Glass-Reinforced Interacting Blends of Epoxy / Polyurethane Based on Castor Oil: Synthesis and Characterization. II

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Synopsis

Mechanical and dielectric properties of rubber mixtures of epoxy/polyurethane based on castor oil loaded with glass fiber is of great interest from a technological point of view. Epoxy resin was prepared from bisphenol A and epichlorohydrin in alkaline medium. Polyurethane was prepared from the hydroxyl group of castor oil reacted with 2,4-toluene diisocyanate. Elemental analysis and infrared (IR) spectra are presented as evidence for the formation of these materials. A homogeneous solution of epoxy resin and polyurethane was prepared in acetone containing a curing agent 1,3-propane diamine. The glass-reinforced laminates were prepared by interacting polymer blends on the glass fiber through compression moulding. Chemical resistance to solvents, flexural strength, izod impact strength, and Rockwell hardness studies on a series of specimens were investigated. It was observed that they behave as tough materials. An attempt was made to study the effect of electrical conductivity by changing the compositions of rubber mixtures during reinforcement with glass fibers. The dielectric constant (E') dielectric loss (E''), and loss tangent ($\tan \delta$) of the specimens and their dependence of temperature was studied.

INTRODUCTION

The incorporation of elastomers into epoxy resins has been an active area of research for the past few decades.[1-5] The primary reason for this interest has been the improved toughness of modified materials. Recently, novel IPNs incorporating epoxy resin and polyurethanes,[6-8] have been extensively studied. In our previous work, we reported the IPNs of polyesters derived from castor oil and polyacrylamide.[9] With a view to investigating the properties of modified materials, we have used epoxy resin derived from bisphenol A in the present investigation. The liquid resin was interacted with polyurethane obtained from castor oil in presence of glass fibers. Thus obtained glass-reinforced epoxy/polyurethane laminate was characterized in terms of important mechanical, electrical, and thermal properties.

EXPERIMENTAL

Chemicals

All the chemicals employed in this present study were of analytical-grade purity. Bisphenol A was obtained commercially and recrystallized twice prior to use. 1,3-Propanediamine was purchased from Schuchardt, Munich,

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Germany. 2,4-Toluene diisocyanate was purchased from Fluka AG, Basel, Switzerland.

Synthesis of Epoxy Resin

A mixture of bisphenol A (456 g, 2 moles), epichlorohydrin (740 g, 8 moles), and water (10 mL) was placed in a 2-L three-necked flask equipped with a stirrer, thermometer, and condenser. Sodium hydroxide (12 g) was added to the mixture in the first installment and heated on water bath with stirring. The temperature was maintained at 100°C. When the temperature was lowered, sodium hydroxide (12 g) was added and the temperature was controlled to 100°C. Thus, a total of 44 g of sodium hydroxide were added during the reaction time of 4 hours. The mixture was cooled, liquid product was separated from solid sodium chloride, and treated with benzene (100 mL). The liquid mixture was distilled in vacuum (10 mmHg) to remove excess epichlorohydrin, benzene, and water. Thus obtained epoxy resin was a transparent and very thick liquid.

Epoxide gram equivalent of the resin was established to be 0.047/g of resin by the pyridinium hydrochloride method.[10] The molecular weight was computed on the basis of epoxide group analysis and was found to be 914. The resin contained C%, 76.18 and H%, 6.92 and these values are comparable with those calculated on the basis of the structure of repeat unit ($C_{18}H_{20}O_3$) of the resin molecule.

The IR spectrum of epoxy resin showed typical epoxy absorption bands at 830 and 1250 cm^{-1}. The other characteristic vibrational bands as shown in Figure 1 are indicative of the structure of epoxy resin. Thus, the possible

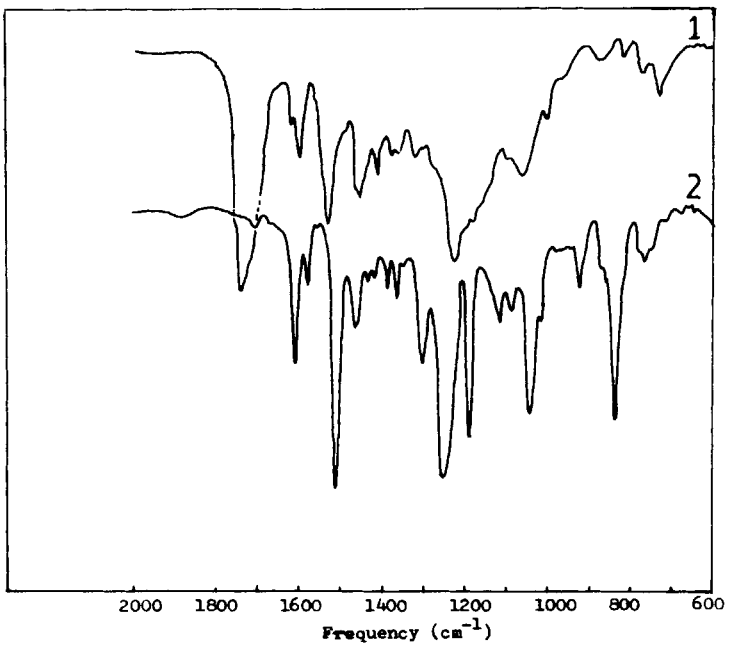
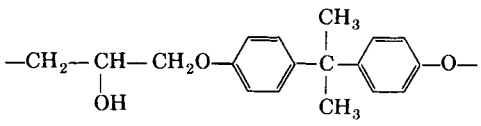


Fig. 1. IR Spectra of (1) PUR from castor oil; (2) Epoxy resin from bisphenol A.

structure of epoxy resin was



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Synthesis of Polyurethane from Castor Oil

Castor oil (150 g, 0.15 moles) was reacted with 2,4-toluene diisocynate (59.25 g, 0.34 moles) in order to maintain NCO/OH ratio 2. This will result in isocyanate-ended polyurethane. The reaction was carried out at 45°C under continuous stirring for one hour. The polymer was isolated in the form of thick syrup. IR spectrum indicated characteristic frequency of ester linkage around $\nu_{C=O}$1746 cm^{-1} and amide linkage at $\nu_{C=O}$1655 cm^{-1}. The typical IR spectrum is shown in Figure 1.

Lamination Process

The laminate of epoxy/polyurethane was made according to ASTM procedure (D-20) by compression moulding. A 50% solution of resin blend (epoxy/PUR of various composition) in acetone (250 mL) and 1,3-propane diamine (5 g) were mixed for homogeneous solution. Seven layers (12 in. × 12 in.) of epoxy-compatible *E* glass cloth (10 mil thick, plain Weave) were impregnated with the above solution and the prepregs were stacked on a flat mould and clamped to maintain a pressure of 75–80 psi. The mould was kept in a preheated air-circulating oven maintained at 100°C. The laminate was cured at 100°C for 20 minutes and postcured for 17 hours at 120°C to ensure complete curing. The mould was cooled slowly and the laminate was removed.

Following the above procedure, other laminates of varying composition of epoxy/PUR contents mentioned in Table I were prepared.

TABLE I
Experimental Details of Synthesis of Laminates

Sample code	Epoxy resin (g)	Polyurethane (g)	Epoxy/PUR[a] content in the laminate (%)
Laminate-1	112.	12.5	90/10
Laminate-2	100	25	80/20
Laminate-3	94	31	75/25
Laminate-4	87.50	37.50	70/30

[a]Epoxy/PUR content below 70/30 was not possible in lamination due to experimental difficulties, i.e., Epoxy/PUR is not compatible with the glass fiber.

TABLE II
Chemical Resistance Study of the Laminates as per ASTM Technique

Solvent	Laminate-1			Laminate-2			Laminate-3			Laminate-4		
	Physical appearance	% Change in weight	% Change in thickness	Physical appearance	% Change in weight	% Change in thickness	Physical appearance	% Change in weight	% Change in thick-ness	Physical appearance	% Change in weight	% Change in thick-ness
1 25% H_2SO_4	No effect No change in color No change in gloss	0.964	0.662	No effect	0.851	0.657	No effect	0.773	0.662	No effect	0.642	0.662
2 15% HCl	Color of the specimen becomes light	0.720	1.33	Color of the specimen becomes light	0.957	1.33	Color of the specimen becomes light	1.686	0.657	Color of the specimen becomes light	2.228	0.662
3 5% HNO_3	No effect	1.073	1.33	No effect	1.426	1.32	No effect	1.381	0.662	No effect	1.719	0.657
4 5% NaOH	Color of specimen becomes white	1.039	0.657	Color of the specimen becomes white	0.517	1.307	No effect	0.499	0.662	Color of the specimen becomes white	0.384	0.657
5 10% NH_4OH	Color of the specimen becomes white, patches appear on the surface	3.178	3.70	Color of the specimen becomes white No appearance of patches on the surface	4.011	4.268	Color of the specimen becomes white	5.796	4.458	Color of the specimen becomes white patches appear on the surface	5.716	5.298

6	25% CH_3COOH	No effect	6.147	5.16	No effect	8.484	7.00	No effect	10.14	3.92	No effect	8.989	4.605
7	5% H_2O_2	No effect	0.854	1.33	No effect	2.057	1.986	No effect	2.85	1.315	No effect	2.781	1.315
8	Methylethyl ketone	Color of the specimen becomes light Surface gloss disappears Delamination	2.468		Color of the specimen becomes light Surface gloss disappears Delamination	1.989		Surface gloss disappears Delamination	2.448		Surface gloss disappears Delamination	2.57	4.575
9	Distilled water	No effect	0.930	1.92	Color of the specimen becomes white	1.761	1.898	Color of the specimen becomes white	2.007	2.547	Color of the specimen becomes white	2.297	2.564
10	Carbon tetrachloride	Color of the specimen becomes light	0.051	5.00	Color of the specimen becomes light	6.185	5.55	Color of the specimen becomes light	7.301	5.55	Color of the specimen becomes light	7.76	5.095
11	40: NaCl	No effect	0.231	0.662	No effect	1.737	1.307	No effect	1.886	0.649	No effect	2.054	0.653
12	Toluene	No effect	2.092	4.00	Specimen becomes transparent surface gloss disappears	3.626	4.635	No effect	4.910	3.31	No effect	4.625	2.597

RESULTS AND DISCUSSION

Characterization of Laminates

Solvent resistance of epoxy/PUR laminates to the series of standard reagents has been studied quantitatively according to ASTM D-543-67 (1978) procedure. The pieces of laminate (20 mm × 20 mm × 1.5 mm) were put in 100 mL standard reagents for 7 days. After exposure to chemical reagent, each of the laminate pieces was examined on the basis of physical appearance such as discoloration, loss of gloss, decrease in weight, and change in thickness. The details of the results were reported in Table II. It is observed these laminates are pretty stable in all the standard reagents. However, in certain solvents, for example 25% CH_3COOH, the loss in weight was found to be 6–10% of the weight of the laminates.

Mechanical Properties

The laminates reported in Table I were compression molded as 12 × 12 in. × 1.5 mm sheets at a temperature of 120°C. There were then cut into required size to give test specimens for property measurements. ASTM procedures were used for measuring flexural strength, flexural modulus (D 790), izod impact unnotched (D 256), and Rockwell hardness (D 785).

Some of the significant mechanical properties of these laminates are listed in Table III. Data of commercial glass-reinforced pure epoxy resin laminate[11] under same condition are included for comparison. Properties such as flexural strength, flexural modulus, izod impact strength, and hardness have been observed to be modified to those of the commercial epoxy laminates. Flexural strength and modulus are lower than the pure epoxy laminate. This is quite obvious from the architecture of the interacting polymer blends of epoxy with castor oil-based polyurethane-containing laminates. It is, in fact, that incorporation of castor oil PUR increased the elastomeric properties of the laminates. This is also reflected in the impact strength and hardness properties which are found to be higher than the commercial epoxy laminate. We intended to take scanning electron microscopy of these laminates. But it is worthwhile to mention that it was difficult for cryogenic fracture, and hence it was not possible to study the morphology of these laminates.

TABLE III
Mechanical Properties of Laminates

Sample code	Density g/mL	Flexural strength MN/m^2	Flexural modulus MN/m^2	Izod impact unnotched J/m	Hardness (Rockwell) R
Laminate-1	1.8108	222.3	1.615×10^4	871.04	101.0
Laminate-2	1.7824	228.9	1.440×10^4	1064.10	91.8
Laminate-3	1.7598	153.9	1.296×10^4	1162.43	89.3
Laminate-4	1.6528	182.6	1.44×10^4	1267.96	88.3
Pure epoxy resin laminate[a]		629.6	2.59×10^4	—	—

[a]Values of pure epoxy resin laminates were taken from *Encyclopaedia of Polymer Science & Technology*, **6**, 257, 1967.

Dielectrical Properties

Since we have claimed that these laminates are tougher, we wanted to examine their dielectric behavior. Specific electrical conductivities are reported in Table IV. The dielectric properties (E', E'' and $\tan\delta$) at two frequencies (10 KHz, 1 KHz) are shown in Figures 2, 3 and 4. Specific

TABLE IV
Thermal and Electrical Conductivities of the Laminates

Sample code	Electrical conductivity (δ_0) at 300°K (ohm^{-1} cm^{-1})	Activation energy for electrical conductivity (eV)
Laminate-1	6.16×10^{-13}	1.44
Laminate-2	3.38×10^{-12}	0.972
Laminate-3	3.38×10^{-12}	0.87
Laminate-4	7.94×10^{-12}	0.79

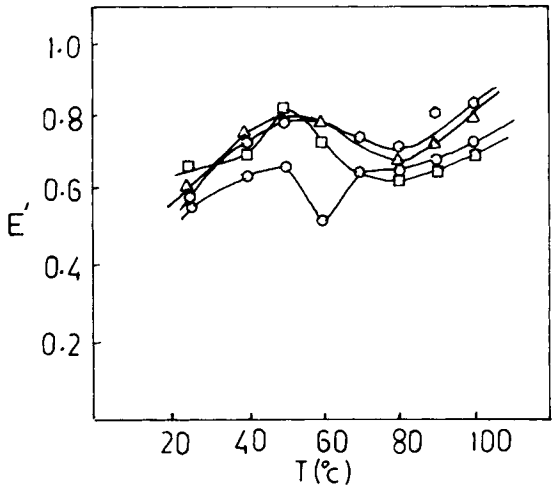

Fig. 2. Dielectric constant (ϵ') vs. temperature for different laminates: (○) Laminate-1; (△) Laminate-2; (○) Laminate-3; (□) Laminate-4.

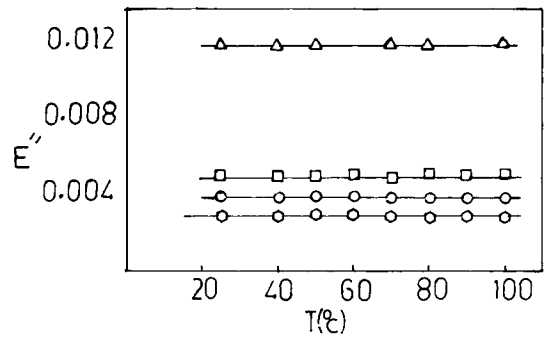

Fig. 3. Dielectric loss (ϵ'') vs. temperature for different laminates: (○) Laminate-1; (△) Laminate-2; (○) Laminate-3; (□) Laminate-4.

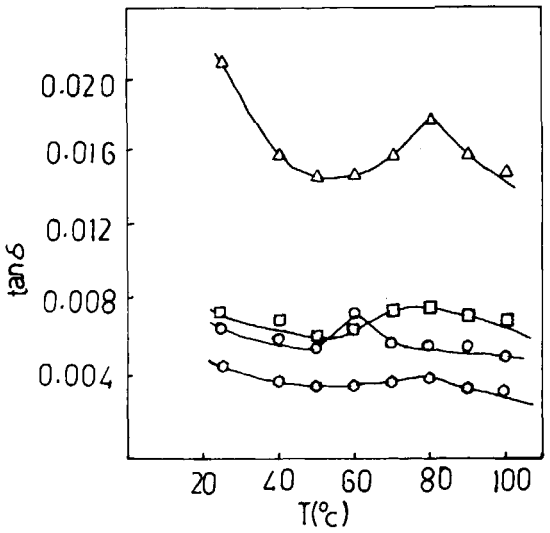

Fig. 4. Loss tangent (tan δ) vs. temperature for different laminates: (○) Laminate-1; (△) Laminate-2; (○) Laminate-3; (□) Laminate-4.

conductivity of these laminates places them in the category of electrical insulators.

Thermogravimetry (TG)

TG thermograms of these laminates indicate a characteristic behavior of thermal degradation. The weight loss in all the laminates is almost uniform and does not show any trend of thermal stability among the series. However, thermal behavior reveals that laminates are stable up to 300°C and lose weight 5, 8, 9, and 10% beyond the temperatures 400, 500, 600, and 700, respectively.

CONCLUSION

Glass reinforcement has been achieved by interacting blends of epoxy resin and polyurethane-based castor oil. Thus laminates were prepared and characterized. These laminates have improved physical properties and electrical properties which are consistent with the present-day research on the glass-reinforced polymer blends.

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