Effect of Diluents and/or Fortifier on the Glass Fiber–Epoxy Composites

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Synopsis

The glass fiber–epoxy composites were fabricated with the E-type glass cloth and diglycidyl ether of bisphenol A (DGEBA) using 12% diethylenetriamine (DETA) as catalyst on the basis of DGEBA. The properties were modified by incorporating diluents such as epoxidized 2,2,6,6-tetra-methylolcyclohexanol (ETMC) and 1,4-butandioldiglycidyl ether (BDDE) with/without 20 parts per 100 g of a condensation product of phenyglycidylether and 4-hydroxyacetanilide (PGEHA) employed as fortifier. The characterization of these epoxy laminates includes resistance to chemical reagents, dynamic mechanical analysis, and mechanical properties like flexural strength, impact strength, and hardness. The dielectrical properties such as breakdown strength, dielectric constant (ϵ'), dielectric loss (ϵ''), and loss tangent ($\tan \delta$) were estimated.

INTRODUCTION

The resin matrix material for fiber-reinforced composites plays an important role in determining the mechanical and chemical properties of composite itself.[1] Varma and Raj[2] have fabricated the glass fiber–epoxy composites with aromatic diamines containing imide groups as hardeners, having good processibility with the resin and with improved mechanical properties. The mechanical and chemical properties were modified by increasing functionality and absolute viscosity control brought about through the use of a diluent[3] and fortifier.[4] The present work deals with the synthesis and characterization of BDDE and tetrafunctional ETMC diluent, which were incorporated with DGEBA to modify certain properties using 12% diethylenetriamine (DETA) as curing agent, and its effect on the laminated properties was studied along with the effect of 20 parts per 100 g (phr) of PGEHA fortifier. The laminated samples were characterized in terms of resistance to chemical reagents and in terms of mechanical properties, namely, flexural strength, impact strength (izod), hardness (Rockwell), and dynamic mechanical analysis (DMA). The dielectric properties such as breakdown strength, dielectric constant (ϵ'), dielectric loss (ϵ''), and loss tangent ($\tan \delta$) were also estimated.

EXPERIMENTAL

Materials. The bisphenol type liquid epoxy resin DGEBA was prepared by a method based on the one described by Sorenson and Campbell.[5]

Synthesis of Diluent. 2,2,6,6-Tetramethylolcyclohexanol was prepared by hydroxmethylation with simultaneous cannizzaro reaction proposed by Roach and Wittcoff.[6] Epoxidation of 2,2,6,6-tetramethylolcyclohexanol was carried

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out by the reaction with epichlorohydrin at 95–100°C with stirring. The general reaction scheme is shown below:
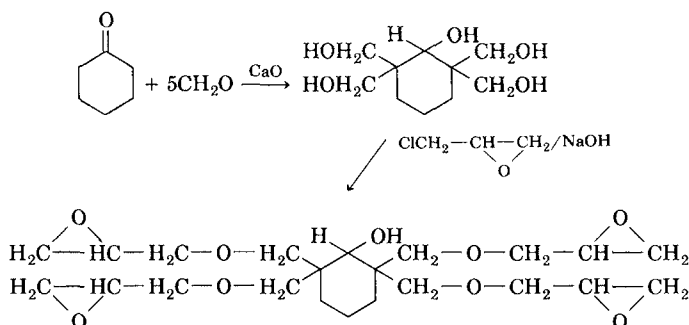
1,4-Butandiol diglycidyl ether (BDDE) was a laboratory grade (Aldrich Chemical Company, Inc.) Chemical.

Synthesis of Fortifier. The reagents required for the preparation of fortifier (i) phenylglycidyl ether (PGE) was prepared by the published method[7] and (ii) 4-hydroxy acetanilide (HA) was a pharmaceutical grade chemical which was recrystallized from distilled water. The fortifier (PGEHA) was prepared by condensing PGE and HA using 0.1 wt% diethylamine hydrochloride as catalyst and purified by recrystallization from acetone (mp 128°C).[8]

The reaction scheme is shown below:
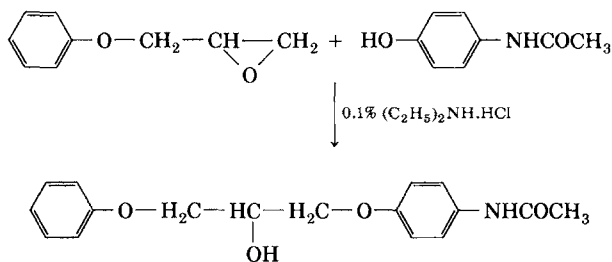
The viscosity of DGEBA, ETMC, and BDDE was 0.031, 0.035, and 0.025 dL g^{-1}, respectively, in chloroform at 30°C.

The epoxy equivalents of DGEBA, ETMC, BDDE, and PGEHA were determined as 190.0, 132.0, 134.0, and 0.0 g/eq, and the number average molecular weights, by vapor pressure osmometry, were 380, 444, 200, and 300, respectively.

Fabrication of Glass Laminates. A mixture of DGEBA (40%) on the basis of weight of glass cloth and diethylenetriamine (12% on the basis of DGEBA) was dissolved in solvent ether (100 mL) and was applied on 14 × 14 in. square pieces of the glass fabric on both sides with the help of a brush.

The cut pieces were soaked uniformly with the resin mixture and hung in air to evaporate the solvent. Fourteen such soaked pieces were stacked one above the other and pressed between the two steel plates previously heated to 100°C. The screws attached at definite places on the two steel places were tightened one by one to the extent of applying a pressure of ~ 100 psi. The whole system was left in an oven at 110°C for 1 h. The pressure was then

raised to ~ 500 psi and the temperature of the oven was raised up to 170°C for all the systems under investigation except the system in which ETMC was used as a diluent; the latter required a higher curing temperature, ~ 200°C. The system was left in the oven for 1 h and was then allowed to cool to room temperature and left for 12 h.

The laminate was removed, cut to a particular size, and shaped as per requirement of the ASTM standard tests for different properties.

Characterization

Resistance to chemical reagents was estimated according to ASTM D 543-67 (1978). Flexural strength was measured according to ASTM D 770 on Universal Instron testing machine (Model A 74-37) at room temperature. DMA measurements were made on DuPont 981 dynamic mechanical analyzer at the heating rate of 10°C/min in air. The impact strength test and hardness test were done according to ASTM D 256 and ASTM D 785, respectively.

In order to study the dielectrical properties of laminated samples, the resistance was measured by a Hewlett packard 4329-A high resistance meter. In this arrangement, a voltage of 500 V was applied through the end of sample, and the corresponding resistance was read directly. Properties such as dielectric loss (ϵ''), dielectric constant (ϵ'), dissipation factor (D), and power factor were also measured on 1615-A capacitance bridge at a frequency of 1 KHz at a temperature of 35°C. The temperature at which the highest tan δ was observed has also been measured. The relations employed for the calculations are as follows:

$$\text{dielectric constant} = \frac{C \cdot l}{\epsilon_0 \cdot A}$$

where C = capacitance, l = thickness (mm), $\epsilon_0 = 0.08851 \times 10^{-12}$ f/cm, and A = area of the sample,

$$\text{dielectric loss} = \tan \delta \times \epsilon'$$

$$\text{power factor} = \sin \delta$$

RESULTS AND DISCUSSION

The composites were fabricated with E-type glass cloth and DGEBA as resin matrix with/without 20 PHR PGEHA fortifier and/or diluent following the details fabricated in Table I using 12% diethylenetriamine as catalyst on the basis of DGEBA resin.

Mechanical properties such as flexural strength, impact strength and hardness of the laminated systems are furnished in Tables II–IV.

Flexural Strength. Examination of the data listed in Tables II–IV indicates that the polymerization of composite material is related to the nature of diluent and/or fortifier incorporated with resin system. Table II reveals that incorporation of ETMC diluent shows a slight loss in flexural strength, even though it is a tetrafunctional diluent, which normally may lead to higher crosslinking. The loss in flexural strength may be due to the steric hindrance

TABLE I
Proportion of Glass Cloth to DGEBA Resin and DGEBA Resin to Diluent and/or Fortifier
Used for Fabrication of the Laminates

System	Glass Cloth: DGEBA resin (% wt/wt)	DGEBA resin: Diluent– Fortifier (% wt/wt)
A (DGEBA)	(60 : 40)	(80 : 20)
B (DGEBA–ETMC)	(60 : 40)	(80 : 20)
C (DGEBA–BDDE)	(60 : 40)	(80 : 20)
D (DGEBA–PGEHA)	(60 : 40)	(100 : 20)
E (DGEBA–ETMC)–PGEHA	(60 : 40)	(80 : 20)–20
F (DGEBA–BDDE)–PGEHA	(60 : 40)	(80 : 20)–20

exerted by the four bulky groups at 2,6- position of ETMC diluent and which may permit comparatively a less compact structure. The system E (DGEBA–BDDE) shows an appreciable increase in flexural strength over that of the system A (DGEBA): This may be attributed to the linear alkyl four methylene groups responsible for improved flexibility present in BDDE diluent.

Alkali Resistance of the Laminates. The laminated systems (A–F) when treated with 25% NaOH solution showed the reduction in the flexural strength (Tables II–IV). Looking at the structure of the composite, it is a three-phase one which contains glass fibers, resins as matrix, and pores. The resin in the composite protects the fibers and, especially, forms a bond between them. Notable factors with the fiber and resin are the critical fiber length and effective bond. When 25% NaOH solution treatment was given, a corrosive effect on the glass-reinforced matrix has been observed that might have resulted in the destruction of the crosslinked structure that formed in the

TABLE II
Properties of Laminates Prepared from A (DGEBA) and D (DGEBA/PGEHA)
with 12% Diethylene Triamine Catalyst

Property (ASTM)	Value A	Glass base D
1 Color of resin	Yellow	Yellow
2 Water absorption (%)	4.20	3.88
3 Thickness (mm)	2.8–2.9	2.8–2.9
4 Resin content (%)	34–35	34–35
5 Impact strength notch (kg cm)	9.60	10.0
6 Hardness (Rockwell)	112.0	117.0
7 Flexural strength (kg cm^{-2})	2.79×10^3	3.11×10^3
Flexural strength[a] (kg cm^{-2})	1.58×10^3	1.81×10^3
8 Electrical strength in oil at 90°C (kV/mm)	11.25	13.26
9 Temp at which maximum tan δ observed (°C)	150	140
10 Resistance (Ω) at 500 V	0.61×10^{11}	0.83×10^{11}

[a] Flexural strength after 7 days exposure to 25% alkali solution at 30°C.

TABLE III
Properties of Laminates Prepared from B (DGEBA/ETMC) and
E (DGEBA/ETMC/PGEHA) with 12% Diethylene Triamine Catalyst

Property (ASTM)	Value B	Glass base E
1 Color of resin	Yellow	Yellow
2 Water absorption (%)	6.08	4.23
3 Thickness (mm)	3.1–3.2	3.1–3.2
4 Resin content (%)	35–36	35–36
5 Impact strength notch (kg cm)	10.30	12.83
6 Hardness (Rockwell)	85.0	99.2
7 Flexural strength (kg cm^{-2})	2.73×10^3	3.08×10^3
Flexural strength[a] (kg cm^{-2})	1.92×10^3	2.91×10^3
8 Electrical strength in oil at 90°C (kV/mm)	3.33	8.86
9 Temp at which maximum tan δ observed (°C)	90	85
10 Resistance (Ω) at 500 V, Rh 55%, temp 30°C	1.31×10^{11}	1.60×10^{11}

[a] Flexural strength after 7 days exposure to 25% alkali solution at 30°C.

glass reinforced matrix. Debonding or deformation of the bonds takes place which may be accounted for the reduction in the flexural strength. Higher reduction in the flexural strength is observed for system C (Table IV) compared to system B (Table III) as two epoxy groups separated by four methylene groups provided more flexible space, which increases the alkali penetration. The alkali penetration in system B is lower due to the sterically hindered structure of ETMC.

TABLE IV
Properties of Laminates Prepared from C (DGEBA/BDDE) and
F (DGEBA/BDDE/PGEHA) with 12% Diethylenetriamine Catalyst

Property (ASTM)	Value C	Glass base F
1 Color of resin	Yellow	Yellow
2 Water absorption (%)	3.38	2.12
3 Thickness (mm)	2.9–3.0	2.9–3.0
4 Resin content (%)	35–36	35–36
5 Impact strength notch (kg cm)	6.80	13.20
6 Hardness (Rockwell)	121.0	128.0
7 Flexural strength (kg cm^{-2})	5.81×10^3	5.99×10^3
Flexural strength[a] (kg cm^{-2})	3.80×10^3	4.13×10^3
8 Electrical strength in oil at 90°C (kV/mm)	8.80	9.82
9 Temp at which maximum tan δ observed (°C)	120	115
10 Resistance (Ω) at 500 V, Rh 55%, temp 30°C	1.08×10^{11}	1.10×10^{11}

[a] Flexural strength after 7 days exposure to 25% alkali solution at 30°C.

TABLE V
Dielectrical Properties of Systems (A–F)[a]

System	Capacitance C	Dissipation factor D	$\tan \delta$ = D.f.	Dielectric constant ($\times 10^1$)	Dielectric loss f	Power factor
A (DGEBA)	172	0.130	0.130	31.09	4.04	0.1289
B (DGEBA–ETMC)	180	0.700	0.700	83.98	59.78	0.5734
C (DGEBA–BDDE)	170	0.140	0.140	47.22	6.72	0.1386
D (DGEBA)–PGEHA	173	0.133	0.133	32.10	4.49	0.1324
E (DGEBA–ETMC)–PGEHA	178	0.682	0.682	85.41	56.24	0.498
F (DGEBA–BDDE)–PGEHA	167	0.123	0.123	48.01	5.29	0.124

[a] Frequency 1 kHz; temp. 35°C.

Impact Strength and Hardness. The impact strength of the laminated samples prepared from DGEBA only (Table II) is lowered down by the incorporation of BDDE while it increased to some extent with incorporation of ETMC. The hardness of the laminated samples has been also increased with the incorporation of BDDE diluent and decreased in the presence of ETMC. Here also the structural features of the diluents plays an important role as described above.

Dielectrical Properties. Examination of the data (Table V) reveals that, among the resin–diluent system, the system B (DGEBA–ETMC) has higher dielectric constant than the system C (DGEBA–BDDE). The difference in this property of the two systems can be possibly attributed to the difference in the compactness of the structures of these two systems as described earlier.

Glass Transition Temperature Modification. The glass transition temperature (T_g) of a matrix in most cases can be correlated with heat deflection temperature (HDT), with the T_g being slightly lower than the HDT.[11] Several potential multifunctional diluents were investigated to increase T_g. Furthermore, these diluents can influence the network structure and ultimately the mechanical and physical properties.[11] Several low temperature studies of the dynamic mechanical properties of DGEBA cured with different types of amines have been reported in the literature.[12–15]

The results of the dynamic mechanical properties in the temperature range of 30–250°C are presented in Table VI. The Young's modulus (E) and $\tan \delta$ calculated[16] for all the systems (A–F) are plotted against temperature. The

TABLE VI
Comparative Data of Glass Transition Temperature (T_g) of the Different Systems
with/without 20 PHR PGEHA Fortifier

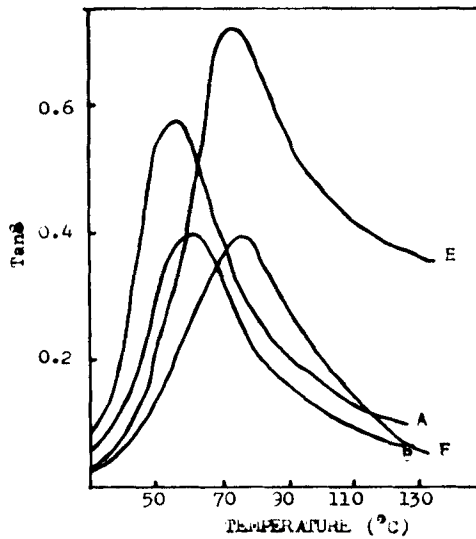| System	Glass transition temp (T_g) (°C)
A (DGEBA)	56
B (DGEBA–ETMC)	111
C (DGEBA–BDDE)	71
D (DGEBA)–PGEHA	61
E (DGEBA–ETMC)–PGEHA	119
F (DGEBA–BDDE)–PGEHA	76

Fig. 1. Plot of tan δ against temperature (°C) for systems A (DGEBA), B (DGEBA–PGEHA), E (DGEBA–BDDE), and F (DGEBA–BDDE)–PGEHA.

selected plots are shown in Figures 1 and 2 for observing glass transition temperature (T_g). The results listed in Table VI reveals that the T_g of laminated sample prepared from DGEBA only increases with incorporation of ETMC and BDDE. The highest increase in T_g among the systems (A–C) is observed for system B (DGEBA–ETMC). This is consistent with the fact that the DGEBA–ETMC system required a higher curing temperature (200°C). That the higher functionality leads to highly crosslinked network structure on curing is reflected in the comparatively higher T_g of both the resin–diluent
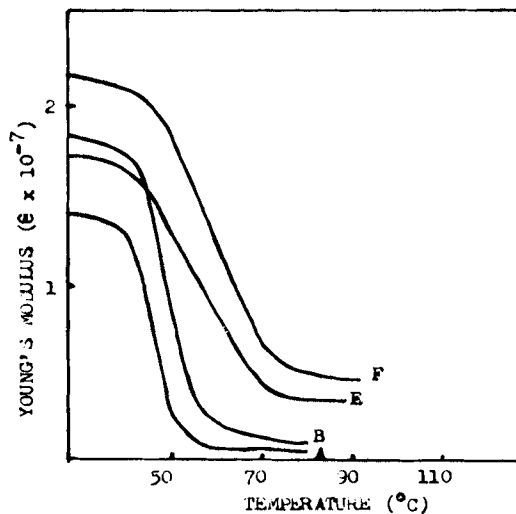

Fig. 2. Plot of Young's modulus (N/m²) against temperature (°C) for systems A (DGEBA), B (DGEBA–PGEHA), E (DGEBA–BDDE) and F (DGEBA–BDDE)–PGEHA.

TABLE VII
Effect of Chemical Resistance on the Laminated Samples Prepared from Different Systems
Using 12% Diethylenetriamine

System	% Weight gain, (after 7 days)			
	Water	25% NaOH	25% HCl	Acetone
A (DGEBA)	4.20	3.17	1.72	3.45
B (DGEBA–ETMC)	6.08	4.59	3.88	5.66
C (DGEBA–BDDE)	3.38	2.13	1.96	2.29
D (DGEBA–PGEHA)	3.88	2.61	1.18	2.90
E (DGEBA–ETMC)–PGEHA	4.23	3.26	2.26	3.98
F (DGEBA–BDDE)–PGEHA	2.12	1.86	1.11	1.44

systems. T_g also increased on incorporation of BDDE diluent (Table VI). Incorporation of PGEHA fortifier (20 phr) further increases the T_g of all the systems.

Chemical Resistancy. The pieces of each laminated sample (20 × 20 × 0.65 mm) were put in 100 mL standard reagents (water, 25% NaOH, 25% HCl, acetone) for 7 days. After exposure to chemical reagents, each sample piece was examined on the basis of physical properties like discoloration, loss of gloss, change in weight, and change in thickness. The related data are presented in Table VII. It is observed that the system B fabricated by incorporation of ETMC diluent shows higher absorbance of water, alkali, acid, and acetone than the other systems presented in Table VII. The large difference in the chemical resistance of the systems B and A is also attributed to the difference in the compactness of the structures of these two laminated systems.

Effect of PGEHA Fortifier. The PGEHA fortifier (20 phr) to all the resin diluent systems exerts the catalytic effect, improving the mechanical, electrical, and chemical properties of all the laminated samples (Tables II–VII).

These observations may be explained as follows: When low molecular weight fortifier is introduced to resin–diluent system which, by virtue of intermolecular interactions and a favorable geometry, reduces the free volume available for motion of the polymer. Reduced polymer mobility on a molecular scale translate into increased properties because the polymer network responds less easily to an applied force. Moreover, PGEHA fortifier contains the free hydroxyl group, which provides strong possibilities for the formation of a highly crosslinked network structure, which is reflected in increased properties of laminated samples.

CONCLUSIONS

The present study has revealed that:

i. Flexural strength of laminates increases on incorporation of BDDE as diluent and decreases slightly on incorporation of ETMC diluent.

ii. Incorporation of BDDE increased the impact strength and decreased the hardness of the laminates while that of ETMC brought about the reverse effect.

iii. Incorporation of both the diluents ETMC and BDDE increased the T_g.

iv. Incorporation of BDDE diluent increased the chemical resistance and that of ETMC decreased the chemical resistance of the laminates.

v. Incorporation of PGEHA fortifier to the resin–diluent system has increased the mechanical, chemical, and electrical properties. This observation seems to have an implication as to the role which this and such fortifiers can play when epoxy–amine systems are employed as resin matrix.

References

1. M. F. Cheung, D. L. Garreett, J. Parsons, and H. V. Oene, *Ind. Eng. Chem., Prod. Res. Dev.*, **25**(2), 296 (1986).

2. D. S. Varma and R. G. Raj, *Bull. Mater. Sci.*, **6**(1), 99 (1984); *Chem. Abstr.*, **101**, 172270h (1984).

3. C. A. May and Y. A. Tanaka, *Epoxy Resin Chemistry and Technology*, T. F. Mika, Ed., Dekker, New York, 1973.

4. P. D. McLean, R. F. Scott, and A. Garton, *Br. Polym. J.*, **15**, 66 (1983).

5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, 2nd ed., Wiley-Interscience, New York, 1966, p. 465.

6. J. R. Roach and H. Wittcoff, *Org. Synth.*, **31**, 101 (1951).

7. H. Lee and K. Neville, *Epoxy Resins*, McGraw-Hill, New York, 1957.

8. J. Daly, A. Britten, and A. Garton, *J. Appl. Polym. Sci.*, **29**, 1403 (1984).

9. J. R. Thakkar, R. G. Patel, and V. S. Patel, *Eur. Polym. J.*, **23**(10), 795 (1987).

10. R. D. Patel, R. G. Patel, and V. S. Patel, *Br. Polym. J.*, **19**, 37 (1987).

11. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974.

12. D. E. Kline, *J. Polym. Sci.*, **47**, 237 (1960).

13. R. P. Kreahling and D. E. Kline, *J. Appl. Polym. Sci.*, **13**, 2411 (1969).

14. R. K. Jenkis, *J. Appl. Polym. Sci.*, **11**, 171 (1967).

15. J. C. Patterson, J. C. Jones, and D. A. Smith, *J. Appl. Polym. Sci.*, **12**, 1601 (1968).

16. E. A. Turi, *Thermal Characterization of Polymeric Materials*, Academic, London, 1981.