Mechanical Properties of E-Glass Fiber Reinforced Siliconized Epoxy Polymer Composites

M. ALAGAR, T. V. THANIKAI VELAN, *and* A. ASHOK KUMAR

Department of Chemical Engineering
Anna University
Alagappa College of Technology
Chennai - 600 025, India

Siliconized epoxy-matrix systems have been developed by an interpenetrating mechanism using epoxy resins GY 250 and LY 556 (Ciba-Geigy) and hydroxyl terminated polydimethylsiloxane with γ-aminopropyltriethoxysilane as crosslinker in the presence of dibutyltindilaurate catalyst. Aliphatic amine (HY 951, Ciba-Geigy), aromatic amine (HT 972, Ciba-Geigy) and polyamidoamine (HY 840, Ciba-Geigy) are used as curing agents for epoxy resins. The tentative level of 10% siloxane introduction into epoxy resin has been ascertained from experimental studies to obtain reasonable improvements in the impact behavior without compromising other mechanical properties. The impact behavior of E-glass reinforced composites made from the siliconized epoxy resin is enhanced to 2–4 times over that measured on the composites made from a pure epoxy resin. Composites cured with aromatic amine impart better mechanical properties than those cured with aliphatic amine and polyamidoamine.

INTRODUCTION

A number of elastomeric materials such as acrylates and nitrile rubbers have been used as toughening agents for epoxy resins, but their usage is restricted because of their limited compatibility and strength characteristics. The toughening process is used to absorb the fracture energy and to improve the impact resistance of the polymer by the introduction of flexible molecular structure (1). The toughening process was developed in order to enhance the utility of polystyrene in the form of a high impact product using elastomeric toughening agents (2). This enabled the transformation of a number of brittle thermoplastic materials into strong, tough, and impact resistant products that have a number of industrial applications. This mechanism of thermoplastic toughening was extended to thermosetting plastics in order to make them strong, impact resistant, and suitable for coatings, adhesives, and matrix materials for advanced composites (3–5). Epoxy resins are widely used as thermal resistant coatings, structural adhesives, and matrix materials for a considerable number of engineering applications because of their characteristic properties (6). However, their inferior impact characteristics limit their usage in many advanced engineering applications. Hence, an improvement in the impact behavior of epoxy resins is essential.

In the present investigation an attempt has been made to improve impact strength of epoxy resin by incorporating hydroxyl terminated polydimethylsiloxane as a toughening agent. Though a number of toughening agents are available, hydroxyl derivative of polydimethylsiloxane is preferred because of its inherent characteristics (9), such as constant physical properties over a wide range of temperature, flexible molecular structure, resistance to weather and ozone, corona discharge and aging, good dielectric strength, good wetting, high thermal stability, good hydrophobic behavior and excellent physiological inertness.

EXPERIMENTAL

The experimentation involves the following steps 1: Preparation of prepolymer mix. 2. Curing of prepolymer mix. 3. Siloxane introduction into epoxy system. 4. Fabrication of composites. A short discussion about materials used precedes the experimental steps mentioned above.

Materials

Siliconized epoxy interpenetrating network systems are developed using epoxy resin GY250 (DGEBA-diglycidyl ethers of bisphenol-A) (Ciba-Geigy) LY 556 (DGEBA) (Ciba-Geigy) and they are termed as systems X and Y. The curatives aliphatic amine (HY 951, Ciba-Geigy), aromatic amine (HT 972,Ciba-Geigy) and polyamidoamine (HY 840, Ciba-Geigy) are referred to as A, B, and C respectively. The siloxane component used in the present work for the development of interpenetrating network system of hybrid siliconized epoxy matrix is derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany) through controlled equilibration polymerization reaction. A silane derivative, viz., γ-aminopropyltriethoxysilane (Union Carbide), is used for curing hydroxyl terminated polydimethylsiloxane and for the formation of network structure with epoxy resins along with dibutyltindilaurate catalyst. The nomenclature of curatives, epoxy resin, and the concentration of siloxane present in the hybridized matrix systems is presented in *Table 1*.

Preparation of Prepolymer Mix

For the preparation of siliconized epoxy prepolymer a known amount (w/w) of hydroxyl terminated polydimethylsiloxane is thoroughly mixed with calculated percentages of epoxy resin at 30°C. The prepolymer mix is subjected to vacuum to remove the trapped air inside the blend.

Curing of Prepolymer Mix

The siliconized epoxy matrix systems X and Y and their varying compositions along with different curatives A, B, and C and catalyst are presented in *Table 2*. The calculated amount of curative (aliphatic amine (A) and polyamidoamine (C) are used separately), silane crosslinker (γ-aminopropyltriethoxysilane), and dibutyltindilaurate catalyst (*Table 2*) are sequentially added to the prepolymer blend [hydroxyl terminated polydimethylsiloxane and epoxy resin (w/w)], and the resulting product is cast in the mold at 30°C. Before casting the entrapped air, the by-product ethanol formed during the curing reaction is removed. The sample is post cured at 70°C for ten hours. In the case of curative B, (aromatic amine) the curative is melted at 90°C and is mixed with siliconized epoxy prepolymer at 120°C. This is followed by the addition of stoichiometric equivalent of γ-aminopropyltriethoxysilane and dibutyltindilaurate catalyst (*Table 2*). The resin blend and curing agents are thoroughly mixed and cooled to about 60°C and vacuum is applied. The mixture is poured into the preheated (70°C) mold and kept for three hours and then post cured at 120°C for two hours and 160°C for one hour.

The curing schedule of siliconized epoxy matrix systems is characterized by differential scanning calorimetry (DSC). From the DSC studies, the rise in temperature obtained during the chemical reaction between epoxy groups and amino groups of silane crosslinker is 120°C and that of epoxy groups and amino groups of curative B is 175°C (*Fig. 1*). The formation of network structure proceeds in two steps. In the first step, the reaction occurs between the epoxide ring of the epoxy resin and amino group of the γ-aminopropyltriethoxysilane, and is confirmed by infrared spectra. This is to be seen by the appearance of OH band (3420 cm^{-1}) and the disappearance of epoxy band (915 cm^{-1}). Absorption peaks appeared at 2980 cm^{-1} and 2850 cm^{-1}, 1370 cm^{-1} confirming the presence of $\text{-Si-OCH}_2\text{CH}_3$ and $\text{Si-(CH}_2)_3$, respectively (10). In the second step, ethoxy groups of γ-aminopropyltriethoxysilane react with hydroxyl groups of hydroxyl terminated polydimethylsiloxane. These reactions indicate that the hydroxyl terminated polydimethylsiloxane is covalently bonded with epoxy resin through γ-aminopropyltriethoxysilane (11).

Table 2. Composition of Curatives, Crosslinker and Catalyst.

Ratio of Siloxane/Epoxy	Amount of Curative (g) A	B	C	Crosslinker (g)	Catalyst (g)
0/100	10	27	50	—	—
10/90	9	24.3	45	1.473	0.1
20/80	8	21.6	40	2.946	0.1
30/70	7	18.9	35	4.419	0.1

Siloxane Introduction Into Epoxy System

To obtain reasonable improvement in impact behavior without compromising other mechanical characteristics, the tentative requirement of siloxane component is taken as 10% (w/w). This has been ascertained from the data obtained from mechanical, electrical, thermal and aging characteristics of cured siliconized epoxy matrix having varied percentages of siloxane content (viz., 10, 20, and 30%).

Fabrication of Composites

Composites materials are prepared by hand lay-up technique (12, 13), using 10 mil bi-directional woven E-glass fabric. Fabric pieces of size 20 × 12.5 cm weighing 50 g are heated to 150°C in a hot air oven for two hours to remove moisture and then cooled to 30°C. A preweighed mixture of siliconized epoxy prepolymer with stoichiometric quantity of curative is applied over fabric sheet using rubber roller. The resin

Table 1. Nomenclature of Epoxy and Siliconized Epoxy Matrix Systems.

Curative	Siliconized Epoxy Matrix System							
	System X (Ciba-GY 250)				System Y (Ciba-LY 556)			
Siloxane/Epoxy (w/w)	0/100	10/90	20/80	30/70	0/100	10/90	20/80	30/70
Aliphatic amine A(HY 951)	AX_0	AX_{10}	AY_{20}	AY_{30}	AY_0	AY_{10}	AY_{20}	AY_{30}
Aromatic amine B (HT 972)	BX_0	BX_{10}	BY_{20}	BY_{30}	BY_0	BY_{10}	BY_{20}	BY_{30}
Polyamidoamine C (HY 840)	CX_0	CX_{10}	CY_{20}	CY_{30}	CY_0	CY_{10}	CY_{20}	CY_{30}

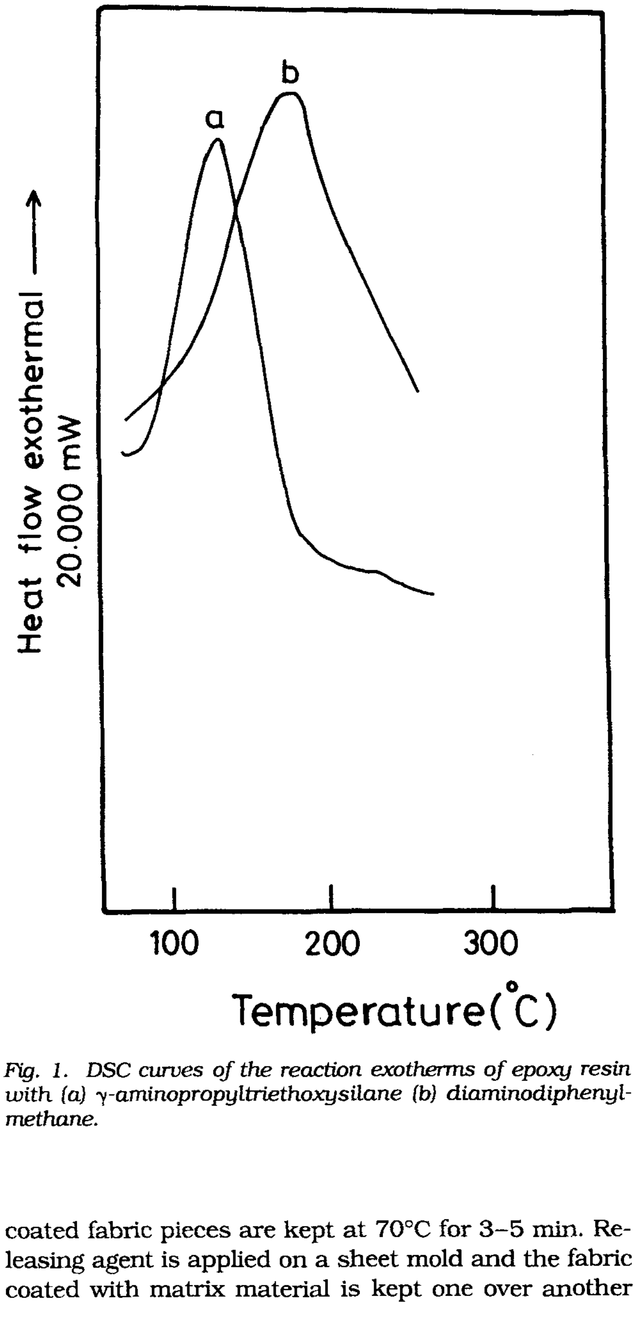

Fig. 1. DSC curves of the reaction exotherms of epoxy resin with (a) γ-aminopropyltriethoxysilane (b) diaminodiphenylmethane.

coated fabric pieces are kept at 70°C for 3–5 min. Releasing agent is applied on a sheet mold and the fabric coated with matrix material is kept one over another in the mold and pneumatic pressure of 2 kg/cm^2 is applied for a period of 30 min. The mold is taken out and cured at 30°C for ten hours. Composite is then removed from the mold and post-cured at 70°C for ten hours. The specimen composites of siliconized epoxy systems X & Y cured by aliphatic amine and polyamidoamine are prepared by the method described above. For aromatic amine curative, curing is carried out at 70°C for three hours and subsequently step cured at 120°C for two hours and 160°C for one hour.

RESULTS AND DISCUSSION

In this section, the effect of introduction of siloxane in to epoxy resin on the mechanical properties is discussed.

Tensile Strength

The matrix specimen and specimen composites having dimensions 25 mm width, 200 mm length, and 5 mm thickness are used in Universal Testing Machine (Instron) as per ASTM D638-89 for determination of tensile strength. Five specimens are tested for each sample and the average value is noted. The value of the tensile strength for epoxy, siliconized epoxy matrix, E-glass reinforced epoxy system, and E-glass reinforced siliconized epoxy system are compared in *Table 3*.

Among the curatives used, the aromatic amine (B) cured system exhibits higher tensile values (14) than the systems cured with A and C. This has been explained as being due to the orientation of rigid molecular structure (*Fig. 2*). The introduction of siloxane into the epoxy skeleton decreases the value of tensile strength according to an increase in percentage of siloxane moiety (*Table 3*). The tensile strength value for the matrix system containing 10% siloxane units AX_{10} is 40%, BX_{10} is 37% and CX_{10} is 52%. Similarly for the system containing 30% siloxane units, AX_{30} is 65%, BX_{30} is 62% and CX_{30} 78%. The value of tensile strength for the epoxy system containing 20% siloxane lies between these two extremes. A similar trend is observed for the matrix systems AY, BY, and CY having varied percentages of siloxane (*Table 3*).

Table 3. The Values of Tensile Strength and Flexural Strength for Cast Matrix and Composites.

Percentage of Siloxane	Tensile Strength kg/cm^2						Flexural Strength kg/cm^2					
	AX	AY	BX	BY	CX	CY	AX	AY	BX	BY	CX	CY
0	708.72	692.56	806.10	739.64	509.04	522.40	1054.65	1013.87	1185.15	1164.33	899.97	826.14
10	428.12	433.11	507.63	494.98	244.39	250.94	694.66	663.02	800.55	774.82	568.81	539.98
20	365.33	368.42	435.22	409.91	188.36	196.16	487.95	483.03	615.70	615.21	419.05	400.71
30	248.05	255.23	303.74	314.99	112.50	122.69	390.92	382.49	550.53	548.41	290.38	284.05
% fiber	**AX_0**	**AY_0**	**BX_0**	**BY_0**	**CX_0**	**CY_0**	**AX_0**	**AY_0**	**BX_0**	**BY_0**	**CX_0**	**CY_0**
60	2449.60	2373.67	2615.53	2524.13	1989.77	2050.94	2556.50	2614.83	2931.93	2919.27	2149.03	2193.67
	AX_{10}	AY_{10}	BX_{10}	BY_{10}	CX_{10}	CY_{10}	AX_{10}	AY_{10}	BX_{10}	BY_{10}	CX_{10}	CY_{10}
30	1043.40	928.09	1387.22	1268.39	889.42	870.09	1173.47	1230.43	1589.00	1551.74	961.14	923.87
60	2308.98	2181.01	2572.64	2467.26	1760.56	1823.84	2439.76	2457.33	2857.39	2833.49	1902.59	1978.52

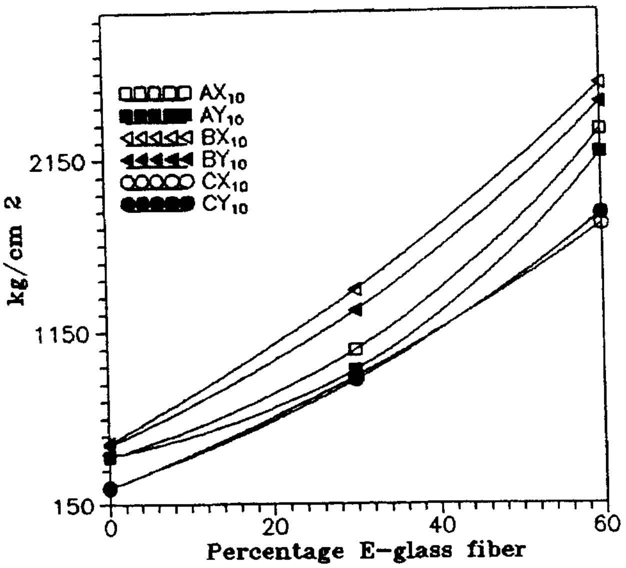

Fig. 2. Plot of percentage E-glass fiber versus tensile strength.

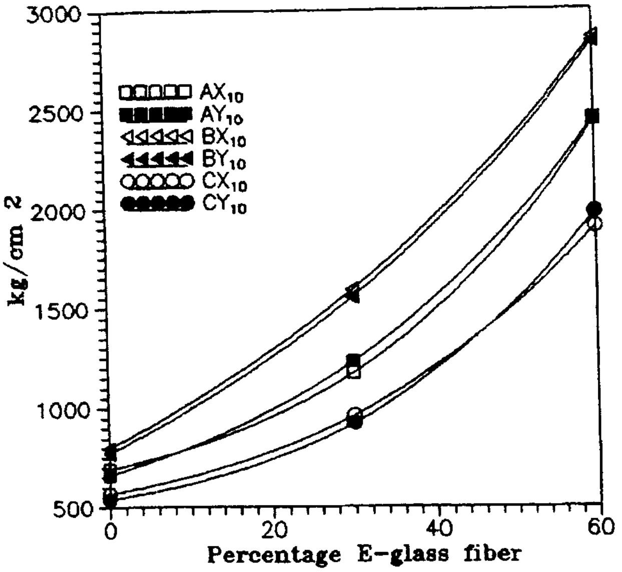

Fig. 3. Plot of percentage E-glass fiber versus flexural strength.

An appreciable increase in the value of the tensile strength is observed when epoxy matrix and optimized siliconized epoxy matrix systems are reinforced with E-glass (*Table 3*). Among the E-glass reinforced matrix systems, siliconized epoxy matrix systems exhibit lower value of tensile strength when compared with those obtained for pure epoxy matrix systems (*Table 3*). This is due to the flexible molecular structure of siloxane. However, the inorganic skeleton of siloxane units intimately bonds and efficiently wets the inorganic nature of silicates present in the E-glass reinforcement and prevents drastic reduction in the value of tensile strength. Further, less appreciable effect of change in the value of tensile strength is observed in the case of E-glass reinforced siliconized epoxy systems cured with aromatic amine (*Fig. 2*).

Flexural Strength

Flexural strength is the maximum stress developed when a bar-shaped composite test specimen is subjected as a single beam to a bending force perpendicular to the bar. The flexural strength of composite specimen of 3.2 mm depth, 12.7 mm width, and 200 mm length is tested using the Instron testing machine. The flexural strength data obtained for matrix systems as well as composites are presented in *Table 3*. The effect of introduction of siloxane and E-glass reinforcement on flexural strength follows the similar trend as observed in the case of tensile strength (*Table 3*).

Decrease in the value of flexural strength values of the matrix systems AX_{10} is 34%, BX_{10} is 33% and CX_{10} is 37% and for the systems AX_{30} is 63%, BX_{30} is 54% and CX_{30} is 68% when compared with the values of pure epoxy systems. However, the systems AX_{10}, BX_{10}, and CX_{10} reinforced with 60% E-glass, the flexural strength values are lowered by 5%, 3%, and 12% when compared with the values of pure epoxy systems reinforced with 60% E-glass (*Table 3*). A plot of percentage E-glass fiber reinforced versus flexural strength is presented in *Fig. 3*.

Impact Strength

Impact strength is defined as toughness or the ability of a composite material to withstand a sharp blow, such as that from a hammer. The impact strength of a composite specimen of 3.22 mm thickness and 12.77 mm cross section is tested using a pendulum testing machine, and the results obtained for matrix systems and composites are presented in *Table 4* (*Fig. 4*). Among the curatives used, the C (polyamidoamine) cured system imparts higher impact character than the other two curatives A and B, owing to its long flexible molecular chain (*Table 4*). The impact characteristics of siliconized epoxy matrix systems are found to be higher than pure epoxy matrix systems. The increase in impact value is based on the percentage concentration of siloxane and the enhancement is mainly influenced by the flexible siloxane molecular structure, energy absorption characteristics and free rotation of Si-O-Si skeleton. From *Table 4* it can be seen that the introduction of siloxane into epoxy resin enhances the impact strength two to four fold and the reinforcement about six to eight fold.

Percentage Elongation

Percentage elongation at break for the matrix specimens and composites is obtained from calculating the change in length divided by original length of the specimen used in tensile strength measurement; the values are presented in *Table 4*. The value of elongation increases with increase in percentage of siloxane

Table 4. The Values of Percentage Elongation and Impact Strength for Cast Matrix and Composites.

Percentage of Siloxane	Percentage Elongation						Impact Strength (kg/cm/cm²)					
	AX	AY	BX	BY	CX	CY	AX	AY	BX	BY	CX	CY
0	5.18	5.26	5.06	5.00	6.40	6.78	5.10	6.24	4.53	3.78	7.85	7.45
10	5.92	6.03	5.72	6.05	7.70	8.20	10.32	12.25	7.21	6.10	16.80	16.30
20	6.71	7.35	7.08	7.20	8.93	9.12	13.85	16.80	10.70	9.20	21.90	21.10
30	9.72	9.78	7.96	8.40	10.80	10.20	19.03	22.91	14.63	12.90	29.65	30.28
% fiber	AX_0	AY_0	BX_0	BY_0	CX_0	CY_0	AX_0	AY_0	BX_0	BY_0	CX_0	CY_0
60	6.06	5.90	5.60	5.45	7.36	7.48	38.60	35.10	30.44	29.60	44.75	45.60
	AX_{10}	AY_{10}	BX_{10}	BY_{10}	CX_{10}	CY_{10}	AX_{10}	AY_{10}	BX_{10}	BY_{10}	CX_{10}	CY_{10}
30	6.35	6.40	5.85	6.25	7.98	8.56	28.33	21.24	36.20	39.35	40.42	42.52
60	7.51	7.02	6.62	6.89	9.40	9.10	42.80	38.62	58.20	61.13	50.74	51.95

and reinforcement (*Fig. 5*). For example, 10% siloxane introduced epoxy systems cured with curatives A, B, and C (AX_{10}, BX_{10}, and CX_{10}), the percentage elongation value enhanced from 0.8% to 1.4%, and in the case of 30% siloxane introduction the enhancement is between 3.5% and 4.5% (*Table 4*). Similarly, the reinforcement enhances the percentage elongation several times more than non-reinforced systems (*Table 4*).

CONCLUSION

Based on the experimental work conducted in the investigation, the following conclusion are made. The siloxane moiety of varying percentage has been incorporated into two types of epoxy resin systems using silane crosslinker with dibutyltindilaurate. The mechanical properties of matrix systems and composites such as tensile strength, flexural strength, impact strength, and percentage elongation at break are tested as per ASTM methods. From the data gathered in mechanical studies, it is inferred that the siloxane introduction imparts flexibility to the epoxy resin system and in turn improves the impact behavior and percentage elongation at breaking level. Hence, the siliconized epoxy matrix resin system is more suitable than pure epoxy resin system for the fabrication of composites for high performance engineering applications.

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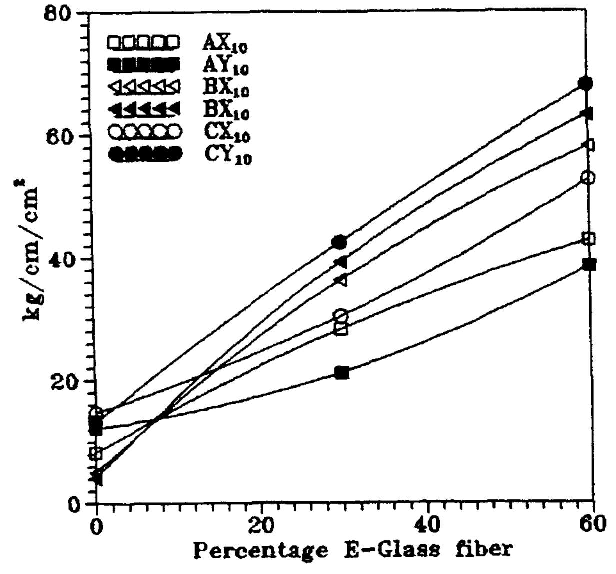

Fig. 4. Plot of percentage E-glass fiber versus impact strength.

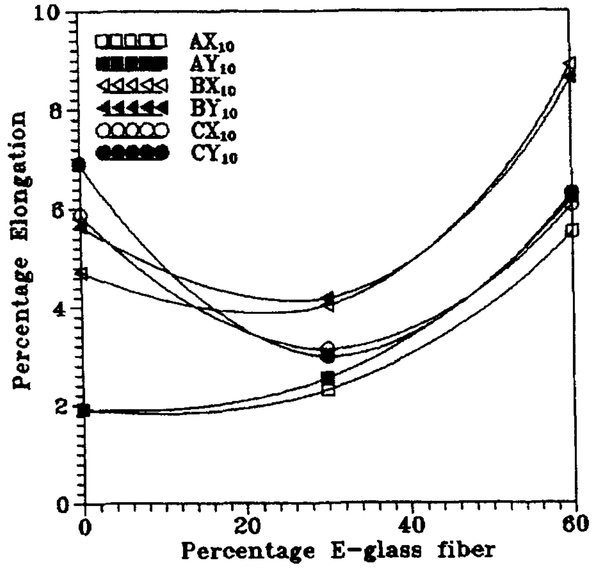

Fig. 5. Plot of percentage E-glass fiber versus percentage elongation.

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