

ESOA modified unsaturated polyester hybrid networks: A new perspective

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ABSTRACT: Hybrid polymer networks based on unsaturated polyester (UPE) and epoxidized soybean oil acrylate (ESOA) were synthesized by reactive blending through free radical addition polymerization reaction. ESOA was prepared by acrylation of epoxidized soybean oil (ESO). The physical, mechanical, thermal and electrical properties of the cured blends were compared with the neat resin. ESOA resin bearing reactive functional groups showed good miscibility and compatibility with the UPE resin. The co-cured resin showed substantial upgrading in the toughness, impact resistance, thermal properties, and downgrading brittleness up to the addition of 20 wt % of ESOA content. The muddled phase structure was corroborated by Fourier transform infrared spectroscopy, scanning electron microscope, and transmission electron microscopy and proved the formation of excellent hybrid polymer network. An improvement in overall properties has been achieved without seriously affecting any other properties. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44345.

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INTRODUCTION

Petroleum derived unsaturated polyester resins are well known over the last four decades due to their relatively low cost and ease of processing. They exhibit poor damage tolerance, low mechanical strength and stiffness relating to other engineering materials such as metals.¹ Again the brittleness of this class of nonbiodegradable thermosetting material is one of their major drawbacks.² Therefore, their utilization in industrial applications has been restricted to some extent. For that reason, various different methods of blending or mixing of different types of polymers have been conducted to successfully tailor the physical, mechanical, and thermal properties of polymers.³ Because blending provides a more refined and versatile procedure for achieving a higher level of structural homogeneity in the mixture of two chemicals with improved properties. Various blending and mixing techniques like mechanical blending, simple melt mixing, solvent casting, latex blending, fine powder blending, etc., are also used for this purpose. Among them mechanical blending is the easiest, cheapest, and user friendly method of blending that combines two chemicals in a unified smoothed manner.

Vegetable oils are very demanding raw materials for the preparation of green composites. Epoxidized soybean oil is a class of vegetable oil having low cost, ready availability, low toxicity, biocompatibility, good lubricity, low volatility, high viscosity

index, solvency for lubricant additives, and easy miscibility with other fluids.⁴⁻⁷ Epoxidized soybean oil acrylate (ESOA) are synthesized from the reaction of epoxidized soybean oil with acrylic acid. When this functionalized⁸ product is cured alone or even with styrene as reactive co monomer, yield rubberlike materials.^{9,10} This substance reduces the tension of deformation, hardness, density, viscosity, and electrostatic charge of a polymer. At the same time it increases the polymer chain flexibility, resistance to fracture, thermal resistance, and dielectric constant.¹¹ So hybrid networks of this biodegradable material with nonbiodegradable thermosetting one will give an innovative and improved combination with good toughness and excellent properties of high applicability.

In this work, ESOA prepolymer is first synthesized from the reaction of epoxidized soybean oil with acrylic acid and then it is blended with different weight percent of unsaturated polyester resins (UPE). Initially, the blends are characterized with the help of Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and transmission electron microscopy (TEM). Then their mechanical, thermal, and electrical performance tests are studied to determine the most optimum blend composition for their use in structural purposes specifically for low-cost housing projects and as an insulating material. Further, a comparative study of thermal and ageing properties has been made between ESOA and the optimum

blend compositions. Here, specific blend compositions have been mentioned to emphasize only on the important experimental results.

EXPERIMENTAL

Raw Materials

Isophthalic polyester (Unsaturated polyester-UPE) was used as the resin (supplied by Vasavi Bala Resins, VBR-4301 and viscosity—0.3 Pa s). The ESO (Epoxidized Soybean Oil) was purchased from Sigma Aldrich. ESOA (Epoxidized Soybean Oil Acrylate) was synthesized in our laboratory from ESO. Triphenylphosphine (TPP or PPh₃—catalyst), Butylated hydroxytoluene (BHT—stabilizer), and acrylic acid were collected from Sigma Aldrich. Methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate were used as catalyst and accelerator for unsaturated polyester and ESOA blend which were purchased from Sigma Aldrich. All chemicals and solvents were used without any purification.

Methods

Synthesis of ESOA from ESO. About 227.60 g of epoxidized soybean oil (0.40 mol) and 87.0 g of acrylic acid (1.20 mol) were added to a three-necked flask (500 mL) attached with a condenser, thermometer and mechanical stirrer. Then 0.085680 g of BHT (0.03% of the total resin) weight was added as stabilizer or free radical inhibitor. About 2.856 g of TPP (1% by weight) was used as a catalyst and the reaction temperature was raised to 70–75 °C. The reaction was carried out for approximately 6 h. The change of reaction with time can be followed by monitoring the equivalents of epoxides to carboxylic acid and the oxirane oxygen content given in Figure 2. The formed ESOA is not highly viscous and shows a constant viscosity at different shear rates indicating, Newtonian behavior. Therefore, it is not necessary to use reactive diluents to reduce the viscosity of acrylated oils, which is a highly desirable feature for composite application.

Preparation of UPE/ESOA Hybrid Networks. ESOA was added in the UPE resin and stirred properly till clear solutions were obtained. The 3% MEKP (w/w) Catalyst was then mixed and stirring was continued for 4 h to confirm that the catalyst was completely dissolved. Now 0.5% cobalt naphthanate (w/w) was added to the solution. At the beginning of fabrication, gel coat was uniformly brushed in to the finished side of male and female parts of the mold. Then the mold was subjected to hot-press (5 tons). Curing was carried out at 120 °C in a convention oven for 2 h.

CHARACTERIZATION

Acid Value Determination

About 1 g of resin was dissolved in 100 mL of acetone. The acid value was calculated by direct titration of the resin against 0.1N KOH solution with five drops of phenol red:bromothymol blue (1:1 in 90% ethanol solution). The end point was obtained when the color of the solution changed from yellow to green and from green to blue. The value was calculated by using the following equation:

$$AV = \frac{5.61 \times f \times V}{W} \quad (1)$$

where, f is the titration factor of the KOH = 1, V is the volume of the 0.1N KOH, and W , weight of the resin sample.

Oxirane Oxygen Content

About 1 g of resin was dissolved in 100 mL of acetic acid. Samples were titrated against 0.1N HBr using five drops of crystal violet indicator. The percentage of oxirane ring per gram of resin was calculated by using the following equation:

$$\text{Oxirane oxygen (\%)} = \frac{1.6 \times N \times V}{W} \quad (2)$$

where, N is the normality of HBr solution, V is the volume of HBr required for titration, and W is the weight of the sample

Fourier Transforms Infrared (FTIR) Spectroscopy

FTIR spectra of ESO, ESOA, and UPE/ESOA blend were collected using Thermo-Nicolate Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with an Omega 9000-A temperature controller).

Nuclear Magnetic Resonance (NMR)

NMR measurements were conducted on a Bruker AC270 MHz spectrometer. Deuterated solvents such as CDCl₃ were used with concentrations typically between 1 and 10 wt % solids.

Gel Content Determination

The small blocks of solid samples (3 mm × 3 mm × 5 mm) were immersed in acetone solvent at room temperature for 1 week. The swelling equilibrium was determined when the weight of the swelling samples were constant. The networks were first weighed in the swollen test. Then they were washed with fresh solvent and dried under vacuum at 80 °C for 3 days until constant weight was achieved. Gel fraction % was calculated as per the following equation.

$$\text{Gel fraction \%} = \frac{\text{Sample weight before extraction}}{\text{Sample weight after extraction}} \times 100 \quad (3)$$

Scanning Electron Microscopy (SEM)

SEM was utilized to examine the surface morphology of neat ESOA as well as the UPE/ESOA hybrid networks. The samples were gold coated and examined by using a Philips 420T scanning electron microscope with a secondary electron detector, operating at 20 kV in the SEM mode.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy was conducted in JEM-200 FX. Thin sections (90 nm) of the Cured blends were obtained by microtome with diamond knife for TEM analysis. The filament Voltage was kept 200 kV to make a bright field image of the blend.

Mechanical Testing

The tensile and flexural properties of different blends were studied by universal testing machine (HOUNSFIELD; H10KS) in accordance with ASTM D-638 and ASTM D-790. Impact strength was measured as per ASTM D256. All the results were taken as an average of four samples.

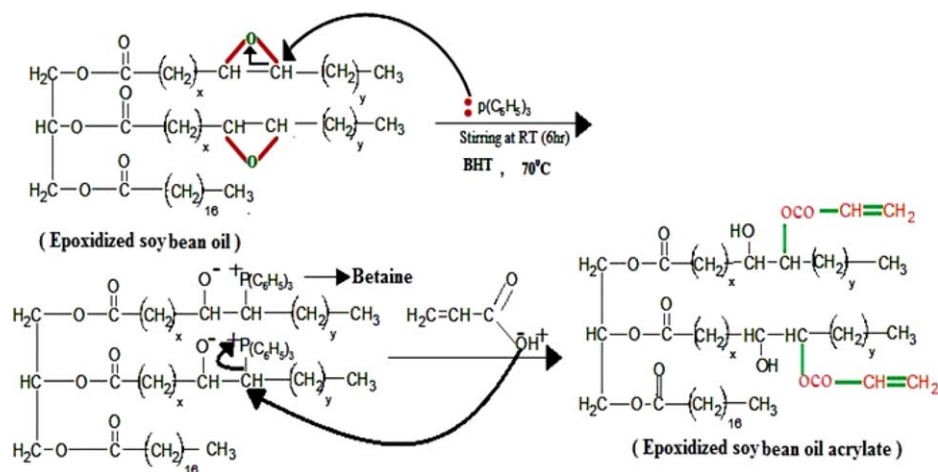


Figure 1. Reaction mechanism of synthesis of ESOA from ESO. [Color figure can be viewed at wileyonlinelibrary.com.]

Dynamic Mechanical Analysis (DMA)

For DMA, five test specimens ($56 \times 13 \times 3$ mm) were cut from the center section of an ASTM type I tensile bar. The dynamic mechanical properties like storage modulus and damping coefficient ($\tan \delta$) were evaluated by using a DMA tester (Model Q800).

Differential Scanning Calorimetry (DSC)

DSC was utilized to determine the glass transition temperatures and to monitor the curing reactions. DSC was conducted on a Perkin Elmer Series 7 thermal analyzer under a nitrogen purge at a heating rate of $10^\circ C/min$. All reported data are from second heating scans.

Thermal Properties Measurement

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Series 7 thermal analyzer with a nitrogen atmosphere at a heating rate of $10^\circ C/min$. The weight loss of the sample was measured as a function of temperature.

Electrical Properties

The volume and surface resistivity were evaluated according to ASTM D257 by using a Keithly 6517A model 8009 resistivity test fixture at room temperature.

Ageing Studies

The ageing of the blends on exposure to water was evaluated by keeping the samples immersed in water. Five specimens ($25 \text{ mm} \times 25 \text{ mm}$) of each sample were kept immersed in distilled water at $25^\circ C$ for 30 days. The samples were taken out, dried at room temperature and their weights were taken. All the results were taken as an average of five samples.

RESULTS AND DISCUSSION

Characterization of ESOA and UPE/ESOA Hybrid Resin

This article aims to present the synthesis procedure of ESOA in details using ESO as raw material. In addition to it the properties of the blend formed by ESOA with UPE have also been studied. During synthesis of ESOA, TPP is used as a pre reaction catalyst to promote the reaction between the epoxy group and the carboxylic acid group through nucleophilic attack by

producing betaine as an intermediate. BHT is used to prevent the autoxidation of ESO by atmospheric oxygen. So the formation of peroxy radical became easy without forming hydro peroxide by autocatalytic reaction. Acrylation of ESO is occurred by acrylic acid via a ring opening reaction. The epoxy groups react with the carboxylic acid groups in the acrylic acid to form the required acrylated ESO. Figure 1 shows the detailed reaction mechanism for synthesis of ESOA and is confirmed through FTIR-analysis. As acrylation reaction involves the intake of the carboxylic groups of the acrylic acid and the oxirane group of ESO; so to know the equivalents of epoxides to carboxylic acid, acid value and oxirane ring percentages of the reaction were calculated according to eqs. (1) and (2) respectively. Figure 2 confirms the decrease in acid value and oxirane ring percentages during the reaction progress with time. Initially the acid value was 44 mg KOH/g . It started to decline rapidly in the first 2 h due to the higher concentration and higher reactivity of acrylic acid and oxirane group. As the reaction progressed, the values decreased slowly and the reaction stopped when the acid value was about 8 mg KOH/g . Again the decreasing trend of the

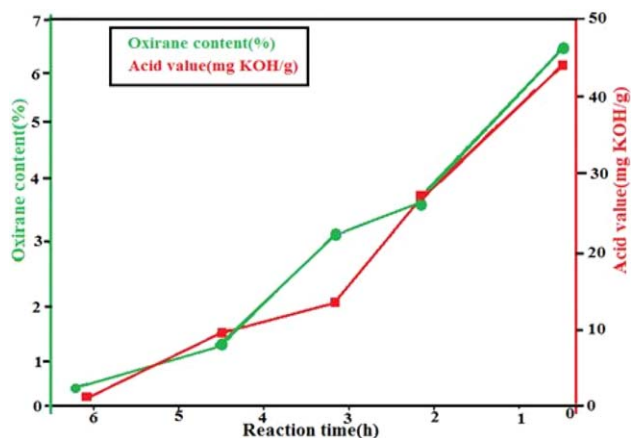


Figure 2. Acid values and oxirane content (%) v. Acrylation reaction time in ESOA synthesis. [Color figure can be viewed at wileyonlinelibrary.com.]

Table I. Analytical Data of the ESO and ESOA

Properties	ESO	ESOA
Oxirane oxygen content (%)	6.4	0.012
Iodine value (g I ₂ /100 g)	6	8
Acid value (mg KOH/g)	1.0	1.15
Viscosity (25°C Pa s)	0.258	23.476

oxirane ring percentage shows the consumption of epoxy groups during the acrylation process. Addition of acrylate groups to the epoxy ring also enhances the viscosity of the starting ESO. Analytical data of ESO and ESOA are presented in Table I. Further characterization by FTIR and NMR confirmed the participation of oxirane group in the acrylation reaction as well as the formation of new acrylate functional groups in ESOA.

The different blends of UPE with ESOA are prepared by using MEKP as free radical initiator.

Figure 3 shows the free radical addition reaction mechanism between UPE and ESOA. The formation of blend is further confirmed by FTIR-analysis which is shown in Figure 4.

FTIR Analysis

Table II presents the IR data; relevant to ESO, acrylic acid, ESOA, and UPE/ESOA hybrid networks. IR of acrylic acid is given in Figure 4(b) for determining the proper formation of ESOA from ESO. Acrylic acid plays a major role for esterification reaction by giving carboxyl ionic group to the epoxy group of the ESO for forming additional polymeric hydroxyl ester. Epoxide resins (ESO) react with carboxylic acid to form ester in the required resin. TPP interacts with acrylic acid by removing its hydrogen as cation and carboxylate as anion for performing nucleophilic addition reaction to electron deficient carbon atom of epoxy group and produces an alcoholate anion. In further step this alcoholate anion abstracts the proton

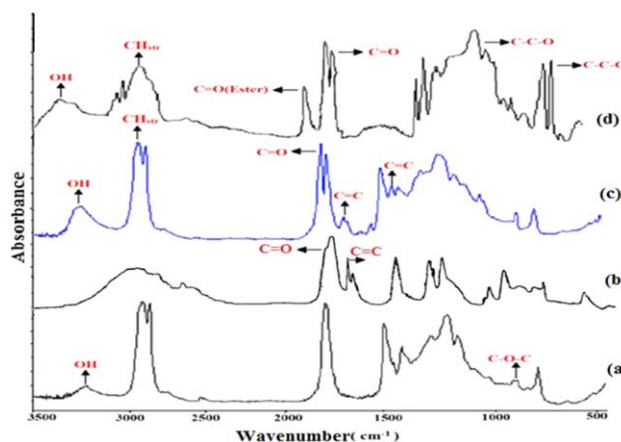


Figure 4. FTIR spectra of (a) ESO, (b) Acrylic acid, (c) ESOA, and (d) UPE/ESOA hybrid network. [Color figure can be viewed at wileyonlinelibrary.com.]

removed in the previous step and completes the reaction with formation of ester. Then carboxylic anion again attacks the unreacted epoxy group till all the epoxy and acrylic acid get used. From the IR of Acrylic acid the most important bands are observed at 1705 cm^{-1} corresponds to C=O band and 1617 cm^{-1} of C=C. Other bands of acrylic acid are given in Table II for taking comparative study. Three important functional groups are shown in Figure 4 in terms of the structural information. These are: oxirane group of ESO, acrylate group and hydroxyl group in the ESOA cured sample and C—O—C ester linkage of UPE in the UPE/ESOA blend. Spectrum of ESO shows several absorbance peaks at 912 and 882 cm^{-1} ascribing to the oxirane group. After acrylation of ESO a new strong absorbance peak at 1637 cm^{-1} is observed that indicated the presence of Vinyl functionality of the acrylate polymer (ESOA). In Figure 4(d) a peak of the blend at 1152 cm^{-1} attributed to the C—O—C ester linkage of unsaturated polyester. Again the

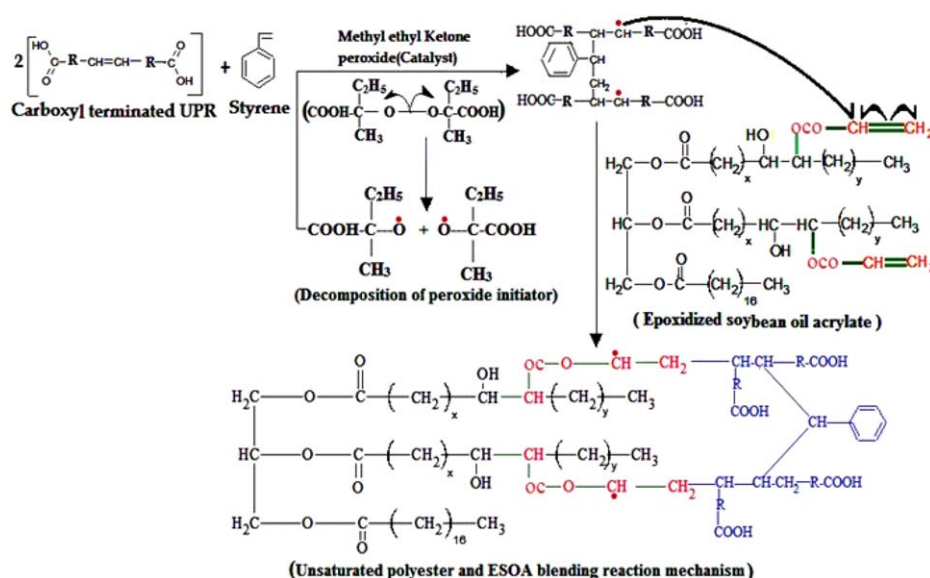


Figure 3. Proposed chemical interactions between UPE and ESOA. [Color figure can be viewed at wileyonlinelibrary.com.]

Table II. FTIR Data of the ESO, Acrylic Acid, ESOA, and UPE/ESO A Blend (Absorption Peak cm^{-1})

ESO	Acrylic acid	ESO A	ESO A/UPE blend
OH _{str} 3443 (Weak)	OH _{str} 3200–2500	OH _{str} 3470 (strong)	OH _{str} 3478
CH _{str} 2944	COH 1384	CH _{str} 2927, 2856	CH _{str} 2985
C=O _{str} 1740	C=O 1705	C=O _{str} 1740	C=O _{str} 1736
CH _{sym band} 1378	CH 1240	CH _{sym band} 1378	CH _{bending} 755 (Benzene ring)
—	C=C 1617	H ₂ C=CH _{str} 1637	—C=CH _{weak} 1004
CO _{str} 1282	CH _{2cis} 1068	C—O _{str} 1270	C—O _{ester} 1755
C—C—O _{str} 1142	C—C—O _{str} 1279	C—C—O _{str} 1189, 1057	C—C—O _{str} 1045
C—O—C 912, 882	CH ₂ 1432	C—C—O _{asyband} 967, 810	C—O—C _{esterlinkage} 1152
CH _{sci band} 1468 oxirane group	—	CH _{scissoring band} 1461	CH _{end} 1461
	CH _{2 trans} 1046	H ₂ C=CH 1406	
	scissoring band for terminal alkene		

synthesized hybrid network of UPE/ESO A blend gave an interesting peak of lower peak height than normal $-\text{CH}_3$ and $-\text{CH}_2$ peak at 2955 cm^{-1} denotes $-\text{CH}_{\text{str}}$.

This confirms the occurrence of poly addition reaction during the hybrid network formation.

NMR Analysis

Figures 5 and 6 present the ^1H -NMR spectra of ESO and ESO A, respectively. In Figure 5 the terminal methyl groups and the methyl group in α -position to it showed peaks at 0.82 and 1.32 ppm. A signal at 1.29 corresponds to the backbone methylene protons in the triglyceride chain. In ESO the methine of the epoxy ring proton showed peaks in the 3.1–3.5 ppm region. The peaks at 4.1–4.4 ppm originate from the protons in the methylene group of the triglyceride.

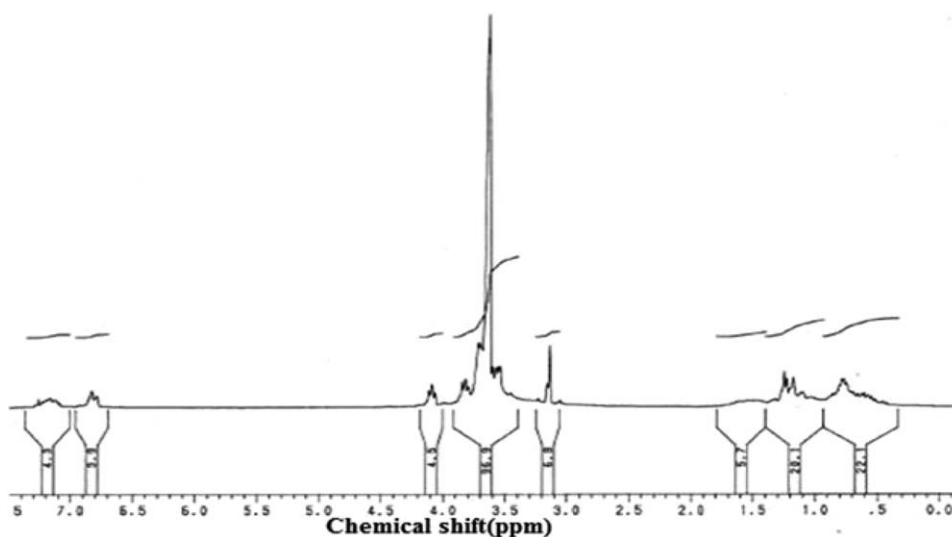
In Figure 6 the vinyl protons associated with the acrylic group are detected at 5.6, 5.8 (methylene protons), and 6.4 ppm

(methine proton). The protons are not equivalent and they have different chemical shifts due to the effect of their orientation. As synthesis of epoxy acrylate involves opening of epoxy rings with the formation of acrylate moieties and hydroxyl groups in the triglyceride chain this NMR analysis provides strong evidence for the presence of the required groups. The chemical shift at 3.5–4.0 ppm showed the proton peak of CH group α to the $-\text{OH}$ group ($\text{HO}-\text{CH}$). The signal at 3–3.5 ppm is related to the hydroxyl group peak formed after the acrylation reaction. The acrylation percentage can be calculated from this NMR-study by using the following equation.

$$\text{Acrylation\%} = \frac{A_{\text{Epoxy}}}{A_{\text{Epoxy}} + A_{\text{Acrylate}}} \times 100 \quad (4)$$

where, A_{Epoxy} is the integrated area of the methine epoxy protons = 3.1 ppm; A_{Acrylate} is the integrated area of the acrylate protons = 5.8–5.6 ppm = 0.2 ppm.

By putting all these values in eq. (4) the calculated result is:

**Figure 5.** NMR analysis of ESO.

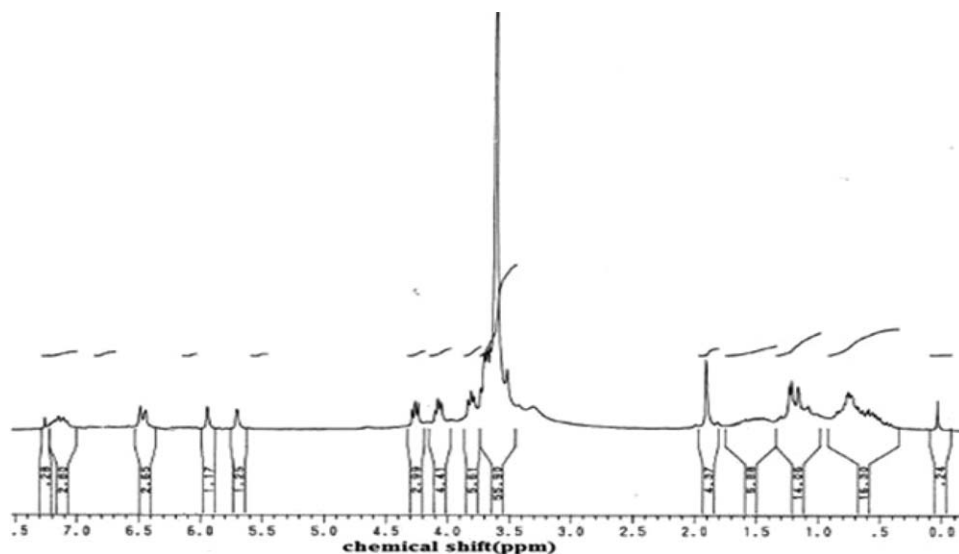


Figure 6. NMR analysis of ESOA.

$$\text{Acrylation percentage} = \frac{3.1}{3.1+0.2} \times 100 = \frac{3.1}{3.3} \times 100 = 93.9393 \approx 94$$

The acrylation percentage is found as 94% which is in a good agreement with the results obtained from FTIR and NMR analysis.

Gel Content Determination

From eq. (3) the low volume fractions of Gel content (V_p) in the modified resins during swelling studies are listed in Table III indicate reductive cross linking. The cured modified samples yielded highest amount of soluble matter compared with the unmodified sample. This is confirmed by the slightly lower gel content values of the modified samples obtained from the swelling studies. This indicates cross linking between UPE and ESOA.

SEM Analysis

The SEM micrographs of pristine UPE, ESOA, UPE/ESO—(90/10), (80/20), (70/30) are shown in Figure 7(a–e), respectively. The SEM image of pristine UPE has a smooth, glassy, and homogeneous microstructure without any plastic deformation whereas the normal ESOA has irregular rubberlike elastic surface. UPE/ESO (90/10) shows one phase with small crack which means a very weak toughening effect suggests morphology of cross linked continuous structure of the hybrid network.¹² The miscibility of ESOA in the UPE resin is confirmed from Figure 7(c). It depicts smooth and regular morphology with prominent and persistent co-continuous phase of both the resin matrices.

The two phases are mixed together which created an idea of a homogeneous phase. It is a strong basis for the formation of a hybrid polymer network structure with possibility for co-reaction. This can prevent the material deformation and crack initiation. Increasing the amount of ESOA reduces the crystallinity and roughness of the surface of the hybrid systems. This is an indication for the improvement in fracture energy. Detection of a heterogeneous structure in 30 wt % of bio-resin

content has done in Figure 7(d). The morphology shows some irregular ridges and phase-separated domains on the continuous phase of the UPE-ESO blend. This may be the free acrylic acid groups present in the ESOA resin. It indicates that this polymer possesses longer molecular chain and less miscibility with unsaturated polyester resin.

TEM Analysis

The performance of a hybrid network depends on the compatibility of the two blends. TEM is a widely used technique to evaluate the successful coordination of two polymers to determine the strength of the hybrid network system. Thus, TEM micrograph is collected to achieve better understanding of intermingled network created between the UPE/ESO hybrid networks shown in Figure 8. Figure 8(a) demonstrated the TEM of UPE. It is single phase with brittle glassy and crystalline surface. At the composition of 90/10 blend ratio the co-continuous phase has not yet been formed. When the reaction starts the ESOA first forms a copolymer with the resin, then phase separates. Thus, the cured thermoset possess a dispersed elastic phase. Here the elastic domain participates during cure to form a toughened UPE material. It revealed that the two phases remained intact with each other and a layer of crystalline phase was clearly visible with the presence of an elastic phase. As the

Table III. Gel Content Study of the UPE, ESOA, and UPE/ESO Blend

Materials	Soluble matter (%)	Gel content (V_p)
UPE	4.677	0.923
UPE/ESO (90/10)	5.282	0.907
UPE/ESO (80/20)	5.42	0.883
UPE/ESO (70/30)	5.9	0.775
ESO	6.2	0.692

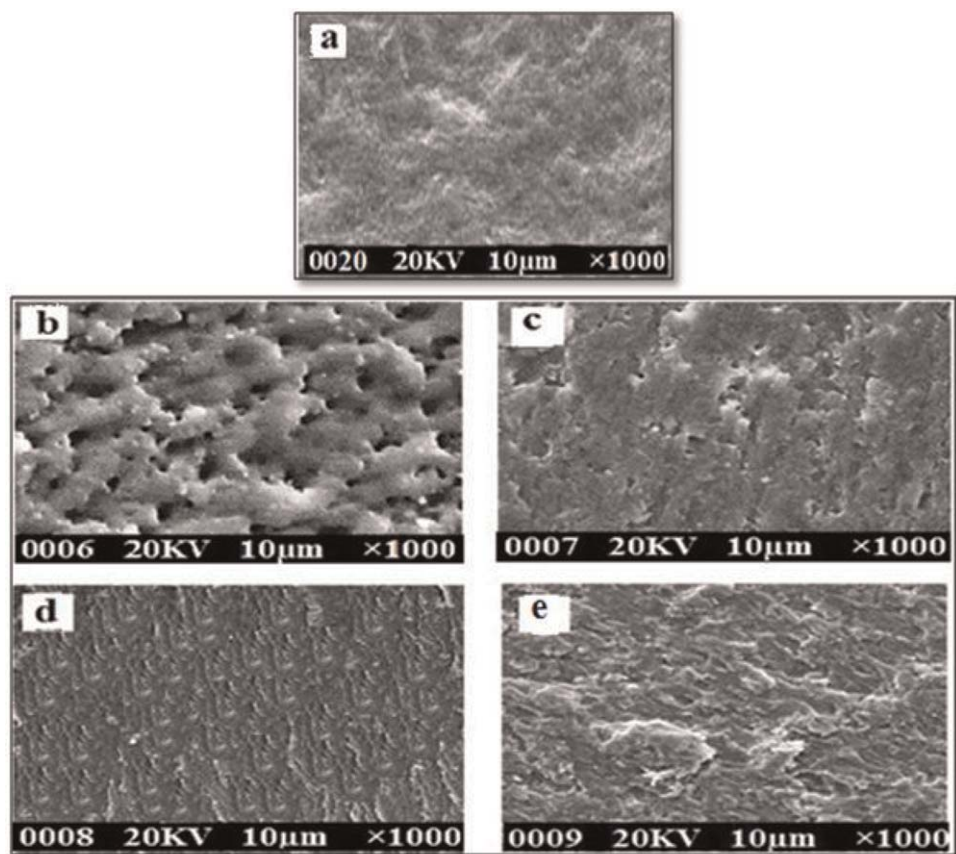


Figure 7. SEM of (a) UPE, (b) ESOA, and UPE/ESOA—(c) 90/10, (d) 80/20, (e) 70/30.

acrylate unit content of ESOA increases, the size of the dispersed UPE network become smaller and the shape of the UPE domains appear less elongated.

The higher reactivity of both the resins confirmed the formation of a good hybrid polymer network. Better co-ordination restricted the mobility of cross linked chain segment in spite of

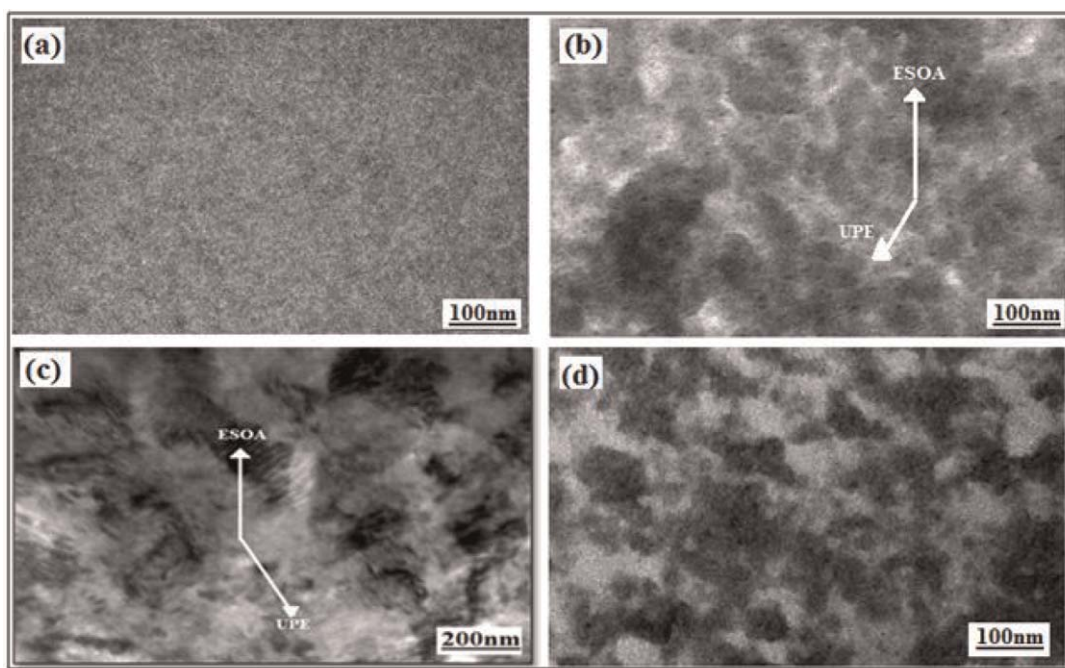


Figure 8. TEM of (a) UPE, (b) UPE/ESOA (90/10), (c) UPE/ESOA (80/20), and (d) UPE/ESOA (70/30).

Table IV. Tensile and Bending Properties of the UPE, ESOA, and UPE/ESOA Blend

Material	Properties					
	Tensile			Bending		
	Stress (MPa)	Strain (%)	Modulus (GPa)	Stress (MPa)	Strain (%)	modulus (GPa)
UPE	48 ± 4	1.0 ± 0.2	5.1 ± 0.1	58 ± 3	2.6 ± 0.3	2.2 ± 0.1
UPE/ESOA (90/10)	41 ± 3	1.05 ± 0.1	4.2 ± 0.2	49 ± 4	2.9 ± 0.1	1.8 ± 0.2
UPE/ESOA (80/20)	37 ± 4	1.12 ± 0.1	3.1 ± 0.2	44 ± 2	3.2 ± 0.2	1.5 ± 0.2
UPE/ESOA (70/30)	26 ± 4	1.4 ± 0.2	2.8 ± 0.3	39 ± 5	3.9 ± 0.3	1.2 ± 0.2
ESOA	20 ± 0.3	1.52 ± 0.1	2.1 ± 0.2	24 ± 4	2.3 ± 0.2	1.04 ± 0.3

its long molecular structure and enhanced the compatibility. The two networks exhibit good blending properties.

Mechanical Properties

Referring to Table IV the tensile and bending properties obtained by variable content of ESOA (10, 20, 30 wt %) in UPE/ESOA hybrid network suggested a slight diminish in the values. For blends with 30 wt % of ESOA the tensile strength decreased from 48 MPa for pure UPE, to 26 MPa and the Young modulus changed from 5.1 GPa for UPE to 2.8 GPa. Again Table IV demonstrated the reduction in bending strength from 58 to 39 MPa and bending modulus from 2.5 to 1.5 GPa for pure UPE and 30 wt % ESOA content, respectively. This value is expected as ESOA has lower tensile and bending properties than UPE. So this is only due to the contribution of ESOA chain that makes the blend more flexible and enhances the ductility which leads to deformation of the sample before fractured.^{13,14}

Meanwhile the values of fracture strain, toughness and impact strength showed in Table V increased than neat UPE at about 20 wt % of ESOA content and began to decrease with increasing the amount of the ESOA.

At 20 wt % of ESOA content the values of fracture strain, toughness and impact strength showed an increment of about 60.15%, 23.17%, and 33% than the pristine UPE resin. It is due to the networks obtained from cross linking carbon-carbon double bonds present in the acrylic acid group of ESOA that prevented propagation of the molecular chain. It helped to absorb the energy of impact and enhance the properties. So ESOA is acting as a plasticizer and reduce the brittleness of the resulting blend. Here the result is obvious as the rigidity of the bio-resin is lower than that of pristine UPE. The qualitative

incorporation of more ESOA result free chain ends which give weak points to nucleate voids under stress. Hence, it reduced both the toughness and fracture strain of the hybrid composite.^{14,15} So the system showed higher values of fracture strain in comparison with neat UPE. The positive values can be accredited for the enrichment of adhesion between the unsaturated polyester and bioresin.¹⁶

At 30 wt % of ESOA the following properties decreases due to the phase separation of the blends. This may take place due to the presence of acrylic acid which reduces the tendency of grafting between UPE and ESOA.

Dynamic Mechanical Analysis

Storage modulus (E') and damping coefficient ($\tan \delta$) of ESOA, UPE, and the UPE/ESOA hybrid networks (w/w = 90/10, 80/20, 70/30) as a function of temperature are listed in Table VI and shown in Figure 9(a,b), respectively. The storage modulus (E') decreased with increasing the amount of ESOA. UPE has higher storage modulus than ESOA but during addition the modulus decreased at slower rate. It is because UPE undergone transition from the fully formed glassy state to the rubbery state. For all samples the storage modulus remained almost constant between 20 and 50 °C. The storage modulus of the UPE homopolymer decreased rapidly at 70 °C due to the glass transition temperature of UPE-ESOA hybrid network polymer. That proved that two polymers are miscible with each other. For a highly compatible blend the curve showed a broadening of T_g . As here it gives a single and broader peak so the hybrid networks are compatible with each other.^{17,18} The enhanced molecular motion and reduced glass transition are obtained by the addition of ESOA. So T_g of UPE has shifted to lower temperature from 105 to 90 °C and remained constant up to 20 wt %. The damping of the blends increased with increasing concentration of ESOA.

Table V. Fracture, Toughness, and Impact Properties of the UPE, ESOA, and UPE/ESOA Blend

Material	Properties		
	Fracture strain (%)	Toughness (MJ/m ³)	Impact strength (J/m)
UPE	2.56 ± 0.2	0.6 ± 0.5	32 ± 5
UPE/ESOA (90/10)	2.78 ± 0.2	1 ± 0.3	39 ± 3
UPE/ESOA (80/20)	4.1 ± 0.3	2.3 ± 0.5	48 ± 3
UPE/ESOA (70/30)	3.2 ± 0.2	1 ± 0.5	39 ± 3
ESOA	10.2 ± 0.2	2 ± 0.3	50 ± 4

Table VI. Glass Transition Temperatures of the UPE, ESOA, and UPE/ESOA Blend

Materials	Properties			
	DSC T_g (°C)	DMA		
		Storage modulus (MPa)	T_g (°C)	Maximum tan delta
UPE	105	4002	105	0.28
UPE/ESOA (90/10)	93	3400	95	0.42
UPE/ESOA (80/20)	90	3200	90	0.49
UPE/ESOA (70/30)	72	2800	82	0.55
ESOA	60	2000	68	0.60

It is because the mobility of molecular chain increases at the interface due to the presence of flexible ESOA bio-resin. Again 30 wt % replacement decreases the T_g to 82 °C because of the reduction of crosslink density and that supported the formation of a hybrid polymer network. They cannot form a homogeneous mixture as ESOA floated on the surface of UPE of the mixture because of different densities.

Figure 9(b) represented the damping coefficient ($\tan \delta$) values which are also shifted to lower temp. This shows the resin is elastic in nature. So with increasing ESOA content the storage modulus that is stiffness is decreasing in the glassy state.

Differential Scanning Calorimetry (DSC)

The DSC results showed in Figure 10 are in agreement with the DMA analysis.

With increasing the amount of ESOA content the glass transition temperature is shifted toward lower temperature. It can be explained by the fact that introduction of biobased monomer in UPE makes a miscible hybrid thermosetting blend by decreasing the crosslink density as well as glass transition temperature gradually. The DMA and DSC properties of the systems studied are listed in Table VI.

Thermogravimetric Analysis

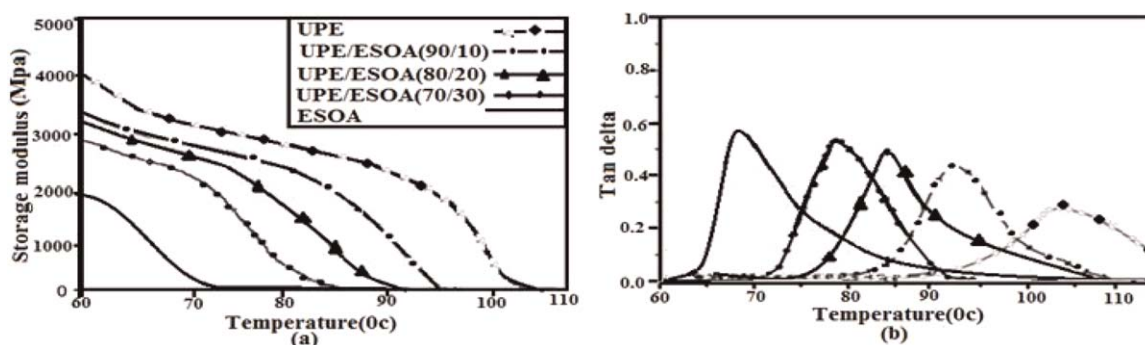
Figure 11 depicted the thermal degradation of the UPE, ESOA and UPE/ESOA hybrid networks. The maximum rate of decomposition of UPE polymer chain occurs at around 360 °C. The weight loss below 150 °C has been assigned to water loss^{19,20} and above 150 °C referred the loss of bonded water and extra acrylic acid present in the blend. The main degradation step is observed in the temperature range above 400 °C. At that

temperature the weight loss is associated with the degradation of the polymer chain structure, in agreement with the literature.^{21,22} This can be supported by the reactive cross linked blending of the ESOA/UPE networks that avoided the thermal degradation and consequent dispersion of the degraded products. The thermal degradation of ESO, ESOA, and UPE/ESOA blend was studied with the first derivative (DTG) and the important characteristic temperature obtained is listed in Table VII. The presence of a large content of bulky groups on the cross linked network structure and improved free radical induced interaction between the acrylic acid group of ESOA and free radical sites of UPE made the ESOA/UPE hybrid network thermally stable.

This result implies that the initial degradation temperature of the blend of 20 wt % ESOA is 275 °C which is higher than the pristine UPE, indicating a better thermal stability. It is only due to the better cross-linking density. Moreover, the T_{max} (temperature of maximum degradation rate) shows higher value, confirming the higher thermal stability.

Electrical Properties

The electrical resistance (volume resistance) was decreased monotonically with formation of the hybrid networks of UPE with 10, 20, and 30 wt % of ESOA. Because of UPE and ESOA have 10^{15} and 10^{12} Ω cm volume resistivity and 10^{14} and 10^{11} Ω surface resistivity, respectively. As ESOA content is increased from 0 to 20 wt % the volume resistivity of the hybrid networks decreased from 10^{15} to 10^{12} Ω cm and same case occurred in surface resistivity as shown in Figure 12(b). It is due to the longer chain of ESOA molecules which resulted higher stress distribution at each cross linking site and enhanced the degradation

**Figure 9.** DMA study of UPE, ESOA, and UPE/ESOA hybrid networks.

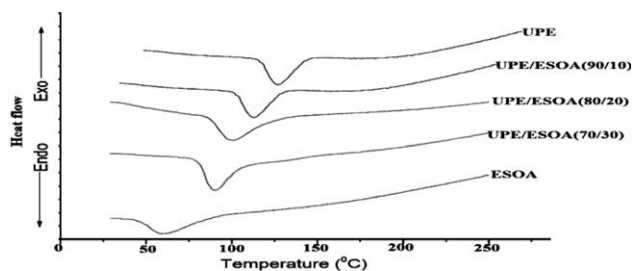


Figure 10. DSC study of UPE, ESOA, and UPE/ESOA hybrid networks.

rate. After 20 wt % the values remained constant. This was the impact of ESOA on UPE up to 20 wt % of concentration for formation of better hybrid network. The result confirmed the insulating property of the hybrid network system as the resistivity values are in aggregation of the property of an insulator.

Ageing Studies

This can be determined by the percentage of water absorbed by the hybrid networks by finding the weight difference between the samples, immersed in water and dry samples by using the formula:

$$W(\%) = \frac{W_f - W_i}{W_i} \times 100 \quad (5)$$

where, $W(\%)$ is the moisture content in percentage, W_f is weight of wet samples, and W_i is initial weight of dry samples.

The values obtained from eq. (5) are shown in Figure 13. Here we can observe that the percentage of water absorption

increased in a very negligible rate with increasing the ESOA content. Again the water absorption results demonstrated that the blended network system absorbed less moisture than normal ESOA. It may be due to the strong cross linking between the two matrix resins which avoids the entrance of water molecules within it. After all, the little enhancement can be described due to the presence of $-\text{OH}$ groups in the ESOA part initiated hydrogen bonding with water molecule.

The Application Areas

The utilization of renewable resources in energy and material applications is receiving increasing attentions in both industrial and academic settings, due to concerns regarding environmental sustainability.^{22–24} Due to better thermo physical and thermal properties and low fragility this functionalized vegetable oil can be used to form soft and flexible rubbers as well as hard and rigid plastic. So it is important for the production of commodity plastics as it fulfills the demand of green chemistry partially through efficient use of renewable resources with waste management and lesser byproduct formation.²⁵ Hence it may be called as a promising material to partially replace the petroleum-based plastic. Till now they have been used as paints and adhesives.^{26–29} If further studies will be continued on this biobased blend then it can create a new market strategy in the area of construction, automobile, marine, military, sports, and leisure.

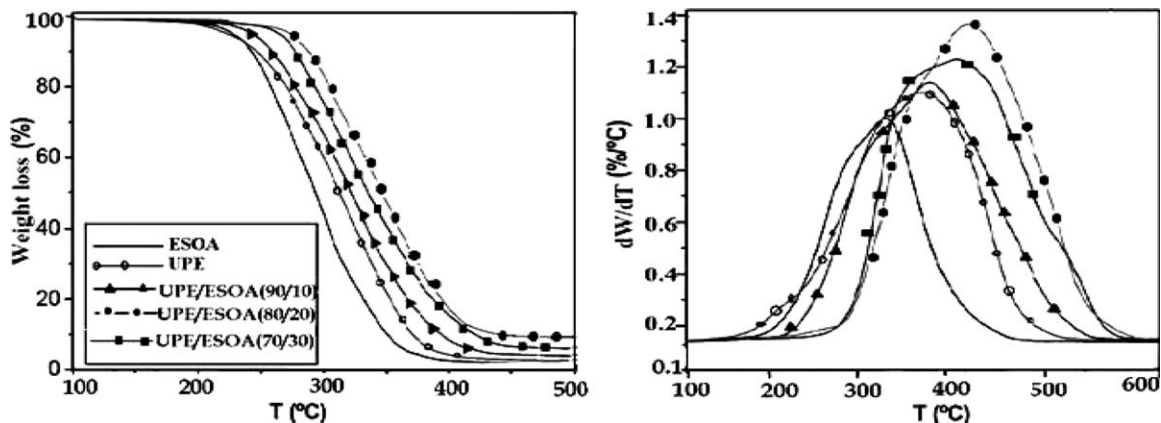


Figure 11. TGA analysis of UPE, ESOA, and UPE/ESOA hybrid networks.

Table VII. Thermal Properties of the UPE, ESOA, and UPE/ESOA Blend from TGA and DTA

Materials	Thermal properties				
	T_5 % (°C)	T_{10} % (°C)	T_{50} % (°C)	T_{end} (°C)	M_{residue} (%)
UPE	212	318	353	490	9
UPE/ESOA (90/10)	247	343	392	510	41.13
UPE/ESOA (80/20)	275	372	430	548	68.87
UPE/ESOA (70/30)	262	364	420	535	38.08
ESOA	235	320	340	478	13

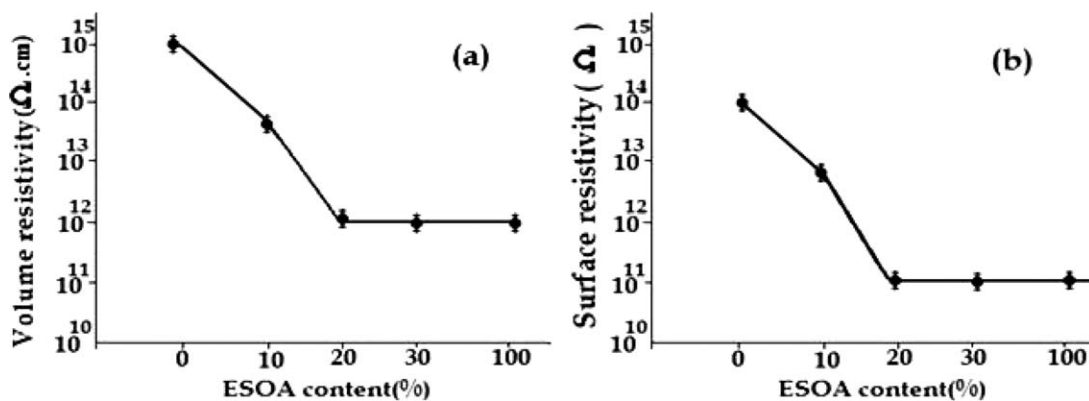


Figure 12. (a) Volume and (b) surface resistivity of UPE, ESOA, and UPE/ESOA hybrid networks.

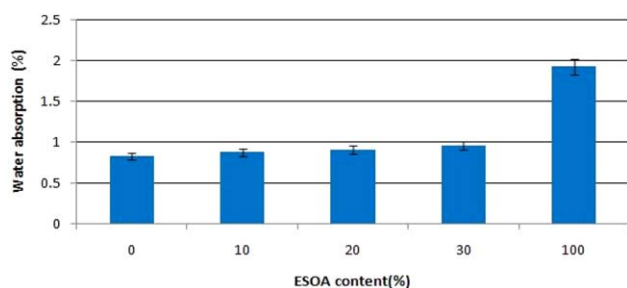


Figure 13. Ageing studies of UPE and varying content of UPE/ESOA hybrid networks. [Color figure can be viewed at wileyonlinelibrary.com.]

CONCLUSIONS

The overall results showed that UPE and ESOA form a miscible hybrid networks with possibility of co-reaction. The produced material has received much concentration due to their prospective to gain properties superior to conventional engineering materials. The novelty of this work includes the use of Epoxidized Soybean Oil Acrylate as a plasticizer in varying proportions for the first time into unsaturated polyester matrix. The studies revealed significant improvement in thermophysical and thermal properties which is very much important for various engineering applications. The optimum properties are achieved at 20 wt % because at higher bio resin content (30 wt %), the crosslink density decreases. Again reduction of brittleness of the pristine UPE after hybridization enhances their potential for application. Because brittle materials do not absorb much energy in mechanical deformation and ductility is usually needed for this to occur. Thus, the above blend could be a better material for a variety of structural and thermal applications with the ability of advanced functioning.

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