Heat-Distortion Temperature of Unidirectional Polyethylene–Glass Fiber–PMMA Hybrid Composite Laminates

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ABSTRACT: Unidirectional (UD) composite laminates based on high-performance polyethylene fibers (PEF) and glass fibers (GF) and their hybrids were prepared with partially polymerized methyl methacrylate (MMA) at room temperature, followed by heating at 55°C (well below the softening point of PEF, 147°C) for 2 h. The heat distortion temperatures (HDT) of the composites were measured and analyzed. The dependency of the HDT correlated with the wettability of the fibers, measured from the contact angle. The HDT of the composites increased with increasing GF content but decreased when PEF was used. An optimum combination of different properties was obtained by using PEF/GF/PMMA hybrid composites, with GF ply/plies on the lower tension side of the UD laminates. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 541–545, 1999

Key words: hybrid composite; unidirectional laminates; contact angle; wettability; heat-distortion temperature

INTRODUCTION

High-performance polyethylene fibers (PEF) are currently produced by solution (gel) spinning of ultrahigh molecular weight polyethylene and possess unique mechanical properties in terms of high strength-to-weight ratios and stiffness-to-weight ratios.[1] Moreover, these PEF possess relatively high energy to break compared with carbon, aramid, and glass fiber (GF).[2] Because of these unique properties, PEF has a high potential for use in composite structures. Unfortunately, however, the low heat-distortion temperature (HDT) of polyethylene is one of the major limitations for its use in certain composite applications because the HDT is the maximum temperature at which a polymer can be used as a rigid material. Therefore GF, a well-known reinforcing fiber, is used in combination with PEF to obtain a good balance of the HDT.

A few workers have used PEF as one of the reinforcing fibers in hybrid composites, but these works are based mainly on a thermoset matrix.[2–7] Composites based upon thermoplastic polymeric matrices potentially offer several advantages compared with those based upon thermosetting resins.[8,9] Thus, one could expect a unique structural material based on poly(methyl methacrylate) (PMMA), a thermoplastic polymer, as the matrix in PEF/GF-reinforced composite.

The present work reports the unidirectional (UD) laminates based on PEF and GF and their hybrid with partially polymerized methyl methacrylate (MMA) well below the softening point of PEF. The work was carried out with the following objectives: (1) to obtain the HDT of UD laminates cast from MMA–PEF, MMA–GF, and MMA–

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PEF/GF (hybrid) and (2) to study the role of PEF ply/plies in the hybrid laminates toward the HDT, depending on the relative position of the ply/plies.

EXPERIMENTAL

MMA (Western Chemical Corp., Calcutta, India) was purified by a standard technique[10,11] and benzoyl peroxide (Bz_2O_2) was recrytallized from chloroform[12] and dried in vacuum. The purification of *N,N*-dimethylaniline (NDA) was achieved by distillation under reduced pressure before use.

The PEF (Spectra 900, Allied-Signal Corp., Petersburg, FL) used for the preparation of composites were surface-treated with chromic acid following refs. 2, 13, and 14. The surface of GF (433 BF-225, Owens Corning Fiberglas Corp., Granville, OH) was already treated by a standard treatment used directly for making composites. The wetting characteristics of PMMA on treated and untreated PEF and GF have been studied by contact-angle determination.[15–17] Improved wetting was found when the treated fibers were investigated.[18]

The UD plies were made on a glass sheet using partially polymerized MMA as the resin and an amine-peroxide (NDA–Bz_2O_2) initiator system in bulk at room temperature.[19] The preimpregnated plies were used to construct multiple-layer systems. Laminated structures were prepared by stacking these plies of PEF and GF unidirectionally in the mold and the composites were made using the same at room temperature until they solidified within the mold and shrinkage was controlled using extra resin in the mold. Finally, the composite was heated to a temperature of 55°C (well below the softening point of PEF) for 2 h to ensure the completion of MMA polymerization. A detailed description of the preparation of laminates is given elsewhere.[18,20–25]

UD laminates were prepared from four to 16 plies for PEF and GF (designated as S_4 to S_{16} and G_4 to G_{16}, respectively) with steps of four plies. The nomenclature and geometry of the different hybrid laminates which were studied are given in Figure 1(a). The first and second number within the brackets stand for the number of GF plies and PEF plies, respectively, present in those hybrid laminates. When a load was applied to the specimen such as I(12,4) on the "U" side, the sample is designated as I(12,4)/U. When the load direction is reversed such that it is applied on the "L" side,

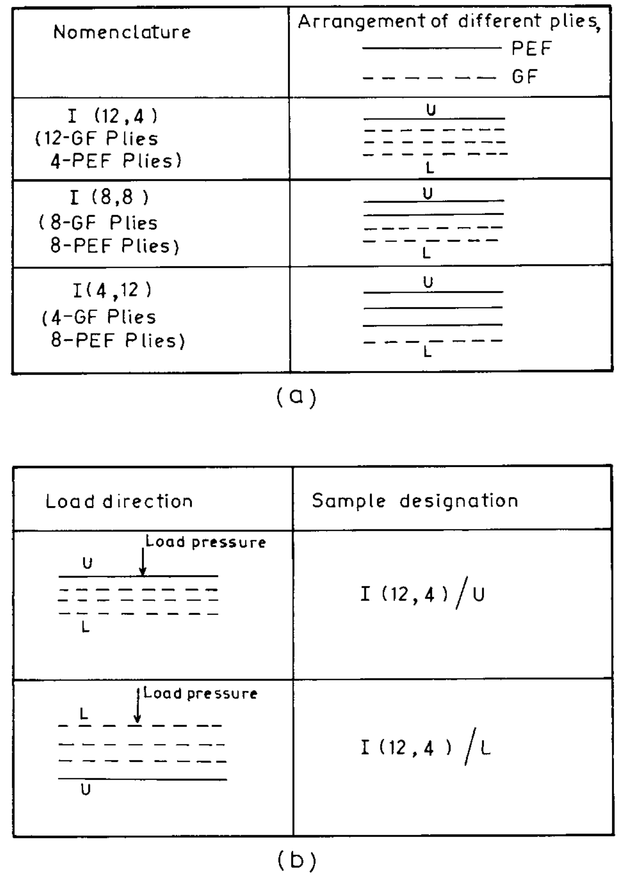

Figure 1 Schematic representation of hybrid laminates (one line equivalent to four plies): (a) nomenclature and geometry of hybrid laminates; (b) load direction with sample designation.

then the sample is designated as I(12,4)/L [Fig. 1(b)]. Similar nomenclature is applied for the other hybrid laminates. The samples for measurements were cut to 127 × 12.7 × 6.35-mm dimensions. In this test, a load of 1.81 MPa (264 psi) was applied to the sample, and the temperature was increased at a rate of 2°C/min. The HDT was determined using ASTM D648. In all cases, 10 specimens were tested and average values are reported.

RESULTS AND DISCUSSION

In Figure 2, the deflection or elongation is plotted against temperature at different fiber volume fractions (V_f). The HDT in this case is defined as the temperature at which the deflection of the test specimens becomes 0.26 mm. The HDT of the glass-fiber-reinforced composites (GFRC) in-

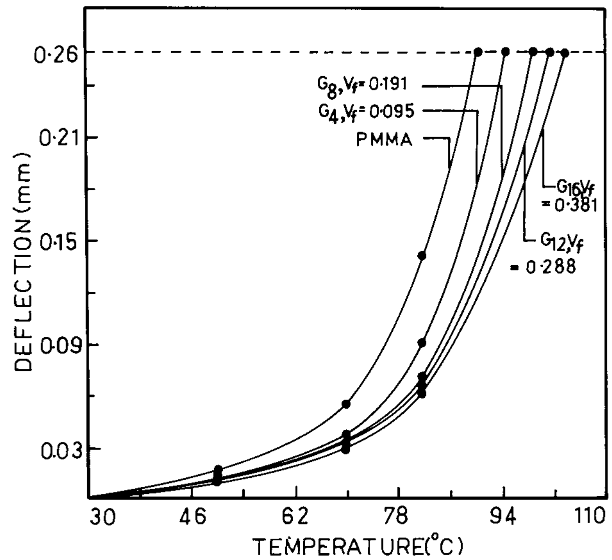

Figure 2 HDT as determined from deflection–temperature curves for GFRC.

creased gradually from 90.5°C (PMMA) to 110°C (G_{16}) with increasing V_f. But in case of PEF-reinforced composites (PEFRC), the reverse results are observed (Fig. 3). In this case, the HDT decreases gradually from 90.5°C (PMMA) to 84°C (S_{16}). This behavior is due to the lower HDT of polyethylene compared to PMMA.[26]

Another factor which also contributes to the lowering of the HDT in the case of PEFRC, con-

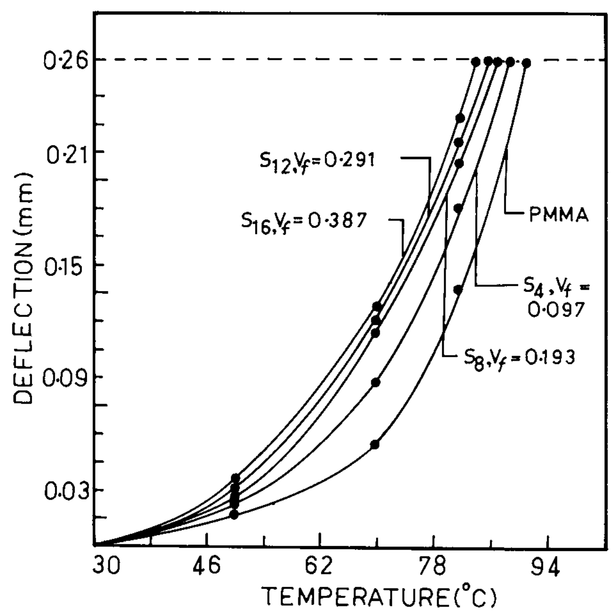

Figure 3 HDT as determined from deflection–temperature curves for PEFRC.

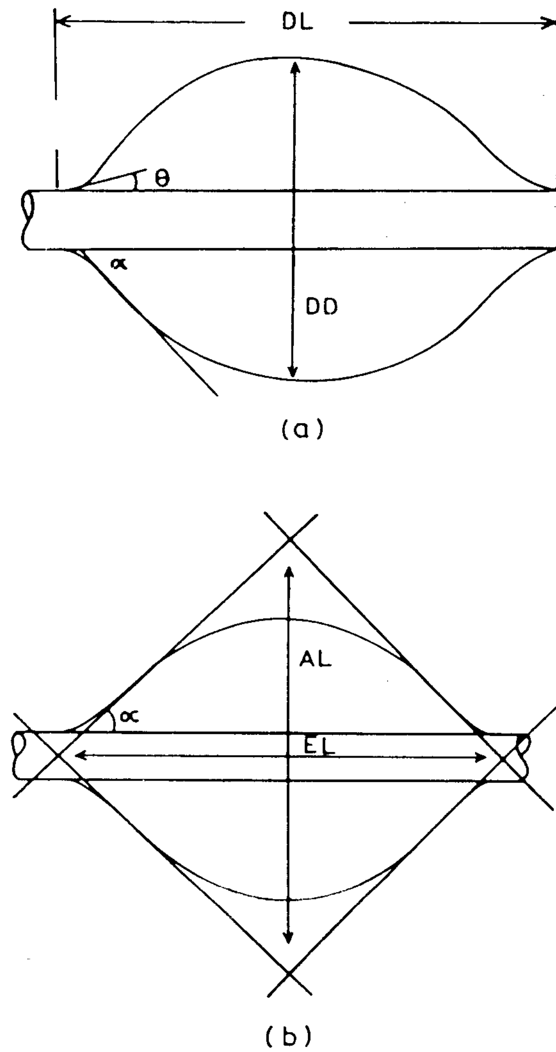

Figure 4 Cross section of a drop and parameters: (a) Contact angle θ; angle α; *DL,* drop length; *DD,* drop diameter. (b) *EL,* equatorial length; *AL,* axial length; angle α.

trary to its increase in the case of GFRC with increasing V_f, is the matrix-to-fiber adhesion strength. From the contact angle (between the fiber and matrix) measurement[27] (Fig. 4 and Table I), it is observed that the contact angle (θ) and the α angle is lower while *DL*/*DD* and *EL*/*AL* are higher in the case of PEF compared to GF, which indicates better wettability of PEF by PMMA, leading to good adhesion. The higher HDT of GF and its comparatively lesser wettability by the PMMA matrix, which means lower efficiency in load transfer between the fiber and matrix, inhibits the deflection, thereby increasing the HDT. From Figures 2 and 3, it is also observed that the slopes of the first part of the curves are much less

Table I Values of Contact Angle (θ), α Angle, and *DL/DD and EL/AL Ratio*

Fiber	θ Angle (°)	α Angle (°)	DL/DD	EL/AL
Treated GF	8 ± 1.9	19 ± 2.0	3.00 ± 0.02	2.57 ± 0.07
Treated PEF	5 ± 2.3	12 ± 2.6	3.76 ± 0.08	3.07 ± 0.11

compared to the higher-temperature region, where deflection is higher, as expected. In the case of PEFRC, as temperature increases and both PEF and PMMA approach their HDT, the whole composite sags and the deflection is enhanced. For the GFRC, although the HDT of GF is much higher, the PMMA matrix softens and distorts on approaching its HDT with increasing temperature, improving the load-transfer efficiency and enhancing the deflection.

An interesting feature of the present study is the effect of the changing position of the PEF and GF ply/plies on HDT in the hybrid laminates. In Figure 5, the HDT is plotted against systems 1–5. All the systems in this figure have approximately same total V_f. From the figure, it is clear that when PEF ply/plies are present at the lower side of the hybrid laminates, the HDT always remains at a lower value. If the layup sequence is reversed, that is, GF ply/plies are present at the lower side, the HDT shows a higher value. Now, when a constant load is applied to a beam, the load is transferred from the upper, compression side to the lower, tension side. As a result, the maximum stress occurs on the lower side of the hybrid laminates. Thus, in the case of hybrid laminates, where PEF ply/plies are on the tension side, the lower HDT of the composite is due to the low HDT of both PEF and PMMA, and also the good adhesion between the two leads to better load transfer and faster distortion. The reason for the improvement in HDT in the case of hybrid composites when the GF ply/plies are on the tension side is due mainly to the much higher HDT of GF compared to PEF. Also, the comparative lower wettability of GF by PMMA may delay the deflection in reaching the required 0.26 mm, due to inefficient load transfer between the matrix and fiber.

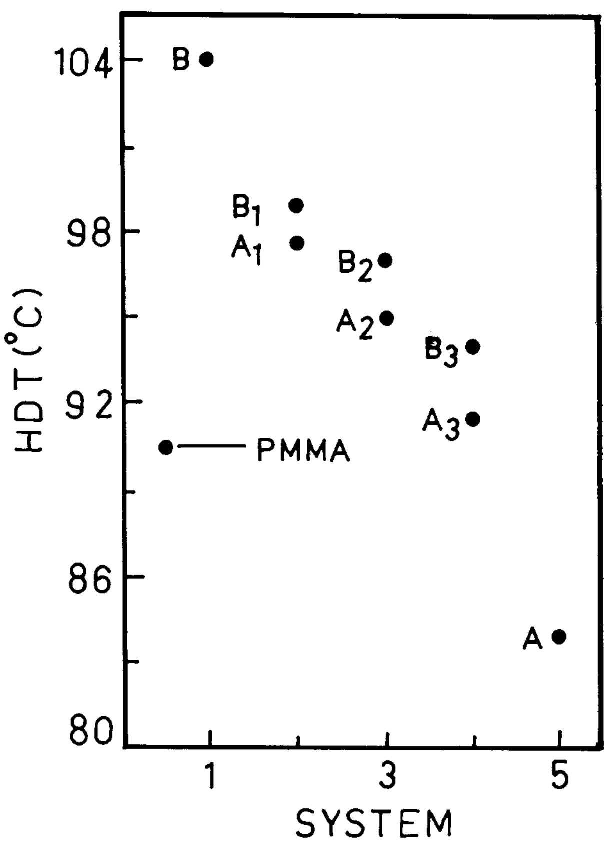

Figure 5 Plot of HDT versus systems 1–5: System 1: B, G_{16}. System 2: B_1, I(12,4)/U; A_1, I(12,4)/L. System 3: B_2, I(8,8)/U; A_2, I(8,8)/L. System 4: B_3, I(4,12)/U; A_3, I(4,12)/L. System 5: A, S_{16}.

CONCLUSIONS

The HDT of fiber-reinforced PMMA composites increases with increasing V_f in the case of GF incorporation, but shows a declining trend when PEF is used. When an optimum combination of different properties is required, a good idea may be to use PEF/GF/PMMA hybrid composites with the GF ply/plies occupying the lower, tension side.

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REFERENCES

1. Lemstra, P. J.; Krischbaum, R.; Ohta, T.; Yasuda, H. Developments in Oriented Polymers-2, Elsevier, London, 1987, pp. 39–77.

2. Peijs, A. A. J. M.; Catsman, P.; Govaert, L. E.; Lemstra, P. J. Composites 1990, 21, 513.
3. Peijs, A. A. J. M.; Venderbosch, R. W.; Lemstra, P. J. Composites 1990, 21, 522.
4. Peijs, A. A. J. M.; De Kok, J. M. M. Composites 1993, 24, 19.
5. Adams, D. F.; Zimmerman, R. S. in Proceedings of the 31st International SAMPE Sympoium, 1986, pp. 1456–1468.
6. Poursartip, A.; Riahi, G.; Teghtsoonian, E.; Chinatambi, N. in Proceedings of the 19th International SAMPE Technical Conference, 1987, pp. 503–514.
7. Peijs, A. A. J. M.; Lemstra, P. J. in Proceedings of of the 3rd Rolduc Polymer Meeting, Elsevier, London, 1989, pp. 218–227.
8. Kodokian, G. K. A.; Kinloch, A. J. J Mater Sci Lett 1988, 7, 625.
9. Hoggatt, J. T.; Oken, S.; House, E. E. U.S. Air Force Report AFWAL-TR-80-3023, April 1980.
10. Ghosh, P.; Mitra, P. S.; Banerjee, A. N. J Polym Sci Polym Chem Ed 1973, 11, 2021.
11. Ghosh, P.; Benerjee, A. N. J Polym Sci Polym Chem Ed 1975, 12, 375 (1975).
12. Ghosh, P.; Biswas, S.; Niyogi, U. J Polym Sci Part A Polym Chem 1986, 24, 1053.
13. Ladizesky, N. H.; Ward, I. M. J Mater Sci 1983, 18, 533.
14. Ladizesky, N. H.; Ward, I. M. J Mater Sci 1989, 24, 3763.
15. Yamaki, J. I.; Katayama, Y. J Appl Polym Sci 1975, 19, 2897.
16. Sellitti, C.; Vargiu, S.; Martuscelli, E.; Fabbro, D. J Mater Sci 1987, 22, 3477.
17. Tissington, B.; Pollard, G.; Ward, I. M. J Mater Sci 1991, 26, 82.
18. Saha, N.; Banerjee, A. N.; Mitra, B. C. Polym Adv Technol 1995, 6, 637.
19. Ghosh, P.; Mukherjee, N. Eur Polym J 1979, 15, 797.
20. Saha, N.; Banerjee, A. N.; Mitra, B. C. Polymer 1996, 37, 699.
21. Saha, N.; Banerjee, A. N. Polymer 1996, 37, 4633.
22. Saha, N.; Banerjee, A. N.; Mitra, B. C. J Appl Polym Sci 1996, 60, 139.
23. Saha, N.; Banerjee, A. N. J Appl Polym Sci 1996, 60, 657.
24. Saha, N.; Banerjee, A. N. J Appl Polym Sci 1996, 62, 1193.
25. Saha, N.; Banerjee, A. N. J Appl Polym Sci 1996, 62, 1199.
26. Brydson, J. A. Plastics Materials, Butterworth, London, 1982, Chaps. 10 and 15.
27. Sellitti, C.; Vargiu, S.; Martuscelli, E.; Fabbro, D. J Mater Sci 1987, 22, 3477.