Polymer Vol. 37 No. 20, pp. 4633-4638, 1996
S0032-3861(96)00322-9
0032-3861/96/\$15.00 + 0.00

Stress relaxation behaviour of unidirectional polyethylene–glass fibres PMMA composite laminates

Nirmal Saha and Amar Nath Banerjee*
Department of Plastics and Rubber Technology, University of Calcutta, 92 A. P. C. Road, Calcutta-700 009, India

(Received 23 February 1996)

Unidirectional composite laminates based on glass fibres (GF) and high performance polyethylene fibres (PEF) and their hybrids were prepared with partially polymerized methyl methacrylate at room temperature, followed by heating at 55°C (well below the softening point of PEF) for 2 h. The stress relaxation behaviour of the composites were determined and analysed. It was found that at all strain levels, the rate of stress relaxation decreased by incorporation of GF in GF-reinforced composite laminates (GFRC) but the reversed behaviour 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 GFRC, it decreased in one step. The rate of stress relaxation was increased with the increase of relative proportion of PEF in the hybrid composites and at a higher proportion of PEF, it decreased in two steps like PEFRC. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyethylene; glass fibres; poly(methyl methacrylate) matrix)

Introduction

A present trend amongst polymer scientists is to prepare thermoplastic and thermosetting composites exhibiting high mechanical behaviour, are light-weight, low-cost and designed to perform in different static and dynamic fields of application. By a permutation and combination of various fibres and polymers, a wide range of composites having unique properties for versatile applications as alternatives to conventional materials like metals, woods, etc., have been prepared.

High performance polyethylene fibres (PEF) possess unique mechanical properties, in terms of high strength-to-weight and stiffness-to-weight ratio[1]. Moreover, these PEF possess a relatively high energy to break compared with carbon, aramid and glass fibres (GF)[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], i.e. the fibre is elongated under static load over a period of time. Thus GF, a well known reinforcing fibre is used in combination with PEF to obtain a good balance of stress relaxation behaviour.

A few workers have used PEF as one of the reinforcing fibres which are mainly based on the use of thermoset matrix[2,5–9]. Composite 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/GF reinforced composites.

The present work has been undertaken with the following objectives: (1) to obtain the stress relaxation characteristic of unidirectional (UD)-laminates cast from MMA–PEF, MMA–GF and MMA–PEF/GF (hybrid) and (2) to study the stress relaxation behaviour of the hybrid laminates at different relative volume of PEF or GF.

Experimental

Fibres and other reagents used were as follows: PEF (Spectra 900) supplied by Allied-Signal Corporation (Petersburg, USA). GF (433 BF-225) supplied by Owens Corning Fiberglass Corporation (Ohio, USA). MMA supplied by Western Chemical Corporation (Calcutta, India). Benzoyl peroxide (Bz_2O_2) supplied by Loba-Chemie Indoaustranal Corporation (Bombay, India). *N,N*-Dimethyl aniline (NDA) supplied by E. Merck Ltd (Bombay, India). MMA was purified by standard techniques[12,13] and Bz_2O_2 was recrystallized from chloroform[14] and dried *in vacuo*. The purification of NDA was achieved by distillation under reduced pressure before use.

The PEF, used for the preparation of composites were surface treated with chromic acid following other papers[2,15,16]. The surface of GF had already been treated with a standard treatment, and was used directly for making composites. The wetting characteristics of PMMA on treated and untreated GF and PEF had been studied by contact angle determination[17–19]. Improved wetting was found when the treated fibres were investigated[20].

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[21]. 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 mould and the composites

---

[*] To whom correspondence should be addressed

Table 1 Volume fraction of fibres of GFRC and PEFRC

Composite	V_f
GFRC	
G_1	0.089
G_2	0.179
G_3	0.267
G_4	0.356
PEFRC	
S_1	0.090
S_2	0.180
S_3	0.266
S_4	0.356

Table 2 Lay-up sequence and PEF fraction of hybrid composites

Lay-up sequence[a]	PEF fraction (%)
[GGGG]	0 (G_4)
[GSGG]	25.4
[SGSG]	50.6
[SSGS]	74.7
[SSSS]	100 (S_4)

[a] G, GF; S, PEF ply

were made from the same resin at room temperature until it solidified within the mould. Shrinkage was controlled by using extra resin in the mould. Finally, the composite was heated to a temperature of 55°C for 2 h in order to ensure the completion of MMA polymerization. A detailed description of the preparation of laminates was given elsewhere[20,22–24]. UD-laminates were prepared with up to four plies for PEF (designated as S_1 to S_4, respectively) and GF (designated as G_1 to G_4, respectively). The volume fractions of fibres (V_f) of both the laminates (GFRC and PEFRC) are given in Table 1. The lay-up sequence and relative proportion of PEF in hybrid laminates are given in Table 2[22]. The total V_f of hybrid composites was held constant at 35.6% and the proportion of PEF was varied from 0 to 100% in steps of approximately 25%.

A stress relaxation experiment was carried out at 25 ± 1°C, using a dumb-bell shaped test specimen in an Instron Universal Testing machine. The specification of the dumb-bell was as follows: gauge length 20 mm, width 6 mm and thickness 1.70 mm, were loaded parallel to the fibres with serrated jaw wedge grips. Specimens were stretched at a speed of 5 mm min^{-1} up to strain levels of 0.5, 1.5 and 2.0%, 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 three strain 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 has been observed that the rate of stress relaxation (as indicated by the slope) increases with the strain level (*Figure 2*).

Figure 3 shows the variation of σ/σ_0 with t for GFRC. The rate of stress relaxation decreases with increasing glass content at all strain levels from G_1 to G_4 (*Figure 2*)—this behaviour may be due to the elastic nature of GF. From *Figure 2* it is clear that the rate of stress relaxation tends to flatten with increasing strain level. This behaviour is probably due to the fact that the fibre–matrix interface bonding has a greater effect at higher strain level.

The results of PEFRC samples are shown in *Figure 4*. Unlike in the case of PMMA and GFRC, experimental points for these systems appear to lie on two straight lines, the first line is of greater slope (Table 3) and applies for short times, whilst the second line is for longer times. The initial relaxation may arise from a rearrangement or reorientation at the viscoelastic PEF–PMMA interface[25].

Unlike GFRC, the rate of stress relaxation (initial slope) of PEFRC increases with the increase in volume fraction of PEF at all strain levels (*Figure 2*). This behaviour of PEFRC is inherently implied from the viscoelastic nature of PEF. At the same V_f and strain level, the slope is much higher for PEFRC than for

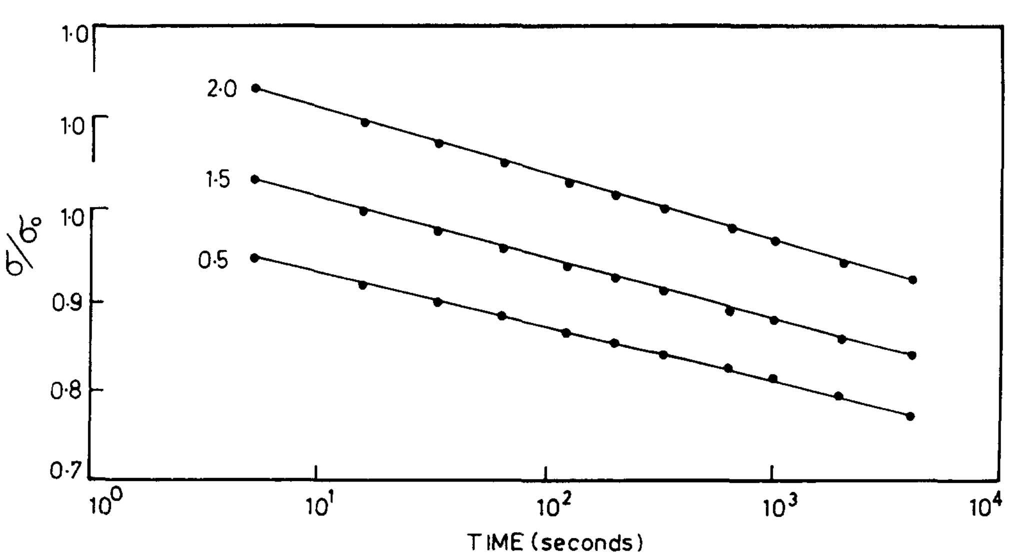

Figure 1 Stress–relaxation curves for PMMA. Successive graphs are displaced upward by 0.1 for clarity. Figures on the left hand side against lines indicate strain (%)

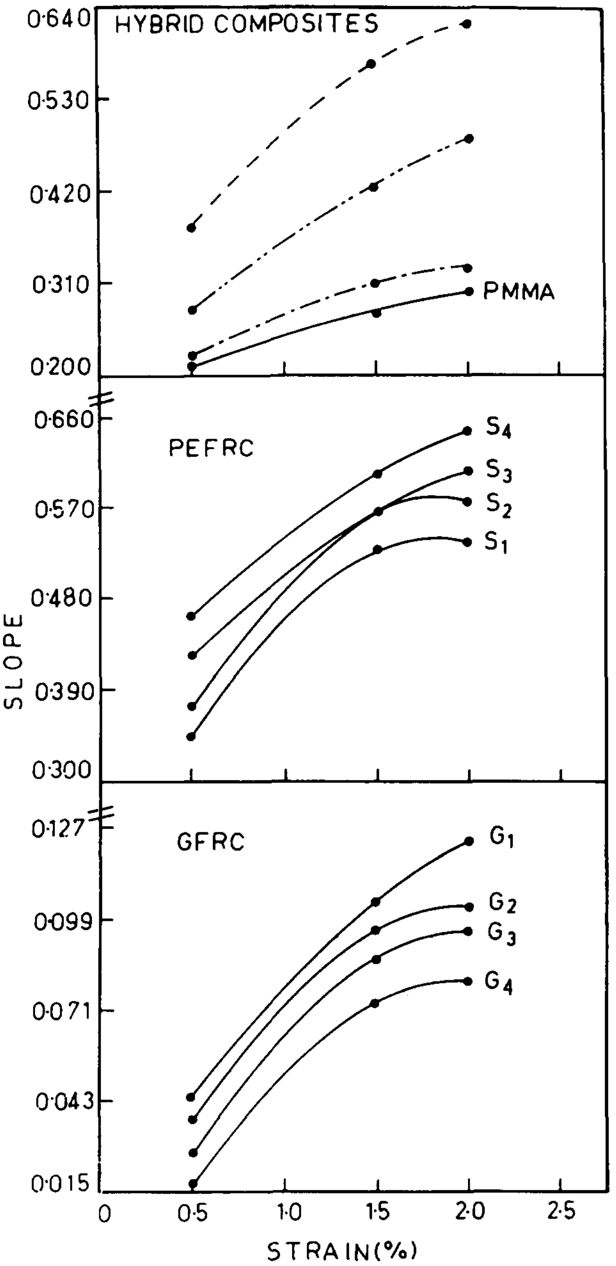

Figure 2 Variation of slope (rate of stress relaxation) with strain (%). For PEFRC and hybrid composite graphs, the initial slope is plotted against strain. (———) 0% PEF; (—·—) 25.4% PEF; (—··—) 50.6% PEF; (- - - - -) 74.7% PEF; (— —) 100% PEF; (●) points for 0.5% strain; (○) points for 1.5% strain; (△) points for 2.0% strain

GFRC. The difference of the slope between these two laminates at the same strain level increases from one ply to four plies because of the differing nature of the fibres. From *Figure 2* it is observed that at higher strain level the PEFRC curves tends to level off, similar to GFRC curves.

A method[26] of estimating the contribution of 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 3*. From *Figure 5* it is seen that at the same V_f, the contribution of the early process increases with strain level initially but tends to be independent or nearly independent at higher strain level, i.e. the bonding at the fibre–matrix interface has a greater effect at higher strain[25] as discussed previously.

Furthermore, it may 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 GF with a viscoelastic PEF, a considerable drawback in long-term properties can be expected. *Figure 6* shows the variation of σ/σ_0 with t for hybrid laminates. When the relative volume of PEF is 25.4%, the rate of stress relaxation decreases with time at all strain levels in a single straight line. But in the case when the relative volumes of PEF are 50.6 and 74.7%, the stress decreases, giving two linear parts or lines, having a greater slope in the first part of the line, and the time of intersection of these two lines is approximately the same as PEFRC (*Table 4* and *Figure 6*). It is clear from *Figure 6* (and *Table 4*) that the long-term properties of GF–PEF hybrids are principally dominated by the viscoelastic nature of PEF. The variation of rate of stress relaxation and contribution of early process with strain level (*Figures 2* and *5*) are the same as PEFRC which also indicates the influence of PEF in hybrid laminates.

Conclusions

The main conclusions can be summarized as follows: the composite laminate as a whole has been made at room temperature, the casting requiring a minimum amount of energy which may be regarded as an

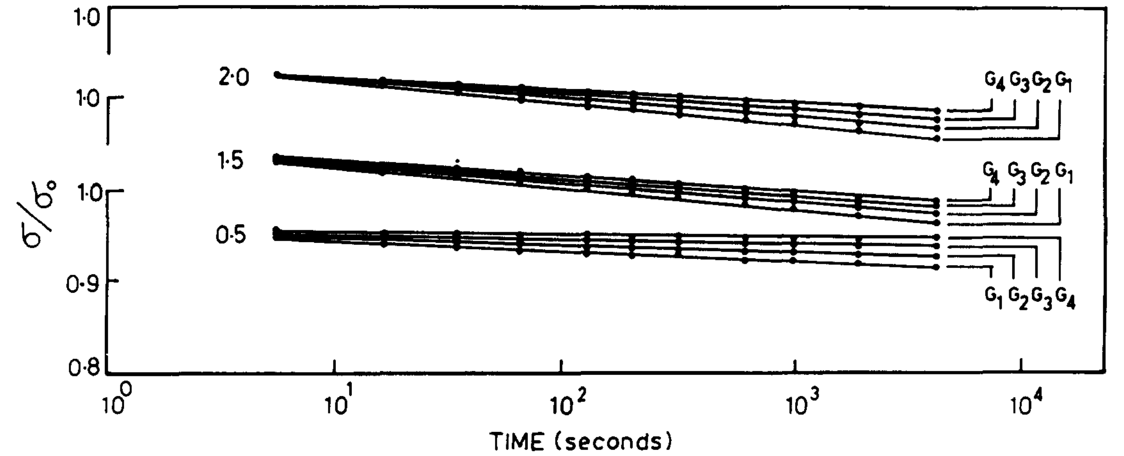

Figure 3 Stress–relaxation curves for GFRC. Successive graphs are displaced upward by 0.1. Figures on the left hand side against curves indicate strain (%)

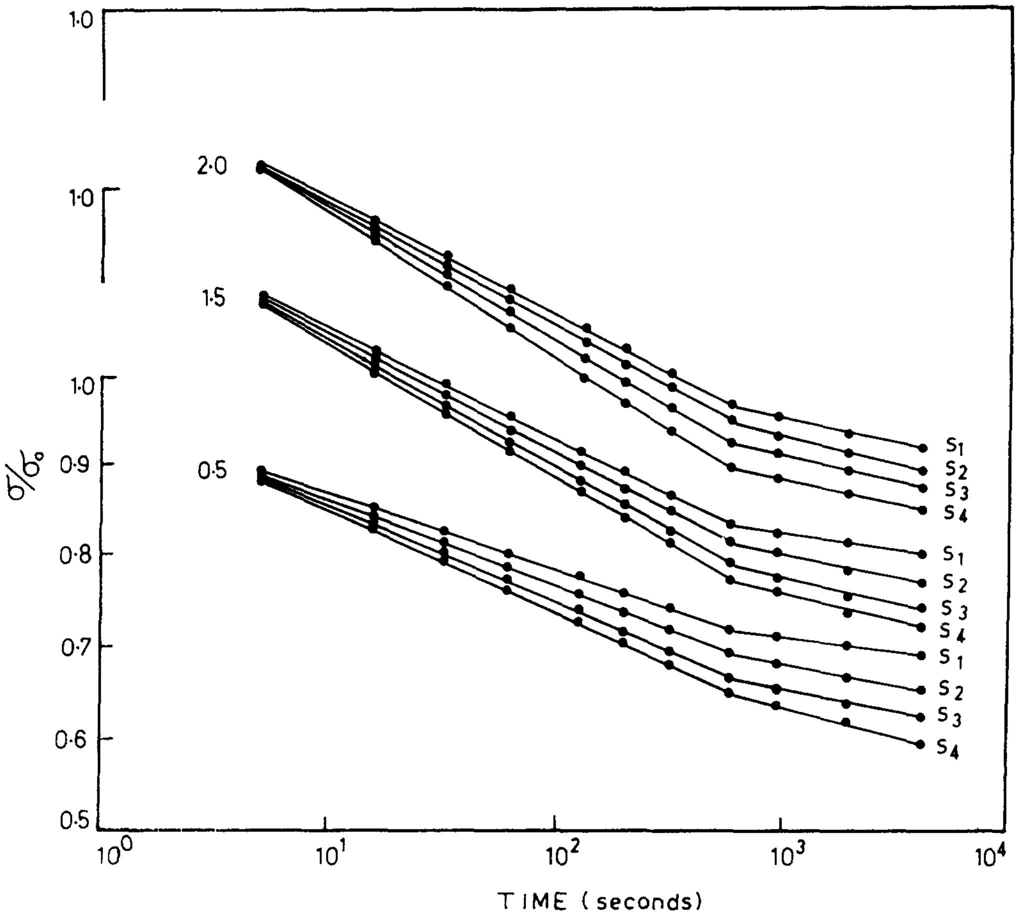

Figure 4 Stress–relaxation curves for PEFRC. Successive graphs are displaced upward by 0.2. Figures on the left hand side against curves indicate strain (%)

advantage of the system[20,22,23]. The rate of stress relaxation decreases from one ply to four plies for GFRC. The rate of stress relaxation increases from one ply to four plies for PEFRC which is the reverse case to GFRC. There are two distinct linear sections in the plot of stress vs time for PEFRC, but in the case of GFRC there is only one linear section. In GF–PEF hybrid laminates, the stress relaxation properties are dominated principally by the PEF.

Acknowledgement

The award of a CSIR, Indian Fellowship (SRF) to Nirmal Saha is gratefully acknowledged.

Table 3 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
	S_4	0.466	0.249	0.217	0.955	0.820	0.135	14.13
1.5	S_1	0.532	0.176	0.356	0.975	0.750	0.225	23.07
	S_2	0.566	0.212	0.354	0.975	0.750	0.225	23.07
	S_3	0.577	0.240	0.337	0.976	0.745	0.231	23.67
	S_4	0.601	0.268	0.333	0.976	0.745	0.231	23.67
2.0	S_1	0.536	0.249	0.287	0.950	0.730	0.220	23.16
	S_2	0.577	0.249	0.328	0.950	0.715	0.235	24.74
	S_3	0.606	0.268	0.338	0.945	0.705	0.240	25.39
	S_4	0.649	0.268	0.381	0.945	0.685	0.260	25.51

Table 4 Results of stress relaxation measurements for hybrid composites

Strain (%)	PEF fraction (%)	Slope (negative)			Intercept at 1 s			Contribution of early process (%)
		Early	Later	Difference	Early	Later	Difference	
0.5	0 (G_4)	0.017	—	—	0.965	—	—	—
	25.4	0.222	—	—	0.961	—	—	—
	50.6	0.277	0.141	0.081	0.957	0.830	0.127	13.27
	74.7	0.374	0.176	0.198	0.955	0.825	0.130	13.61
	100 (S_4)	0.466	0.249	0.217	0.955	0.820	0.135	14.13
1.5	0 (G_4)	0.072	—	—	0.961	—	—	—
	25.4	0.306	—	—	0.957	—	—	—
	50.6	0.424	0.176	0.248	0.970	0.745	0.225	23.20
	74.7	0.577	0.231	0.301	0.971	0.745	0.226	23.27
	100 (S_4)	0.601	0.268	0.333	0.976	0.745	0.231	23.67
2.0	0 (G_4)	0.079	—	—	0.945	—	—	—
	25.4	0.325	—	—	0.945	—	—	—
	50.6	0.488	0.176	0.312	0.941	0.696	0.245	26.04
	74.7	0.625	0.231	0.394	0.945	0.705	0.240	25.40
	100 (S_4)	0.649	0.268	0.381	0.945	0.685	0.260	25.51

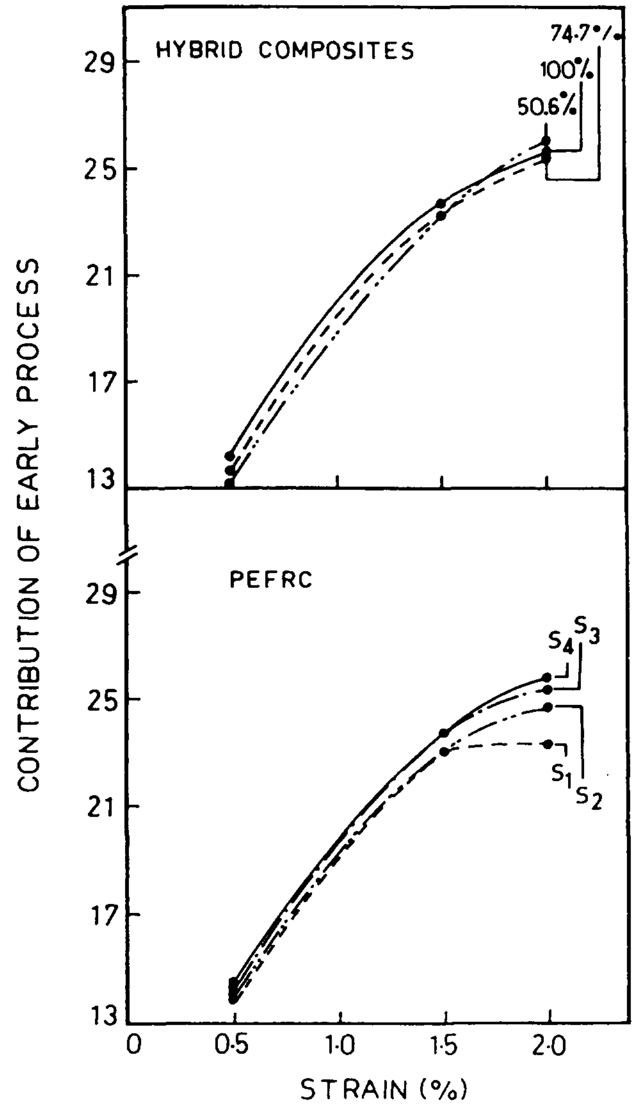

Figure 5 Variation of contribution of early process with strain (%). Figures against curves in hybrid composite graphs indicate relative PEF fraction (%)

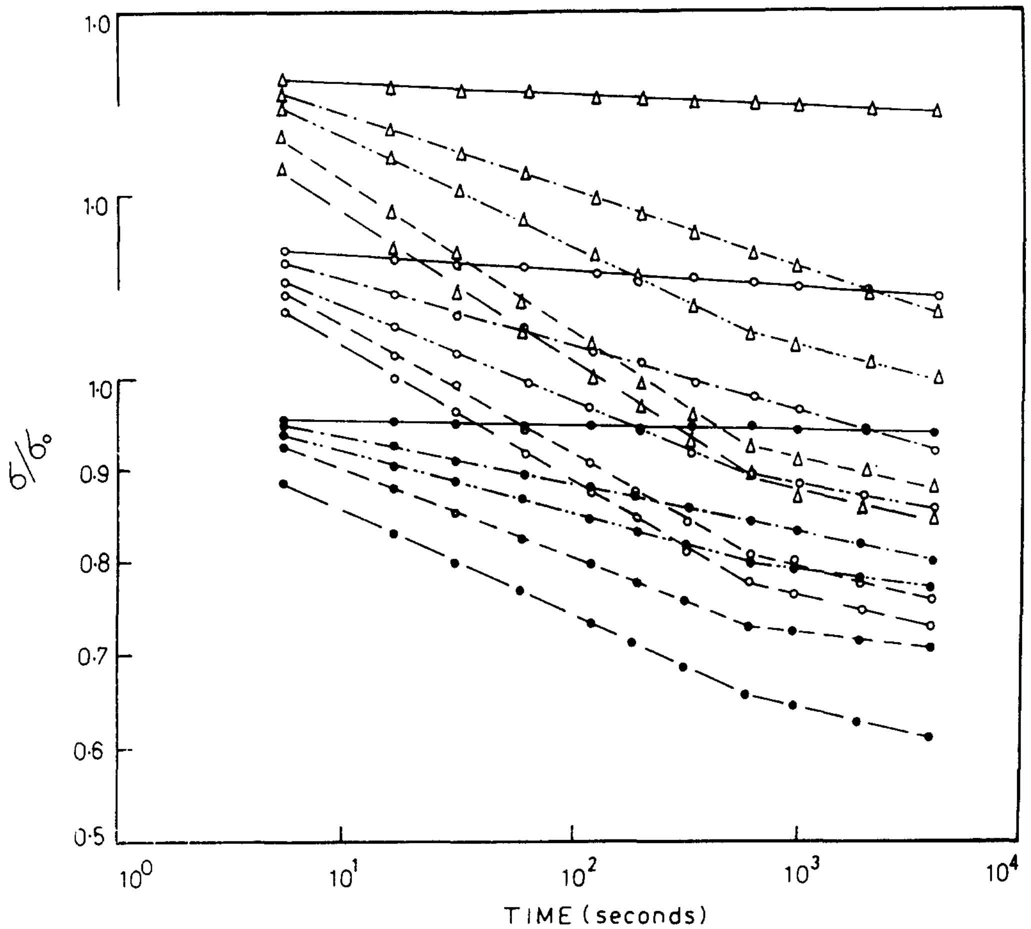

Figure 6 Stress–relaxation curves for hybrid laminates. Successive graphs are displaced upward by 0.2. (———) 0% PEF; (— • —) 25.4% PEF; (— • • —) 50.6% PEF; (- - - - -) 74.7% PEF; (— —) 100% PEF; (●) points for 0.5% strain; (○) points for 1.5% strain; (△) points for 2.0% strain

References

1 Lemstra, P. J., Kirschbaum, R., Ohta, T. and Yasuda, H. 'Developments in Oriented Polymers—2', Elsevier, London, 1987, pp. 39–77
2 Peijs, A. A. J. M., Catsman, P., Govaert, L. E. and Lemstra, P. J. *Composites* 1990, **21**, 513
3 Grubb, D. T. and Li, Z. F. *Polymer* 1992, **33**, 2587
4 Ward, I. M. and Wilding, M. A. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 561
5 Peijs, A. A. J. M., Venderbosch, R. W. and Lemstra, P. J. *Composites* 1990, **21**, 522
6 Peijs, A. A. J. M. and De Kok, J. M. M. *Composites* 1993, **24**, 19
7 Adams, D. F. and Zimmerman, R. S. Proc. 31st Int. SAMPE Symp., 1986, pp. 1456–1468
8 Poursartip, A., Riahi, G., Teghtsoonian, E. and Chinatambi, N. Proc. 19th Int. SAMPE Tech. Conf., 1987, pp. 503–514
9 Peijs, A. A. J. M. and Lemstra, P. J. Proc. 3rd Rolduc Polymer Meeting, Elsevier, London, 1989, pp. 218–227
10 Kodokian, G. K. A. and Kinlock, A. J. *J. Mater Sci. Lett.* 1988, **7**, 625
11 Hoggatt, J. T., Oken, S. and House, E. E. U.S. Air Force Report AFWAL-TR-80-3023, April, 1980
12 Ghosh, P., Mitra, P. S. and Banerjee, A. N. *J. Polym. Sci., Polym. Chem. Edn* 1973, **11**, 2021
13 Ghosh, P. and Banerjee, A. N. *J. Polym. Sci., Polym. Chem. Edn* 1975, **12**, 375
14 Ghosh, P., Biswas, S. and Niyogi, U. *J. Polym. Sci., Part A: Polym. Chem. Edn* 1986, **24**, 1053
15 Ladizesky, N. H. and Ward, I. M. *J. Mater. Sci.* 1983, **18**, 533
16 Ladizesky, N. H. and Ward, I. M. *J. Mater. Sci.* 1989, **24**, 3763
17 Yamaki, J. I. and Katyama, Y. *J. Appl. Polym. Sci.* 1975, **19**, 2897
18 Sellitti, C., Vargiu, S., Martuscelli, E. and Fabbro, D. *J. Mater. Sci.* 1987, **22**, 3477
19 Tissington, B., Pollard, G. and Ward, I. M. *J. Mater. Sci.* 1991, **26**, 82
20 Saha, N., Banerjee, A. N. and Mitra, B. C. *Polym. Adv. Technol.* 1995, **6**, 637
21 Ghosh, P. and Mukherjee, N. *Eur. Polym. J.* 1979, **15**, 797
22 Saha, N., Banerjee, A. N. and Mitra, B. C. *Polym. Commun.* (in press)
23 Saha, N., Banerjee, A. N. and Mitra, B. C. *J. Appl. Polym. Sci.* 1996, **60**, 657
24 Saha, N., Banerjee, A. N. and Mitra, B. C. *J. Appl. Polym. Sci.* 1996, **60**, 657
25 Bhagawan, S. S., Tripathy, D. K. and De, S. K. *J. Appl. Polym. Sci.* 1987, **33**, 1623
26 Mackenzie, C. I. and Scanlan, J. *Polymer* 1984, **25**, 559