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Synthesis and characterization of soybean epoxy resin with phenoxy and glycidyl ether groups

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ABSTRACT

New soybean epoxy resin with phenoxy and glycidyl ether groups (SEPG) was prepared from the renewable source soybean oil. The SEPG was characterized by spectral and titration methods. The prepared SEPG was blended with commercial epoxy resin in different ratios and cured at 85°C for 3h, 150°C for 1h and post cured at 225°C for 2h using m-phenylene diamine (MPDA) as curing agent. The epoxy/SEPG/MPDA with different compositions cured in the temperature range of 120 -153°C as revealed by DSC studies. Composite laminates were fabricated using epoxy/SEPG/MPDA-glass fibre at different compositions. The tensile strength(280-310MPa), tensile modulus(3.1-3.4 GPa), flexural strength(365-395MPa), flexural modulus(7.3-8.0 GPa) and impact strength (33.9-36.1J/cm) were studied. The interlaminar fracture toughness(G_{IC}) values increased from 0.6953 KJ/m² for neat epoxy resin to 0.8423 KJ/m² for the modified epoxy resin in the 20% SEPG. Thermo gravimetric studies reveal that thermal stability of the neat epoxy resin was decreased by incorporation of SEPG.

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KEYWORDS

Epoxy resin;
Soybean oil;
Mechanical properties;
Thermal properties;
Rheology;
Cure studies.

INTRODUCTION

Polymers prepared from renewable and in expensive natural resources, such as carbohydrates, starch, proteins, fats and oils, have become increasingly interesting because of their low cost, ready availability and possible biodegradability^[1-3]. The various sources of oils and fats are animals (tallow, lard) and vegetables (soybean oil, palm oil, rapeseed oil). Oils and fats are triglyceride esters of higher fatty acids which contain two reactive sites one is the double bond in unsaturated fatty acid chain, another is the ester group. Now a days maximum high performance polymer research is going on in oleochemical method^[4].

Higher the iodine value of the vegetable oil, the more advantageous for polymer synthesis soybean oil, sunflower oil, safflower oil and linseed oil have high iodine value but cultivation and availability of soybean oil is more compared to other vegetable oils. Epoxidised vegetable oils show excellent promise as inexpensive, renewable material for industrial applications. Soybean oil is a double bond containing triglyceride. These double bonds may also be converted into the oxirane moiety by reaction with peracids or peroxides. Epoxidised soybean oil is used mainly as plastisizer for PVC chlorinated rubber and polyvinyl emulsion to improve stability and flexibility.

The goal of the present research is the develop-

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ment of inexpensive but highly reactive soy based epoxy resin namely soybean epoxy resin with phenoxy and glycidyl ether from unsaturated soybean oil. We expect that this soy based epoxy resin will possess higher reactivity and therefore provide denser intermolecular crosslinking and yield materials that are stronger than those obtained from commercially available unmodified epoxidised soybean oil (ESBO). Using a high content of a soyate co resin will create an inexpensive but still high performance fibre reinforced composite material from renewable resources. In this present work, soybean epoxy resin with phenoxy and glycidyl ether groups was prepared and blended with commercial epoxy resin and the effects of the loading level on the mechanical and thermal properties of composites were evaluated.

EXPERIMENTAL

Materials

Soybean oil was procured from Ruchi oil industries, India, m-chloroperbenzoic acid and fluoboric acid were purchased from E-MERCK, India. Phenol, isopropanol, chloroform, ethylacetate, epichlorohydrin and acetone, were purchased from SRL, India. Commercial epoxy resin (diglycidyl ether of bisphenol A) of epoxide equivalent weight 180, used in this study was procured from Huntsman, India. m-Phenylene diamine was obtained from Loba chemical, India. All the chemicals were used as purchased. Plain-woven glass fibres with an aerial density of 200g/m² were obtained from Saint Gobain India.

Synthesis of phenoxy soybean polyol

The epoxidised soybean oil(ESBO) was prepared by adopting already reported procedure^[5]. Phenoxy soybean polyol was prepared from the ESBO. Phenol(100g, 1.06 mol), isopropyl alcohol(100ml) and catalytic amount of fluoroboric acid were mixed in a 500 ml RB flask equipped with a thermometer, a dropping funnel and a magnetic stirrer. ESBO(50g, 0.052 mol) was added dropwise to the mixture over a period of 30 min. This mixture was heated to 60°C and maintained at this temperature for a period of 5 h. The reaction was then quenched by adding NH₃ solution and excess phenol was removed by washing with 5% NaOH

solution. The product was extracted with chloroform and dried with sodium sulphate. IR(KBr) vcm⁻¹: 3413(O-H), 2853(CH₂), 1144(O-C-C), 723(CH₂), 1241(C-O-C), 1465(C=C); ¹H NMR(TMS) δppm: 7.2(m, 25 H, phenyl), 5.3(quintet, 1H, CH), 4.15-4.25(d, 4H, CH₂), 2.35-2.45(t, 6H, CH₂), 1.15-1.48(54H, CH₂).

Synthesis of soybean epoxy resin with phenoxy and glycidyl ether

Phenoxy soybean polyol(50g, (0.037 mol) was mixed with of epichlorohydrin (100g, 1.09mol) in a 500ml RB flask equipped with a thermometer, a dropping funnel and a magnetic stirrer, 40ml of 30% aqueous NaOH(12g in 40 ml)was added dropwise to the mixture. After the completion of addition, the mixture was stirred for 16h at 70°C. The excess epichlorohydrin was removed using rotary evaporator. To the reaction mixture methyl ethyl ketone and water were added, shaken well when two layers were obtained. The organic layer was separated and washed several times with water. The solvents were removed by vacuum distillation and a liquid resin was obtained. IR(KBr) vcm⁻¹: 1240 (assym,C-O-Ph), 1074(sym, C-O-Ph), 1169 (C-O-C), 853(oxirane ring), 1739(C=O), 723 (CH₂), 1241(C-O-C), 1465(C=C); ¹H NMR (TMS) δppm: 7.2(m, 25H, phenyl), 5.3 (quintet, 1H, CH), 4.15-4.25(d, 4H, CH₂), 2.35-2.45(t, 6H, CH₂), 0.9(t, 9H, CH₃),1.15-1.48 (54H, CH₂)

Preparation of glass fiber reinforced composite laminates

The laminated composites were fabricated from E glass fibre (woven fabric-plain weave-biaxial) having a density of 200 gsm and epoxy resin/SEPG by hand layup technique .The liquid epoxy resin was taken in a beaker, heated to 85°C, to lower its viscosity and the desired amount of SEPG was added to the resin. The SEPG was varied between 0,5,10,15 and 20% by

TABLE 1 : Blend formulation

Commercial epoxy resin (g)	SEPG (g)	m-phenylene diamine (g)
100	-	15
95	5	15
90	10	15
85	15	15
80	20	15

weight of commercial epoxy resin as given in the TABLE 1. The mixture was degassed in vacuum, MPDA was then added (15% by weight of epoxy resin) and stirred for 5 min at 85°C.

Measurements

Iodine value of soybean oil was found by wj's method, hydroxyl value of phenoxy soybean polyol was measured by acetylation method. Epoxy content of SEPG was measured by pyridinium chloride method^[6].

The FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrometer model RX 1. ¹H NMR spectra was obtained on a AMX-400 NMR spectrometer at 400MHz. Molecular weight data were obtained from PL-GPC 50 using THF solvent. Complex viscosity data of the ESBO and SEPG were obtained from AR 2000 controlled stress rheometer. Thermogravimetric data were obtained on a (TA instruments, SDT Q 600 model) in flowing nitrogen at a heating rate of 20°C/min. The cure characteristics of neat resin and blends were studied using DSC (TA instruments, Q10 model, USA) in the temperature range between 50 and 250°C at a heating rate of 10°C per minute in air. The glass transition temperatures of the composite laminates were evaluated by DMA, NETZSCH DMA 242. The tensile and flexural properties were evaluated as per ASTM D 3039 and ASTM D 790 respectively by using Hounsfield(UK) H50KS screw-driven universal testing machine(UTM). The Izod impact strength was measured according to ASTM D 256-00. The double cantilever beam(DCB) test method was used for determining the G_{IC} fracture toughness, according to the ASTM D 5528 using universal testing machine.

RESULTS AND DISCUSSION

The new type of phenoxy soy polyol was synthesized from epoxidised soybean oil (ESBO) and it was further treated with epichlorohydrin to produce a novel soybean epoxy resin with phenoxy and glycidyl ether. ESBO was prepared from soybean oil by already reported procedure^[5]. Iodine value of the soybean oil is 118 as measured by titration method. Hydroxyl value of the phenoxy soybean polyol is 199mg KOH/g as found by acetylation method. Epoxide equivalent weight of soybean epoxy resin with phenoxy and glycidyl ether

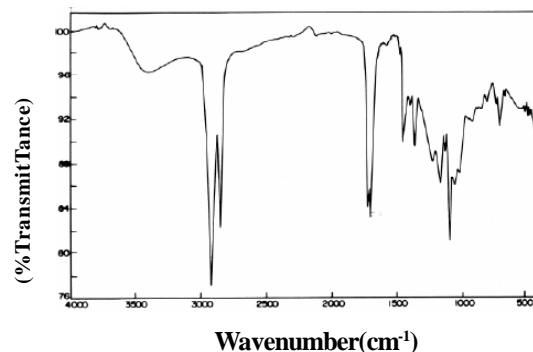


Figure 1 : FT-IR spectrum phenoxy soybean polyol

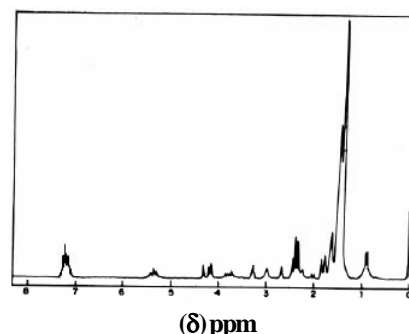


Figure 2 : ¹H-NMR spectrum of phenoxy soybean polyol

is 310. Molecular weight of the synthesized polyol and SEPG is 1350 and 1500 respectively.

Spectral properties

The structure of the prepared phenoxy soybean polyol and soybean epoxy resin with phenoxy and glycidyl ether was confirmed by FT-IR and NMR techniques. The FT-IR spectrum (Figure 1) of phenoxy soybean polyol shows a band at 3413cm⁻¹ due to OH stretching vibration. The absence of band at 1652cm⁻¹ confirms the formation of phenoxy soybean polyol. The band at 2853cm⁻¹ is due to the presence of aliphatic CH₂ group. The disappearance of band at 853cm⁻¹ indicates the absence of oxirane ring. The band at 1144cm⁻¹ shows the -O-C-C stretching of the ester group. The band at 723cm⁻¹ indicates the rocking vibration of CH₂ group. The band at 1241cm⁻¹ indicates the asymmetric stretching of phenyl alkyl ether(C-O-C). The band at 1465cm⁻¹ indicates the aromatic carbon carbon double bond stretching.

Figure 2 shows the ¹H NMR spectrum of phenoxy soybean polyol. The aromatic ring protons in the phenoxy resin appear at 7.2ppm, the methine protons in the glyceryl part of the molecule appear at 5.3ppm, the

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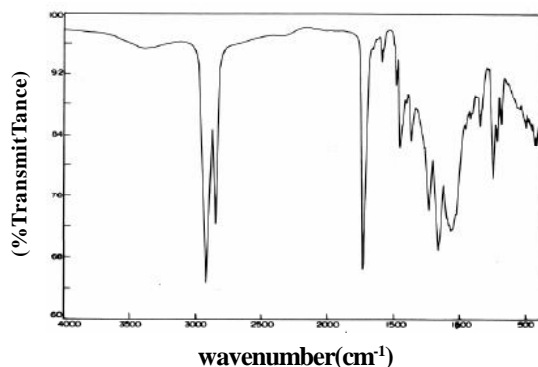


Figure 3 : FT-IR spectrum of soybean epoxy resin with phenoxy and glycidyl ether

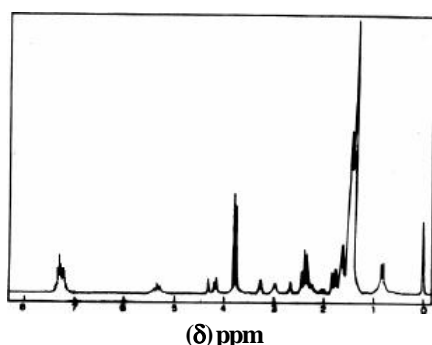


Figure 4 : ¹H-NMR spectrum of soybean epoxy resin with phenoxy and glycidyl ether

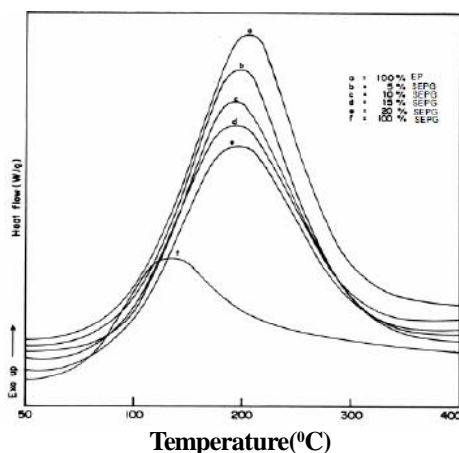


Figure 5 : DSC cure curve of epoxy and SEPG blends

TABEL 2 : DSC cure characteristics of neat epoxy and SEPG modified epoxy systems

Composition	T _i °C	T _p °C	T _f °C
100% EP	105	153	224
5% SEPG+95%EP	101	149	224
10%SEPG+90%EP	99	149	224
15%SEPG+85%EP	97	147	223
20%SEPG+80%EP	96	146	223
100% SEPG	85	120	190

methylene protons in the glyceryl part of the molecule and the hydroxyl protons merge and appear at 4.15 - 4.25ppm, CH₂ protons adjacent to carbonyl group were found at 2.35 - 2.45ppm^[7].

Figure 3 shows the FT-IR spectrum of SEPG. Asymmetric stretching of aryl alkyl ether appears at 1240cm⁻¹. Symmetric aryl alkyl ether stretching appears at 1074cm⁻¹. Symmetric aliphatic ether stretching appears at 1169cm⁻¹. The band at 853cm⁻¹ indicates the presence of oxirane ring. The band at 1739cm⁻¹ is due to the carbonyl stretching vibration of ester.

Figure 4 shows the ¹H NMR spectrum of soybean epoxy resin with phenoxy and glycidyl ether. The aromatic ring protons in the phenoxy resin appear at 7.2ppm, the methine protons in the glyceryl part of the molecule appear at 5.3ppm, the methylene protons in the glyceryl part of the molecule appear at 4.15-4.25ppm, the methylene protons adjacent to carbonyl group were found at 2.35-2.45ppm. The methylene protons adjacent to the oxirane ring appear at 2.95-3.05ppm, methylene protons alpha to carbonyl group appear at 1.65ppm, OCH and OCH₂ protons appear in the region of 3.65-3.73ppm, saturated methylenic protons appear at 1.15-1.48ppm and terminal CH₃ protons appear at 0.9ppm

Rheology studies

Complex viscosity of ESBO/MPDA and SEPG/MPDA with respect to time was studied using AR 2000 controlled stress rheometer in isothermal condition at a strain rate of 20% , frequency 1 Hz and temperature 120°C .For ESBO the complex viscosity 0.56 Pa.s remained constant upto 267s. After 900 seconds the complex viscosity was 1.423 Pa.s. But in the case of SEPG, the initial complex viscosity decreased from 400 Pa.s, to 194 Pa.s (50 s), then it increased at a faster rate. After 900 seconds the complex viscosity was 5200 Pa.s. It indicates that SEPG is more reactive than ESBO.

Thermal properties

The curing reaction of epoxy/ SEPG / MPDA was studied using differential scanning calorimetry (DSC). The data obtained from DSC scans are furnished in TABLE 2. The DSC thermograms of the blends are shown in figure 5.

All the epoxy/SEPG/MPDA blend systems show a

TABLE 3 : TGA data of epoxy and SEPG modified epoxy systems

Composition	T ₁₀ value °C	Char yield (%)
100 % EP	350	20.36
5% SEPG+95%EP	350	17.95
10% SEPG+90%EP	349	16.86
15% SEPG+85%EP	348	14.85
20% SEPG+80%EP	347	13.58
100% SEPG	318	1.12

TABLE 4: Glass transition temperatures of neat epoxy and SEPG modified epoxy-glass fibre composites

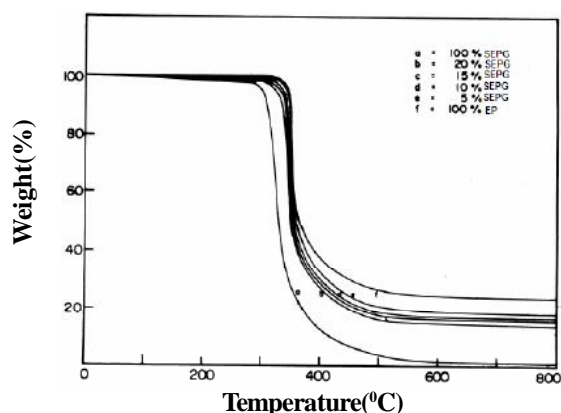
Composition	Tan δ
100 %EP	161
5% SEPG + 95%EP	165
10% SEPG + 90%EP	167
15% SEPG + 85%EP	164
20% SEPG + 80%EP	158

TABLE 5 : Mechanical properties of neat epoxy and SEPG modified epoxy - glass fibre composites

Composition	Tensile strength, MPa	Tensile modulus, GPa	Flexural strength, MPa	Flexural modulus, GPa
100%EP	299	3.4	379	7.8
5%SEPG+95%EP	302	3.4	382	7.9
10%SEPG+90%EP	310	3.5	395	8.0
15%SEPG+85%EP	304	3.4	386	7.9
20%SEPG + 80%EP	280	3.1	365	7.3

TABLE 6 : Impact strength and G_{IC} of epoxy and SEPG modified epoxy glass fibre composites

Composition (%)	Impact strength(J/cm)	G _{IC} (KJ m ⁻²)
100 %EP	34.2	0.6953
5% SEPG+95%EP	34.0	0.7051
10 % SEPG+90%EP	33.9	0.7150
15% SEPG+85%EP	34.8	0.7585
20% SEPG+80%EP	36.1	0.8423

**Figure 6 : TGA curves of neat epoxy and SEPG modified epoxy blends**

single exothermic peak. From the figure, it is also observed that increase in percentage of SEPG decreases the curing temperature of the blends. The decrease in

curing temperature may be due to the fact that SEPG contains pendant epoxy groups which react faster than commercial epoxide system.

The thermal stability of the cured resins was studied by thermogravimetric analysis. The results are presented in TABLE 3.

The thermograms are shown in figure 6. The thermograms of the cured samples reveal that they all degrade in a single step and start their decomposition at around 325°C. The T₁₀ value of the blends is found to be around 350°C. Thermal stability of the epoxy resin decreases with increase in SEPG content. However, compared to other epoxy toughening agents like rubber and polyurethane^[8,9] SEPG imparts better char yield to the epoxy resin.

Dynamic mechanical analysis (DMA) is a powerful technique for measuring the glass transition temperature particularly for polymers with rigid backbones^[10]. The T_g is determined from the temperature of peak maximum of the loss modulus curve. The values are summarized in the TABLE 4. Tan δ is related to crosslink density^[11,12] impact resistance^[13] and toughness of the material. The temperature dependence of the loss factor tan δ for the epoxy/MPDA/SEPG composite varies based on composition. On increasing the percentage of SEPG in the commercial epoxy resin, the T_g value increases up to 10% SEPG, then with further increase in SEPG, it decreases, because up to 10% SEPG the curing reaction is faster and therefore the crosslinking density and T_g are increased. In the case of blends with 15% and 20% SEPG the aliphatic content increases, so the segmental motion increases and hence the T_g value decreases^[14].

Mechanical properties

The tensile strength of the blends increases as SEPG content increases up to 10%. SEPG contains many pendant epoxy groups and its epoxide equivalent is higher than that of the commercial resin. Also these epoxy groups react faster than the commercial resin. Subsequently the crosslinking densities of the blends are higher and hence have higher modulus value. But with 15 and 20% SEPG content the aliphatic chain character is more influencing than crosslinking density thereby decreasing the tensile properties. Tensile modulus was measured from the tensile stress strain curve. The modulus values

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follow the same trend as that of tensile strength. In the case of blend with 20% SEPG, strain value is higher compared to those of 0,5,10%, and 15%^[15]. The flexural strength and modulus values follow the same trend as that of the tensile strength and modulus. The results are given in the TABLE 6.

The unnotched impact specimens were tested in Izod impact testing machine and the results are listed in TABLE 6. The blend with 20% SEPG has a higher impact strength than the neat epoxy system. This increase is due to the incorporation of SEPG containing ether, ester linkages and long aliphatic chains originally from the soybean oil which contributes to the toughness of the composite. But up to 10% SEPG impact values are slightly lower than that of the commercial epoxy resin due to the increased reactivity of the SEPG thereby increasing the crosslinking density of the blend in comparison that of the commercial resin. As the SEPG content in the blend increases the interlaminar fracture toughness value also increases as expected.

CONCLUSIONS

A new multifunctional epoxy resin SEPG containing aliphatic moiety with phenoxy and glycidyl ether groups was synthesized and characterized by FT-IR, NMR method. The prepared SEPG was blended with commercial epoxy resin at 5,10,15 and 20% loading levels. Curing reaction of epoxy/SEPG/MPDA was studied using DSC (all the epoxy/SEPG/MPDA cured systems show a single exothermic peak in the temperature range of $150\pm 3^{\circ}\text{C}$) and rheometer. With increase in SEPG percentage in the blend the mechanical properties like tensile strength, tensile modulus, flexural strength and flexural modulus increase up to 10%. Impact strength remains unaffected up to 10%.SEPG. Incorporation of 20% SEPG increases the impact strength significantly. Thermal stability of the resin decreases with increase in SEPG percentage. Glass transition temperature measured by DMA, is found to be higher for the blend with 10% SEPG. As the SEPG content increases interlaminar fracture toughness value increases. From the results, it can be concluded that SEPG modified epoxy composites may have the potential to provide almost similar performance in engineering and household applications as that of commercial epoxy resin at

concentrations up to 20%.

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