Stress-Relaxation Behavior of Unidirectional Polyethylene–Carbon Fibers: PMMA Hybrid Composite Laminates

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ABSTRACT: Unidirectional composite laminates based on carbon fibers (CF) and high-performance polyethylene fibers (PEF) 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 stress-relaxation behavior of the composites were determined and analyzed. It was found that at all strain levels the rate of stress relaxation decreased by the loading of CF in CF-reinforced composite laminates (CFRC); however, the reverse behavior was found in the case of PEF-reinforced composite laminate (PEFRC). An interesting observation of the study was that the rate of stress relaxation decreased linearly in two steps in the case of PEFRC, whereas in the case of CFRC, it decreased in a single step. In the case of hybrid composites, the stress relaxation decreases in two steps as in PEFRC. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1925–1929, 1998

Key words: polyethylene; carbon fibers; acrylic thermoplastics; hybrid composite; stress relaxation

INTRODUCTION

A present trend among polymer scientists is to prepare thermoplastic and thermosetting composites exhibiting high mechanical behavior. They are lightweight, of low cost, and designed to perform in different static and dynamic fields of application. By permutation and combination of various fibers and polymers, a wide range of composites having unique properties for versatile applications as alternatives to conventional materials like metals and woods were prepared.

The high-performance polyethylene fibers (PEF) possess unique mechanical properties in terms of high strength-to-weight and stiffness-to-weight ratios.[1] Moreover, these PEF possess a relatively high energy to break compared with glass, aramid, and carbon fibers (CF).[2] Because of these unique properties, PEF has a high potential for use in composite structures. Unfortunately, however, an important limitation to the use of PEF is the creep or stress relaxation,[3,4] that is, the fiber is elongated under a static load over a period of time. Thus CF, a well-known reinforcing fiber, is used in combination with PEF to obtain a good balance of stress-relaxation behavior.

A few workers have used PEF as one of the reinforcing fibers which are based mainly on the use of a thermoset matrix.[2,5–9] Composites based upon thermoplastic polymeric matrices potentially offer several advantages compared with those based upon thermosetting resins.[10,11] Thus, one can expect a unique structural material based on the use of poly(methyl methacrylate) (PMMA), a thermoplastic polymer, as the matrix in PEF/CF-reinforced composites.

The present work was undertaken with the following objectives: (1) to obtain the stress-relaxation characteristics of unidirectional (UD) laminates cast from MMA–PEF, MMA–CF, and MMA–PEF/CF (hybrid) and (2) to study the

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Table I Volume Fraction of Fibers of CFRC and PEFRC

Composite	V_f
CFRC	
C_1	0.043
C_2	0.085
C_3	0.128
PEFRC	
S_1	0.090
S_2	0.180
S_3	0.266

stress-relaxation behavior of the hybrid laminates at different volumes of PEF and CF.

EXPERIMENTAL

The fibers and other reagents used are as follows: (1) PEF (spectra 900, 1200 den) supplied by Allied Signal Corp. (St. Petersburg, FL); (2) CF (Indcarf-30, 6K) supplied by Indian Petrochemicals Co. (Boroda, India); (3) MMA supplied by Western Chemical Corp. (Calcutta, India); (4) Benzoyl peroxide (Bz_2O_2) supplied by Lobachemie Indo-austranal Corp. (Bombay, India); and (5) *N*,*N*-dimethylaniline (NDA) supplied by E. Merck (Bombay, India).

MMA was purified by a standard technique[12,13] and Bz_2O_2 was recrystallized from chloroform[14] and dried in a vacuum. The purification of NDA was achieved by distillation under reduced pressure before use.

The PEF used for the preparation of composites was treated with chromic acid following the literature.[2,15,16] The surface of the CF was already treated with a standard treatment and used directly for making composites. The wetting characteristics of PMMA on treated and untreated CF and PEF were studied by contact-angle determination according to the literature.[17–19] Improved wettability was observed in the case of treated fibers compared to the virgin fibers.[20] In this work, only treated fibers were used.

Table II Lay-Up Sequence and V_f of PEF and CF in Hybrid Composites

Lay-up Sequence[a]	Designation	V_f PEF	V_f CF
[CSC]	H-1	0.090	0.085
[SCS]	H-2	0.180	0.043

[a] C, CF; S, PEF ply.

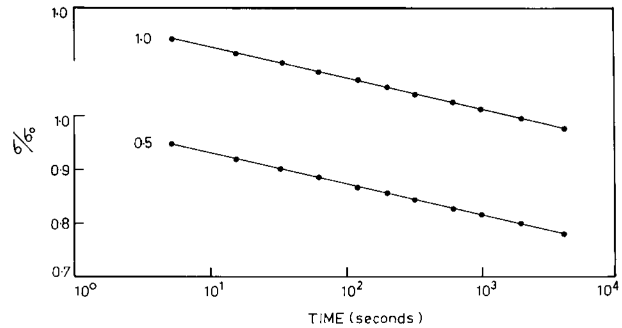

Figure 1 Stress-relaxation curves for PMMA. Successive graphs are displaced upward by 0.2. Numbers on left-hand side against curves indicate strain (%).

The UD plies were made in a dust-free chamber on a glass sheet using partially polymerized MMA as the resin with an amine–peroxide (NDA–Bz_2O_2) initiator system in bulk at room temperature.[21] Laminated structures were prepared by stacking these plies of PEF and CF unidirectionally in the mold, and the composites were made by using the same resin at room temperature until it solidified within the mold. Shrinkage was controlled using extra resin in the mold. Finally, the composite was heated to a temperature of 55°C for 2 h to ensure the completion of MMA polymerization. A detailed description of the preparation of laminates was given elsewhere.[20,22–27]

UD laminates were prepared up to three plies for PEF and CF (designated as S_1–S_3 and C_1–C_3, respectively). The volume fraction of the fibers of both laminates (CFRC and PEFRC) are given in Table I. The lay-up sequence and V_f of the hybrid laminates are given in Table II.

A stress-relaxation experiment was carried out

Table III Results of Stress Relaxation of PMMA and CFRC

Stain (%)	Sample	Slope (Negative)
0.5	PMMA	0.222
1.0	PMMA	0.249
	CFRC	
0.5	C_1	0.052
	C_2	0.044
	C_3	0.035
1.0	C_1	0.079
	C_2	0.107
	C_3	0.087

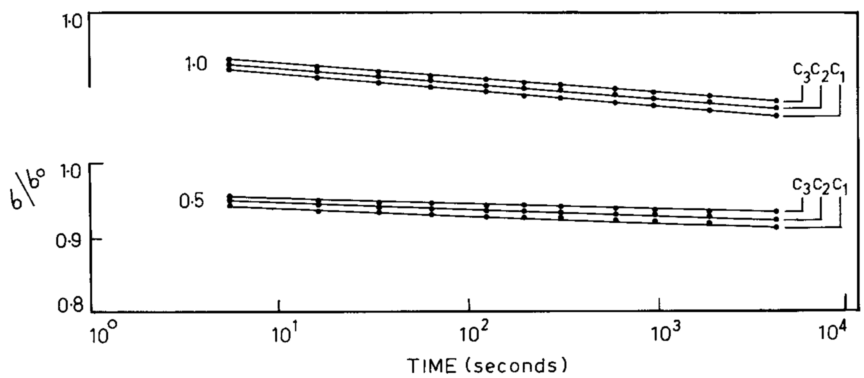

Figure 2 Stress-relaxation curves for CFRC. Successive graphs are displaced upward by 0.2. Numbers on left-hand side against curves indicate strain (%).

at 25 ± 1°C, using a dumbbell-shaped test specimen in an Instron universal testing machine. The specifications of the dumbbell were as follows: gauge length 20 mm, width 6 mm, and thickness 1.70 mm, and it was loaded parallel to the fibers with serrated jaw wedge grips. Specimens were stretched at a speed of 5 mm min^{-1} up to strain levels of 0.5 and 1.0% and kept at these strain levels for 1 h in each case. In all cases, six specimens were tested and average values reported.

RESULTS AND DISCUSSION

Figure 1 shows the variation of σ/σ_0 with time (t) for the samples at two stain levels (where σ_0 is obtained from the maximum load at $t = 0$ when the desired strain is reached and σ is the stress at subsequent times). It was observed that the rate of stress relaxation (as indicated by the slope) increases with the strain level (Table III).

Figure 2 shows the variation of σ/σ_0 with time for CFRC. The rate of stress relaxation decreases with increasing carbon content at all strain levels from C_1 to C_3 (Table III)—this behavior may be due to the elastic nature of CF.[25]

The results of the PEFRC samples are shown in Figure 3. Unlike in the case of PMMA and CFRC, experimental points for these systems appear to lie on two straight lines; the first line refers to a greater slope (Table IV) and applies for short times, while the second line is for longer times. The initial relaxation may arise from a rearrangement or reorientation at the viscoelastic PEF–PMMA interface.[28]

A method[29] of estimating the contribution of

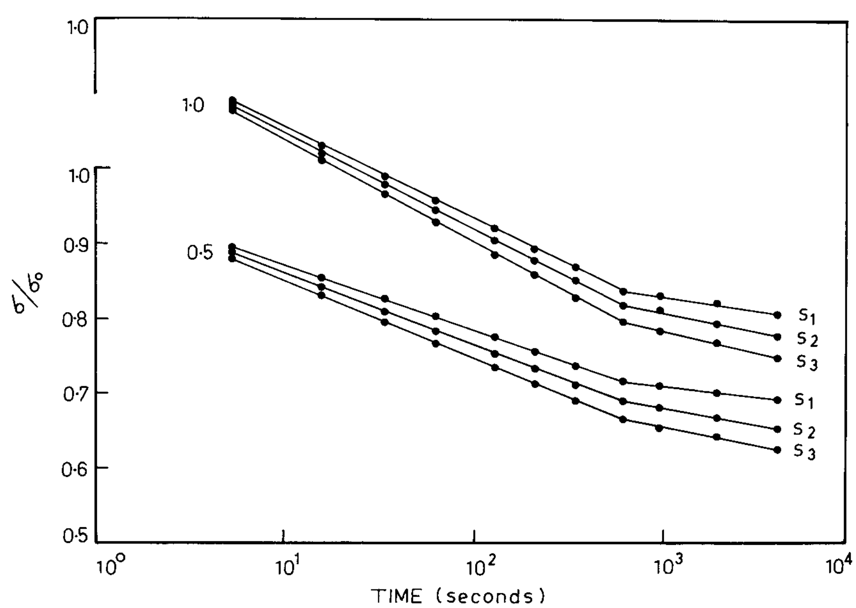

Figure 3 Stress-relaxation curves for PEFRC. Successive graphs are displaced upward by 0.2. Numbers on left-hand side against curves indicate strain (%).

Table IV Results of Stress-Relaxation Measurements for PEFRC

Strain (%)	Composite Sample	Slope (Negative)			Intercept at 1 s			Contribution of Early Process (%)
		Early	Later	Difference	Early	Later	Difference	
0.5	S_1	0.344	0.158	0.186	0.960	0.825	0.135	14.06
	S_2	0.374	0.194	0.180	0.958	0.825	0.133	13.88
	S_3	0.424	0.222	0.202	0.956	0.820	0.136	14.22
1.0	S_1	0.509	0.194	0.315	0.971	0.746	0.225	23.17
	S_2	0.543	0.222	0.321	0.975	0.750	0.225	23.19
	S_3	0.577	0.240	0.337	0.976	0.746	0.230	23.56

the early mechanism to the relaxation in the system is to divide the difference of the intercepts of the two lines by the intercept of the first line at $t = 1$ s. This fraction, expressed as a percentage, is also shown in Table IV.

It may further be noted that the time of intersection of the two lines is approximately constant (about 600 s) and independent of strain level and V_f. This time of intersection represents the change over time at which the mechanism operating at short times becomes exhausted.

In combining an elastic CF with a viscoelastic PEF, a considerable drawback in long-term properties can be expected. Figure 4 shows the variation of σ/σ_0 with time for hybrid laminates. The rate of stress relaxation decreases with time at all strain levels for both the hybrid samples in two straight lines or two linear parts having a greater slope in the first part of the line and the time of intersection of these two lines is approximately same as for PEFRC (Table V). From Table V, it is clear that the rate of stress relaxation and the contribution of the early process increases with strain level and V_f of PEF, indicating that the long-term properties of hybrid composites are principally dominated by the viscoelastic nature of PEF.

CONCLUSIONS

The main conclusions can be summarized as follows: The composite laminates as a whole were made at room temperature, the casting requiring a minimum amount of energy which may be regarded as an advantage of the system.[20,22,23] The rate of stress relaxation decreases from one ply to three plies for CFRC. The rate of stress relaxation increases from one ply to three plies for PEFRC, which is the reverse of CFRC. There are two distinct linear sections in the plot of stress versus time for PEFRC, but in the case of CFRC, there is only one linear section. In CF–PEF hybrid lam-

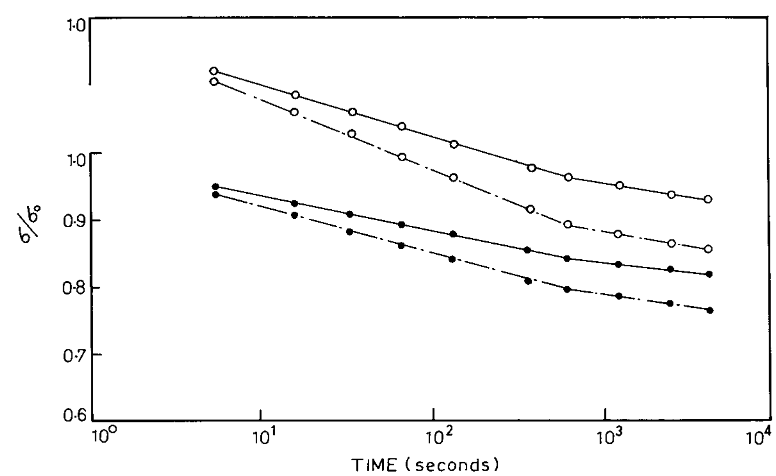

Figure 4 Stress-relaxation curves for hybrid laminates. Successive graphs are displaced upward by 0.2: (——) H-1; (– · –) H-2; (●) points for 0.5% strain; (○) points for 1.0% strain.

Table V Results of Stress-Relaxation Measurements for Hybrid Composites

Strain (%)	Composite Sample	Slope (Negative)			Intercept at 1 s			Contribution of Early Process (%)
		Early	Later	Difference	Early	Later	Difference	
0.5	H-1	0.212	0.140	0.725	0.970	0.830	0.140	14.43
	H-2	0.306	0.176	0.129	0.965	0.790	0.175	18.13
1.0	H-1	0.315	0.176	0.139	0.960	0.750	0.210	21.87
	H-2	0.424	0.203	0.220	0.960	0.640	0.320	33.33

inates, the stress-relaxation properties are dominated principally by PEF.

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REFERENCES

1. P. J. Lemstra, R. Kirschbaum, T. Ohta, and H. Yasuda, *Developments in Oriented Polymers—2,* Elsevier, London, 1987, p. 39.
2. A. A. J. M. Peijs, P. Catsman, L. E. Govaert, and P. J. Lemstra, *Composites,* **21,** 513 (1990).
3. D. T. Grubb and Z. F. Li, *Polymer,* **33,** 2587 (1992).
4. I. M. Ward and M. A. Wilding, *J. Polym. Sci. Polym. Phys. Ed.,* **22,** 561 (1984).
5. A. A. J. M. Peijs, R. W. Venderbosch, and P. J. Lemstra, *Composites,* **21,** 522 (1990).
6. A. A. J. M. Peijs and J. M. M. De Kok, *Composites,* **24,** 19 (1993).
7. D. F. Adams and R. S. Zimmerman, in *Proceedings of the 31st International SAMPE Symposium,* 1986, pp. 1456–1468.
8. A. Poursartip, G. Riahi, E. Teghtsoonian, and N. Chinatambi, in *Proceedings of the 19th International SAMPE Technical Conference,* 1987, pp. 503–514.
9. A. A. J. M. Peijs and P. J. Lemstra, in *Proceedings of the 3rd Rolduc Polymer Meeting,* Elsevier, London, 1989, pp. 218–227.
10. G. K. A. Kodokian and A. J. Kinlock, *J. Mater. Sci. Lett.,* **7,** 625 (1988).
11. J. T. Hoggatt, S. Oken, and E. E. House, *U.S. Air Force Report AFWAL-TR-80-3023,* April 1980.
12. P. Ghosh, P. S. Mitra, and A. N. Banerjee, *J. Polym. Sci. Polym. Chem. Ed.,* **11,** 2021 (1973).
13. P. Ghosh and A. N. Banerjee, *J. Polym. Sci. Polym. Chem. Ed.,* **12,** 375 (1975).
14. P. Ghosh, S. Biswas, and U. Niyogi, *J. Polym. Sci. Part A Polym. Chem. Ed.,* **24,** 1053 (1986).
15. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.,* **18,** 533 (1983).
16. N. H. Ladizesky and I. M. Ward, *J. Mater. Sci.,* **24,** 3763 (1989).
17. J. I. Yamaki and Y. Katyama, *J. Appl. Polym. Sci.,* **19,** 2897 (1975).
18. C. Sellitti, S. Vargiu, E. Martuscelli, and D. Fabbro, *J. Mater. Sci.,* **22,** 3477 (1987).
19. B. Tissington, G. Pollard, and I. M. Ward, *J. Mater. Sci.,* **26,** 82 (1991).
20. N. Saha, A. N. Banerjee, and B. C. Mitra, *Polym. Adv. Technol.,* **6,** 637 (1995).
21. P. Ghosh and N. Mukherjee, *Eur. Polym. J.,* **15,** 797 (1979).
22. N. Saha, A. N. Banerjee, and B. C. Mitra, *Polym. Commun.,* **37,** 699 (1996).
23. N. Saha, A. N. Banerjee, and B. C. Mitra, *J. Appl. Polym. Sci.,* **60,** 657 (1996).
24. N. Saha, A. N. Banerjee, and B. C. Mitra, *J. Appl. Polym. Sci.,* **60,** 139 (1996).
25. N. Saha and A. N. Banerjee, *Polymer,* **37,** 4633 (1996).
26. N. Saha and A. N. Banerjee, *J. Appl. Polym. Sci.,* **62,** 1193 (1996).
27. N. Saha and A. N. Banerjee, *J. Appl. Polym. Sci.,* **62,** 1199 (1996).
28. S. S. Bhagawan, D. K. Tripathy, and S. K. De, *J. Appl. Polym. Sci.,* **33,** 1623 (1987).
29. C. I. Mackenzie and J. Scanlan, *Polymer,* **25,** 559 (1984).