brittle after drying.

#### *Soil burial degradation*

Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degradation. In the present study, there is no weight loss observed in the composites even a period of 2 months. Hence these composites are non-biodegradable.

**Table 7: Soil burial test for composites**

Specimen	Weight(g)	
	Initial	Final
Neat Epoxy(EC) (1:0.5:1.3)	1.54	1.54
EC + 5% coir	1.67	1.67
EC +10% coir	1.98	1.98
EC +15% coir	1.8	1.8
Neat Epoxy(EC) (1:0.5:1.5)	1.93	1.93
EC +5% coir	1.68	1.68
EC +10% coir	1.89	1.89
EC +15% coir	1.88	1.99

#### *Tensile Properties*

**Table 8: Tensile strength, elongation at break and young's modulus of epoxy composites**

Specimen	Tensile Strength (MPa)	% of elongation at break	Youngs Modulus (MPa)
Neat Epoxy(EC) (1:0.5:1.3)	1.8	11	16.36
EC + 5% coir	3.3	12.1	27.5
EC +10% coir	5.9	12.9	45.7
EC +15% coir	10.8	14.04	77.14
Neat Epoxy(EC) (1:0.5:1.5)	2.5	10.64	23.6
EC +5% coir	5.4	10.8	50
EC +10% coir	8.9	11.9	74.8
EC +15% coir	13.73	12.1	113.47

The increase in coir fiber content leads to the increase in the tensile strength and the young's modulus. The elongation at break, however, was decreased, which is in line with the changes of mechanical properties of general natural fiber reinforced polymer composites. Coir fibers possess good mechanical properties. As the content of the coir fibers increased, more fibers shared the tensile





stress to improve the tensile strength and Young's modulus greatly. On the other hand, the limit deformation of coir fibers made the elongation at break decrease. When the mass fraction of coir fiber above 15%, the fibers could not distribute evenly and the defects of the composite increased, which limited the improvement of mechanical properties.

## CONCLUSION

Punnal oil was epoxidised successfully by peroxy acetic acid generated 'insitu' by reacting acetic acid with hydrogen peroxide at the temperature range of 60 – 70°C. The epoxidation was confirmed by iodine value, TLC and FT-IR analysis. Further epoxy composites are prepared from the treated coir fiber of different composites (5, 10 and 15wt %). As the coir fiber content increases, the tensile strength also increases. There is no weight loss observed from the chemical resistance test concluded that these composites are non-biodegradable. The moisture uptake increases with the increase in percentage of fiber content.

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