

Effect of Structure of Epoxy Network on Interfacial Shear Strength in Glass Epoxy Composites. II

NEERAJ GUPTA, I. K. VARMA

Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

Received 31 January 1997; accepted 9 September 1997

ABSTRACT: The effect of the structure of an epoxy network on the interfacial shear strength of glass epoxy composites is described. Diglycidyl ether of bisphenol-A (DGEBA) cured by using stoichiometric amounts of aromatic diamines [i.e., 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, 4,4'-bis(aminophenoxy)benzophenone, bis[4-(4-aminophenoxy)phenyl]sulfone, and 4,4'-diaminodiphenyl methane] was used as the matrix. Interfacial shear strength, determined by using the fragmentation technique, was found to depend on the polarity of the epoxy network and was highest when DGEBA cured with bis[4-(4-aminophenoxy)phenyl]sulfone was used as the matrix. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1767–1771, 1998

Key words: epoxy resin; aromatic diamines; interfacial shear strength; fragmentation; single fiber

INTRODUCTION

In a fiber reinforced composite material, the applied load is transferred from the matrix to the fibers via the interface. A good interfacial bonding is therefore necessary for obtaining high strength and modulus. The wetting of the fibers by the resin and cohesive forces at the interface play an important role in composite performance. Residual stress may develop due to differential shrinkage of the fiber and the matrix during fabrication. Such a differential shrinkage may be advantageous if it results in the gripping of the fibers by the resin, thereby leading to mechanical or frictional adhesion between the two.

The matrix characteristics (such as chemical structure, modulus, cure shrinkage, etc.) are thus important in influencing the interfacial bonding

in fiber reinforced composites. Epoxy resins are versatile resins for studying the effect of structure on interfacial bonding because in these resins the network modification can be easily realized by varying the structure of the epoxy resins or curing agents. The focus in our present study was to evaluate the interfacial shear strength in diglycidyl ether of bisphenol-A (DGEBA) resin cured by a stoichiometric amount of aromatic diamines with different backbone structures.

Several methods are reported in the literature for evaluating the interfacial shear strength. The indirect methods such as the three-point bending test (flexural strength or interlaminar shear strength) give a number that can be correlated with interfacial shear strength. However, the experimental values depend on the fiber volume fraction, and further complications may arise due to fiber–fiber interactions.

Direct methods for evaluating interfacial shear strength are based on single fiber composites. The use of fragmentation (embedded interfacial shear strength),^{1–6} microbonding,^{7,8} fiber pull out,^{9,10} and a curved neck specimen^{11,12} has been reported

This article was presented at the 36th IUPAC International Symposium on Macromolecules, August 4–9, 1996, in Seoul, Korea.

Correspondence to: Prof. I. K. Varma.

Journal of Applied Polymer Science, Vol. 68, 1767–1771 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/111767-05

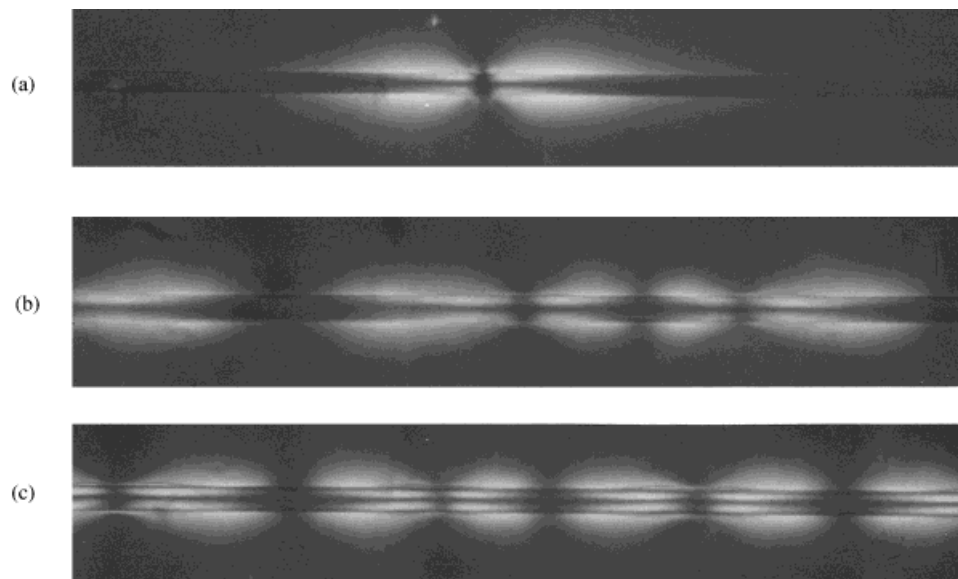


Figure 1 Polarized transmitted light micrographs showing stress birefringence patterns developed during fragmentation of R cured epoxy glass composites ($\times 250$) at (a) 0.8-mm displacement, (b) 1.2-mm displacement, and (c) 1.6-mm displacement (saturation level).

in the literature for the evaluation of interfacial shear strength.

In the present studies the fragmentation method was used. For characterization of the stress transfer at the matrix–fiber interface, a single fiber was embedded in the matrix and the specimen was stretched along the fiber axis until fiber breakage reached a saturation level. The average fiber length (l_c) was then related to interfacial shear strength (τ) according to the relationship¹³

$$\tau = \frac{\sigma_f \cdot d}{2 \cdot l_c}$$

where d is the fiber diameter and σ_f is the fiber tensile strength. Because the fiber matrix interface is placed under shear, the calculated value of τ is therefore expected to be an excellent estimate of the shear strength between the fiber and matrix.

EXPERIMENTAL

Materials

The structure of the epoxy network was varied by using DGEBA (Hindustan Ciba Geigy, grade LY556) and commercially available 4,4'-diamino-

nodiphenyl methane (M) (Fluka). The other aromatic diamines [i.e., 1,3-bis(4-aminophenoxy)benzene (R), 1,4-bis(4-aminophenoxy)benzene (H), 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (B), 4,4'-bis(aminophenoxy)benzophenone (P), and bis[4-(4-aminophenoxy)phenyl]sulfone (S)] were synthesized as reported earlier.¹⁴ The epoxy equivalent of the resin was 176.8.

E-Glass fibers without a surface finish (average diameter of 9.0 μm) were used to prepare single fiber reinforced epoxy coupons. The tensile strength of a single fiber (gauge length of 2 cm) was evaluated on an Instron tensile testing machine (model 1112). A crosshead speed of 1 cm/min and a chart speed of 10 cm/min were used. An average of 25 fibers was determined.

Fabrication of Steel and Rubber Mold

A mild steel mold with eight dogbone-shaped specimens was machined according to ASTM standards. RTV silicone rubber (MetroArch) was used for transfer molding and to obtain 7-cm long dogbone specimen cavities having a width, depth, and gauge length of $0.3 \times 0.15 \times 2.6 \text{ cm}^3$.

Fabrication of Composite Specimens

Single filaments were picked from the fiber bundle and were mounted with the help of a sticking

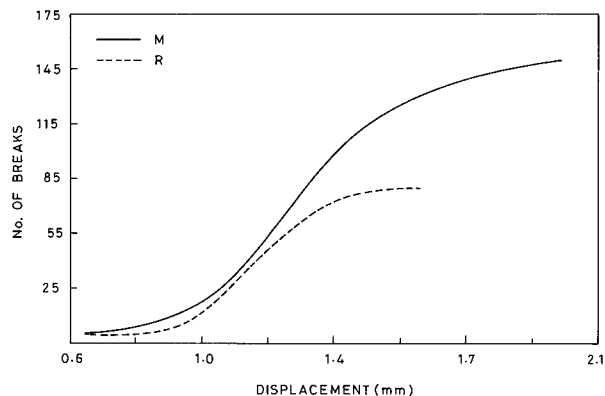


Figure 2 Number of breaks versus the displacement in glass fiber embedded in epoxy resin cured by aromatic diamine M or R.

tape on the silicone rubber mold. The mixture containing the epoxy resin and a stoichiometric amount of diamine was thoroughly mixed and degassed prior to pouring in the mold. The samples were isothermally cured at 100°C for 3 h followed by postcuring at 150°C for 2 h. After cool down the mold was curled away from the specimen parallel to the fiber to prevent fiber damage.

Tensile and Photoelastic Measurements

The epoxy tensile coupons with a single glass fiber at the center were tested on a tensile testing machine (Polymer Laboratories Minimat) that was mounted on a Leitz polarizing microscope with a Wild MPS45 camera facility at the top. The glass fiber encapsulated coupons were loaded in tensile mode. The changes were monitored by a polarized microscope. A tensile stress parallel to the fiber axis was applied to the composite until the fiber broke. The breakage was initially from the weakest fiber defect and progressed to less critical de-

Table I Glass/Epoxy Composites: Effect of Aromatic Diamines on Average Number of Fiber Breaks Observed in Glass Fiber at Saturation Point and Critical Fiber Length (l_c/d)

| Sample | Avg. No. Fiber Breaks | l_c/d |
|--------|-----------------------|---------|
| R | 69 (± 9) | 43.11 |
| H | 79 (± 13) | 38.66 |
| B | 62 (± 13) | 44.88 |
| P | 113 (± 17) | 27.66 |
| S | 116 (± 9) | 27.56 |
| M | 107 (± 15) | 29.55 |

Table II Effect of Aromatic Diamine Hardeners on Matrix Young's Modulus and Interfacial Shear Strength (τ) of Glass/Epoxy Composites

| Sample | τ (MPa) | Matrix Young's Modulus (MPa) |
|--------|--------------|------------------------------|
| R | 19.25 | 1609 |
| H | 21.47 | 1606 |
| B | 18.50 | 1630 |
| P | 30.00 | 1778 |
| S | 30.12 | 1728 |
| M | 28.08 | — |

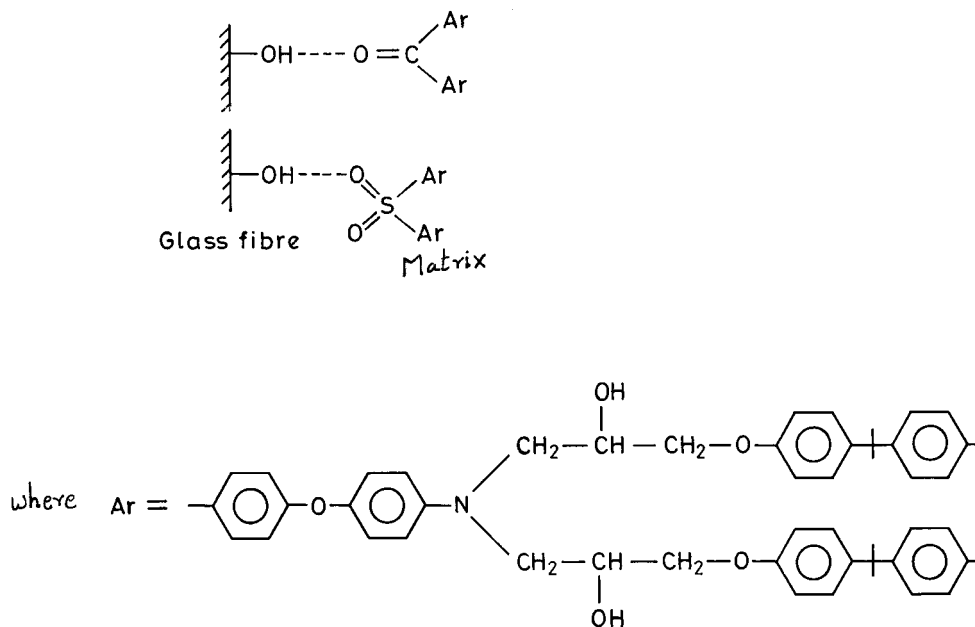
fects. After numerous breaks, the fiber fragments became so short that the shear transfer along their lengths would no longer build up enough tensile stress to cause any further failure with increasing strain. At this point, the fragment length remaining represented the critical fiber length (l_c) of the reinforcement. The length of each of these fragments at the saturation point and the number of total breaks in the fiber were measured using the polarized microscope. Five samples for each formulation were tested, and the average values of the number of breaks in the fiber and critical fiber length were calculated.

RESULTS AND DISCUSSION

The tensile strength (σ_f) of the E-glass fibers was found to be 1660 MPa.

The fragmentation of the embedded fibers in the epoxy network was associated with the development of characteristic birefringence patterns that developed at each break point. The stresses generated within the fiber-matrix interface observed in each specimen were recorded photographically with increasing strain. After a break an intense photoelastic region appeared around the end of the fiber. With increasing strain, this region rapidly expanded down the fragment away from the break. This resulted in a stress pattern that had alternating light and dark areas in the micrograph, thereby leading to an increase in the gap between fragments with increasing strain. Figure 1 shows the stress birefringence pattern that developed during fragmentation of R cured epoxy glass composite.

Figure 2 shows the number of breaks in a 2.6-cm glass fiber length embedded in epoxy resin cured by aromatic diamines M or R. The number of fragments depended upon the applied strain



Scheme 1 Incorporation of a polar carbonyl and sulfonyl group in diamines P and S.

and the structure of the epoxy network. An increase in matrix strain resulted in an increase in the number of breaks. The average number of breaks observed in the glass fibers at saturation level and l_c/d are given in Table I. The number of breaks was higher in resin cured with diamines M, P, or S. At saturation level the number of breaks in the resin cured by B were the lowest. On the basis of the number of breaks observed at saturation level, two groups of epoxy network can be identified: those with fewer fiber breaks (<80 in a fiber of 2.6 cm; e.g., DGEBA cured with diamines R, H, or B) and those with higher fiber breaks (>100 in a fiber length of 2.6 cm; resin cured with P, S, or M diamines).

The interfacial shear strength was determined for the various samples and the results are given in Table II. The observed trend in the interfacial shear strength was as follows:

$$P \approx S > M > H > R \approx B$$

This observed trend can be explained on the basis of matrix characteristics. Recent studies from Wagner⁶ have shown that the energy necessary to initiate or nucleate an interfacial crack from its associated transverse fiber break during single fiber fragmentation depends on the fiber and matrix geometrical and material characteristics. An increase in the Young's modulus of the

matrix resulted in the decrease in debonding energy.⁶ The modulus of the epoxy resins cured by different diamines is given in Table II.¹⁴ A marginal increase in modulus is observed when diamines P, S, and M were used for curing the epoxy resin. In spite of this increase in matrix modulus, the interfacial shear strength was higher in these composites. Therefore, factors other than the matrix modulus, such as the polar interactions between the fiber and matrix, seemed to be more significant.

Incorporation of a polar carbonyl and sulfonyl group in the diamine (P and S) may enhance the interactions of the matrix with the surface hydroxyl groups of the glass fibers (Scheme 1).

Such an interaction may be responsible for increasing the interfacial shear strength. Thus, our studies have shown that the polarity of the epoxy network contributes significantly to the improvement of interfacial shear strength.

REFERENCES

1. Y. Huang and R. J. Young, *Composites*, **26**, 541 (1995).
2. A. S. Wimolklatiasak and J. P. Bell, *Polym. Compos.*, **10**, 162 (1989).
3. A. N. Netravali, R. B. Henstenburg, S. L. Phoenix, and P. Schwartz, *Composites*, **10**, 226 (1989).

4. W. D. Bascom and R. M. Jensen, *J. Adhesion*, **19**, 219 (1986).
5. L. T. Drazl, M. J. Rich, and P. Lloyd, *J. Adhesion*, **16**, 1 (1983).
6. M. Detassis, E. Frydman, D. Vrieling, X. F. Zhou, H. D. Wagner, and J. A. Narin, *Composites*, **27A**, 769 (1996).
7. B. Miller, P. Muri, and L. Rebenfeld, *Compos. Sci. Technol.*, **28**, 17 (1986).
8. D. B. Marshall, *J. Am. Ceram. Soc.*, **67**, 259 (1984).
9. L. Penn, F. Bystry, W. Karp, and S. Lee, in *Molecular Characterisation of Composite Interfaces*, H. Ishida and G. Kumar, Eds., Plenum, New York, 1985, p. 93.
10. C. DiFrancia, T. C. Ward, and R. O. Claus, *Composites*, **27A**, 597 (1996).
11. D. S. Varma, H. L. Needles, D. A. Kourtides, and R. H. Fish, *Polym. Compos.*, **4**, 98 (1983).
12. K. J. Broutman and F. J. McGary, *Mod. Plast.*, **Sept.** (1962).
13. A. Kelly and W. R. Tyson, *J. Mech. Phys. Solids*, **13**, 329 (1965).
14. N. Gupta and I. K. Varma, *J. Appl. Polym. Sci.*, to appear.