JOURNAL OF MATERIALS SCIENCE 29 (1994) 4113–4118

Anisotropy in hysteresis loss and tension set in short-carbon-fibre-filled thermoplastic elastomers

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The effect of short-carbon fibre on the anisotropy in hysteresis loss and tension set of two thermoplastic elastomers, based on natural rubber, high-density polyethylene blend and styrene–isoprene–styrene block copolymer, were studied. The composites based on natural rubber–high density polyethylene blend show anisotropy both in hysteresis loss and tension set, whereas styrene–isoprene–styrene shows lack of anisotropy in both cases. An empirical relationship has been established relating $(\Delta w)_{lt}$, (the difference between the hysteresis loss between systems with longitudinal fibre orientation and transverse orientation) and the strain per cent and volume per cent of fibres.

1. Introduction

Short-fibre-filled rubbers are known to exhibit anisotropy in their physical properties such as stress–strain behaviour and tear resistance [1–3]. It has recently been reported that short-carbon-fibre-filled thermoplastic elastomers based on natural rubber–high density polyethylene exhibit anisotropy in dynamic mechanical properties such as storage modulus and mechanical loss factor [4], while the fibre-filled block copolymer of styrene–isoprene–styrene does not show such anisotropy [5]. This investigation reports the results of studies on anisotropy in hysteresis loss and tension set of short-carbon-fibre-filled thermoplastic elastomers such as styrene–isoprene–styrene block copolymer and 70/30 blend of natural rubber and high density polyethylene.

2. Experimental procedure

2.1. Materials

Natural rubber (NR): Crumb rubber, ISNR-5 grade, obtained from the Rubber Research Institute of India, Kottayam. Density, 0.92 g cm^{-3}.

High-density polyethylene (HDPE): Hostalen GB 7750 obtained from Polyolefins Industries Ltd, Bombay. Density, 0.95 g cm^{-3}; melt flow index, 10 g 10 min^{-1}; crystalline melting range, 128–132 °C.

Styrene–isoprene–styrene block copolymers: Kraton D-1107, with specific gravity of 0.92 and styrene/rubber ratio of 14/86, was obtained from Shell Development Company, USA.

Carbon fibre: RK-30, epoxy treated, obtained from RK Carbon Fibres Ltd, UK, filament diameters, 6.8 μm; density 1.78 g cm^{-3}; tensile strength, 3.0 GPa; tensile modulus, 220–240 GPa; carbon content, 95% mass.

Peroxide: Peroximon F-40, commercial grade, obtained from NICCO (I) Ltd, Calcutta.

Antioxidant: Flectol B, commercial grade, obtained from NICCO (I) Ltd, Calcutta.

2.2. Preparation of composites

Formulations of the composites are given in Table I.

2.2.1. Preparation of composites based on NR–HDPE blend

The composites were prepared in a Brabender Plasticorder (model PLE-330), using a cam-type rotor with the mixer chamber set at 150 °C. Polyethylene was melted in the mixer for 3 min, chopped carbon fibre (6 mm in length) added, and the composite mixed for a further minute. This was followed by the addition of previously masterbatched NR (with antioxidant and peroxide), which was mixed for a further 3 min. The

TABLE I Formulation of the composites

Ingredients (p.h.r.)*	Composite designation	
	B‡	*S*§
NR	70	–
HDPE	30	–
S–I–S	–	100
Carbon fibre	0, 5, 10, 20	0, 5, 10, 20
Antioxidant	1.5	–
Peroxide	0.7	–

* p.h.r. = parts per 100 parts of rubber.
‡ B_0, B_5, B_{10}, B_{20} = compounds containing 0, 5, 10 and 20 p.h.r. fibre, respectively, in NR–HDPE blend.
§ S_0, S_5, S_{10}, S_{20} = mixes containing 0, 5, 10 and 20 p.h.r. fibre, respectively, in S–I–S composites.

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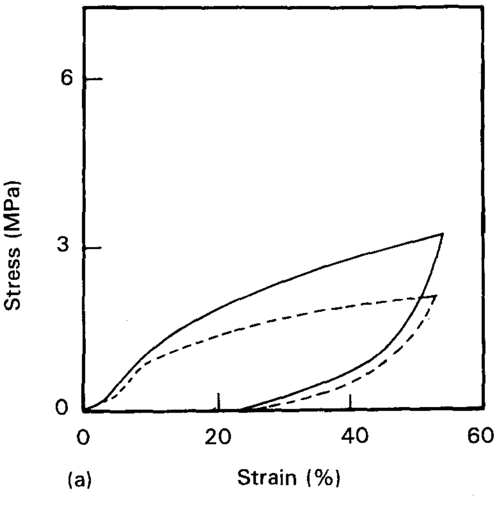
mix was then taken out and sheeted through a laboratory mill with a nip setting of 2 mm. The sheeted material was then remixed in the plasticorder at the same temperature for 2 min, and finally sheeted out through the two-roll mill to ensure uniform dispersion of the fibres and homogeneity of the blend [4]. The sheeted out stock was compression moulded between aluminium foils in an automatic Toyoseiki Labo-Press at 170 °C for 3 min. After 3 min moulding time the sample, still under compression, was cooled to room temperature. Aluminium foils are used between the mould surfaces to reduce shrink marks on the sheet.

2.2.2. *Preparation of composites based on S–I–S*

The composites were prepared in a Brabender Plasticorder (model PLE-330), with the parameters described above. Initially the S–I–S was melted in the mixer for 2 min. Then chopped carbon fibre (6 mm in length) was added to it and mixed for another 3 min. The mix was then taken out and sheeted through a laboratory mill with a nip setting of 2 mm. The sheeted material was then remixed in the plasticorder at 150 °C for 2 min to ensure uniform dispersion of the fibres and homogeneity of the blend, and finally sheeted out through the two-roll mill. The sheeted out stock was then compression moulded as described above.

2.3. Measurement of hysteresis loss

Dumbbell-shaped test pieces were cut in two directions: longitudinal (along the mill direction, hereafter referred to as L-composite) and transverse (across the mill direction, hereafter referred to as T-composite). The measurement of hysteresis at four extension levels (25, 50, 75 and 100%) was carried out at 25 °C using a Zwick Universal Testing Machine 1445, at a cross-head speed of 500 mm min^{-1}. The work done under the first stress–strain cycle was obtained by measuring the area under the loop. The tension set at the end of the hysteresis cycle at 50% extension was measured



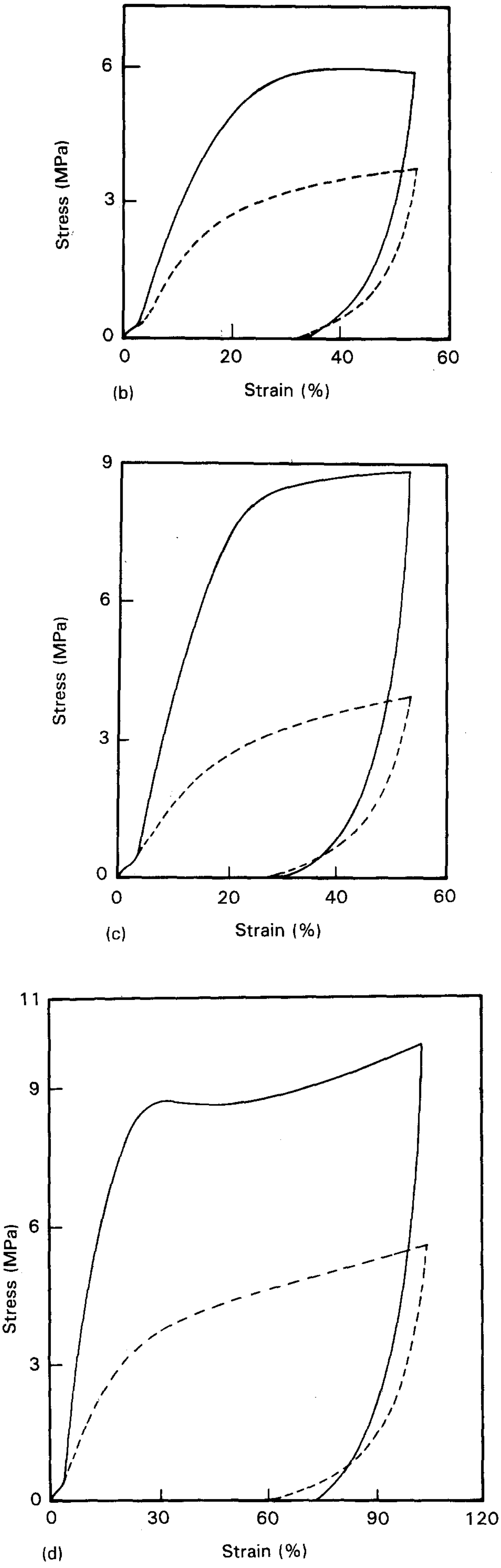


Figure 1 Hysteresis-loss curves for NR–HDPE blend composite, (a) unfilled, 50% extension; (b) 10 p.h.r. fibre-filled, 50% extension; (c) 20 p.h.r. fibre-filled, 50% extension; (d) 20 p.h.r. fibre-filled, 100% extension. (——) L; (– – –) T composites.

by repeating the experiment each time after 0, 3, 6, 12 and 24 h.

3. Results and discussion

Fig. 1a and b shows the hysteresis curves for L and T composites for the unfilled and 10 p.h.r. short-carbon-fibre-filled NR–HDPE blends, respectively, under 50% extension.. It is apparent that anisotropy in hysteresis exists both in the gum and fibre-filled composites. Existence of anisotropy in mechanical properties of this type of blend has been reported previously [6]. Incorporation of short fibre in the blend increases the hysteresis loss for both L and T composites. The hysteresis-loss curves for the 20 p.h.r.-filled composites at 50 and 100% extension are shown in Fig. 1c and d, respectively. It may be observed from the figures that increase in percentage strain causes increase in hysteresis loss. Fig. 2a and b shows the hysteresis curves for the unfilled and 10 p.h.r. short-carbon-fibre-filled S–I–S composites, respectively, at 50% extension. The increase of hysteresis loss with the incorporation of fibres is evident from these figures. Fig. 2c and d represent, respectively, the hysteresis loss of the 20 p.h.r. short-carbon-fibre-filled S–I–S block copolymer at 50 and 100% extension. It is observed that anisotropic effect in these composites is not as prominent as in the case of NR–HDPE blends. Earlier it has been observed that random fibre distribution caused lack of anisotropy in mechanical properties in short-carbon-fibre-filled S–I–S [5] composites.

The anisotropy in the fibre-filled composites is possibly due to the non-random fibre orientation within the matrix. During mixing in the Brabender Plasticorder, lower viscosity of the polymer matrix helps in increasing the degree of randomness in fibre orientation [5]. The S–I–S viscosity is lower than that of NR–HDPE composite under similar conditions [7, 8] (1.16 kPa s^{-1} for S–I–S, and 1.30 kPa s^{-1} for NR–HDPE at 180 °C and 50.6 s^{-1}), and therefore fibres are expected to be more randomly oriented in the former than latter. Scanning electron micrographs showing the different orientation of fibres in the two systems are shown in Fig. 3. The smaller extent of anisotropy in S–I–S composite is therefore thought to be due to increased randomness in fibre orientation as compared to NR–HDPE blends.

The increase in anisotropy with increasing fibre loading is due to the build-up of structural resistance of the matrix to the deformation (i.e. increased modulus: 25% modulus for 0, 5, 10, 20 p.h.r.-filled composites are 1.78, 3.23, 5.0 and 6.10 MPa for NR–HDPE [4] composites, and 0.38, 0.41, 0.67 and 1.0 MPa for S–I–S [5] composites, respectively). To evaluate the relationship between anisotropy and fibre loading, the difference between the hysteresis work

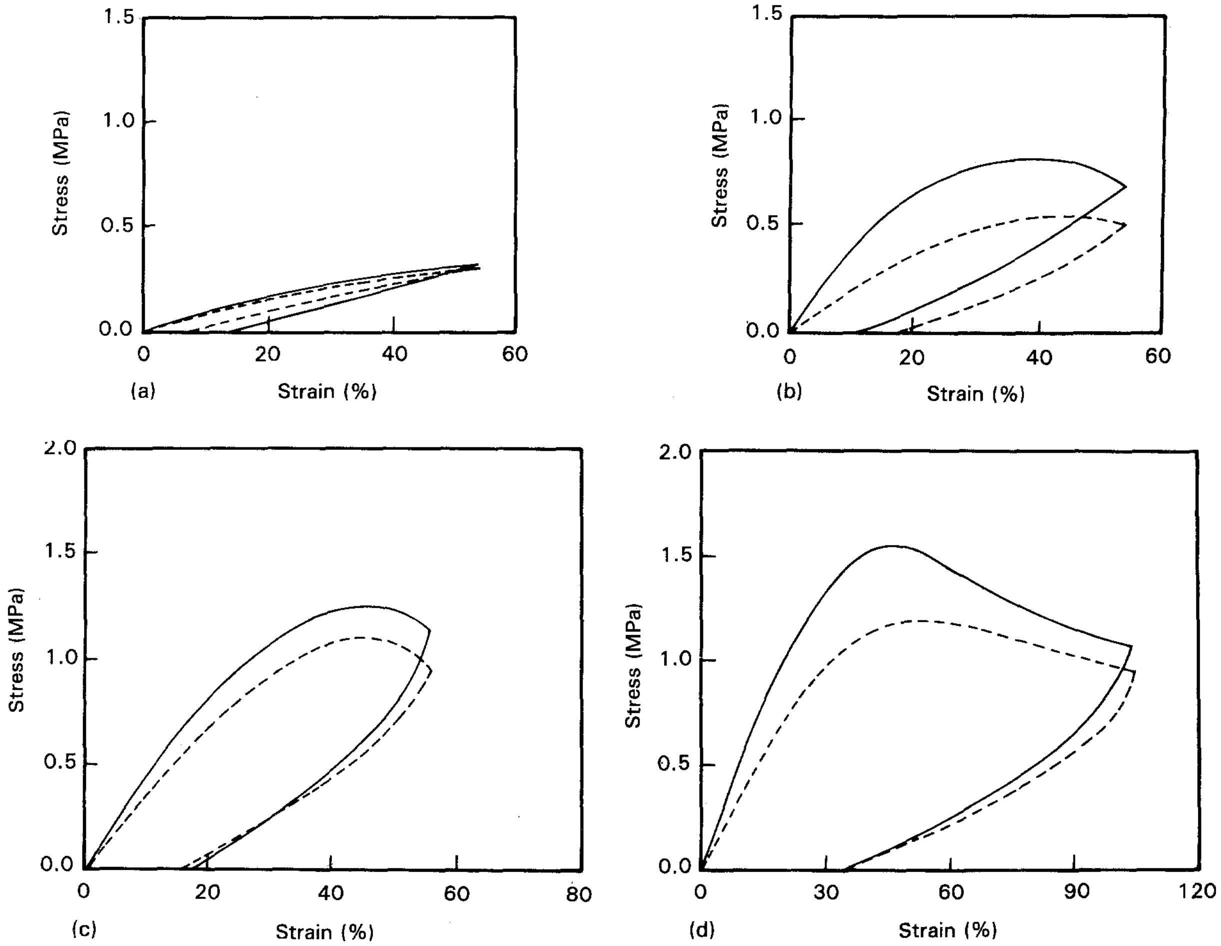


Figure 2 Hysteresis-loss curves for S–I–S composite, (a) unfilled, 50% extension; (b) 10 p.h.r. fibre-filled, 50% extension; (c) 20 p.h.r. fibre-filled, 50% extension; (d) 20 p.h.r. fibre-filled, 100% extension. (——) L; (– – –) T composites.

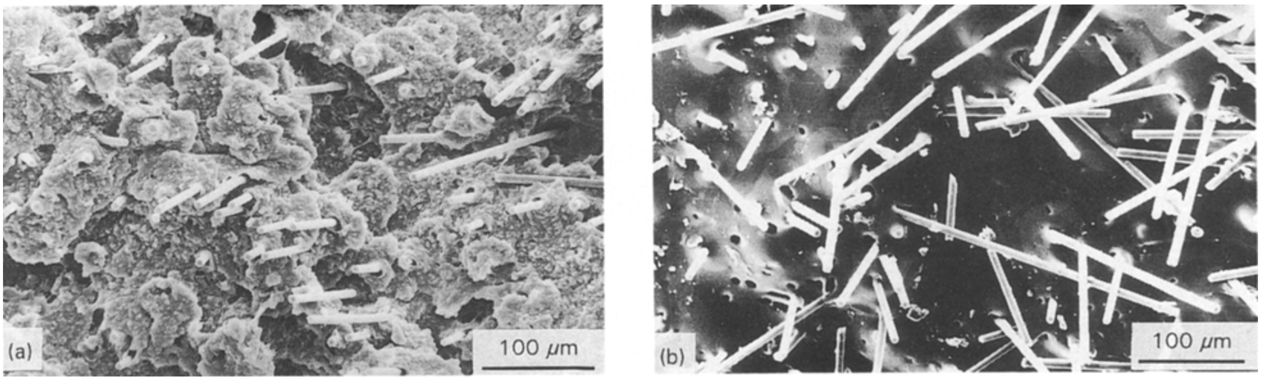


Figure 3 SEM micrograph of fractured surfaces of 10 p.h.r. fibre-filled, (a) NR–HDPE; (b) S–I–S composites.

TABLE II Values of w_1 of NR–HDPE and S–I–S composites

Sample designation		W_1 (J m^{-2}) × 10^3			
		25%	50%	75%	100%
NR–HDPE system					
B_0	L	11.4	35.5	54.6	91.4
	T	6.7	21.7	38.8	63.9
B_5	L	22.6	62.2	98.8	182.0
	T	10.2	35.8	53.3	67.5
B_{10}	L	34.5	95.5	113.5	218.8
	T	12.8	44.5	62.8	94.5
B_{20}	L	38.5	110.0	159.5	292.5
	T	17.8	52.0	81.6	127.5
S–I–S system					
S_0	L	0.16	1.3	1.5	4.0
	T	0.17	1.0	1.5	2.3
S_5	L	1.5	4.1	6.4	15.6
	T	1.1	3.3	6.2	10.6
S_{10}	L	3.4	8.3	1.5	24.8
	T	2.0	5.7	1.1	18.2
S_{20}	L	4.9	13.9	2.2	40.8
	T	4.5	11.2	2.2	30.7

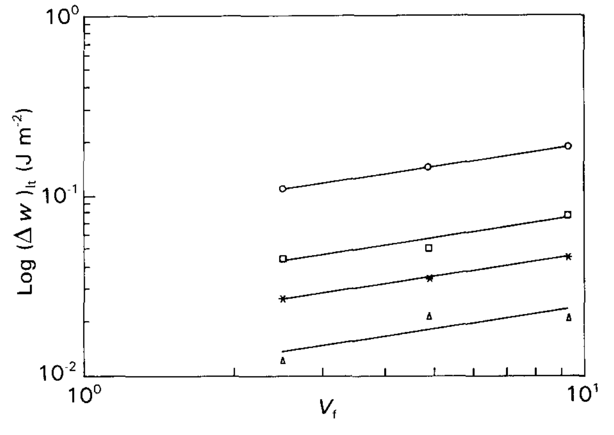


Figure 4 Log–log plot of difference in hysteresis loss (Δw_{lt}) against volume per cent of fibre (V_f) of NR–HDPE composites. ○, 100; □, 75; ×, 50; △, 25%.

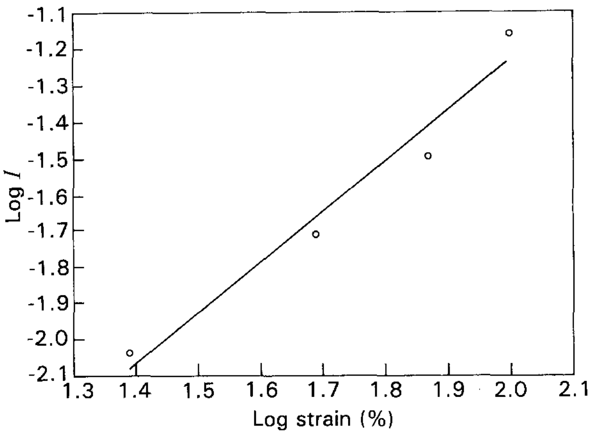


Figure 5 Plot of intercept I (Fig. 4) against percentage strain.

for L and T composites (Table II), Δw_{lt}, is plotted against the volume per cent of fibre loading (Fig. 4) on a log–log plot at different strain rates. For the S–I–S system, as the anisotropic effect is negligible, no correlation has been attempted. For the NR–HDPE system, the plots are parallel straight lines with constant slope and varying intercept, I. The intercept has been plotted against per cent strain, γ, which gives a straight line (Fig. 5). This relationship is represented by the following equations,

$$\Delta w_{lt} = f(\gamma, V_f) \quad (1)$$

$$\Delta w_{lt} = K\gamma^a V_f^b \quad (2)$$

where γ = percentage strain; V_f = volume per cent of fibres; K = intercept of I against γ plot; a = slope of I against γ plot; b = slope of Δw_{lt} against V_f plot. The values of k, a and b are 9.35×10^{-5}, 1.4 and 0.4, respectively.

Hence the relationship can be written as

$$\Delta w_{lt} = 9.35 \times 10^{-5}\, \gamma^{1.4}\, V_f^{0.4} \quad (3)$$

The reverse stress–strain cycle of all composites studied shows a finite strain at zero stress, i.e. these systems show tensile set. The tensile set for the NR–HDPE system is almost twice than that for the S–I–S system (Figs 1 and 2). This shows that the elastic recovery of S–I–S composites is much faster than for the NR–HDPE system. Experiments were carried out to ascertain whether there was anisotropy in tensile set, and the results are plotted in Fig. 6. It can be seen that the percentage tensile set increases up to 6 h and then remains practically constant (permanent set), particularly for the NR–HDPE system, whereas for S–I–S

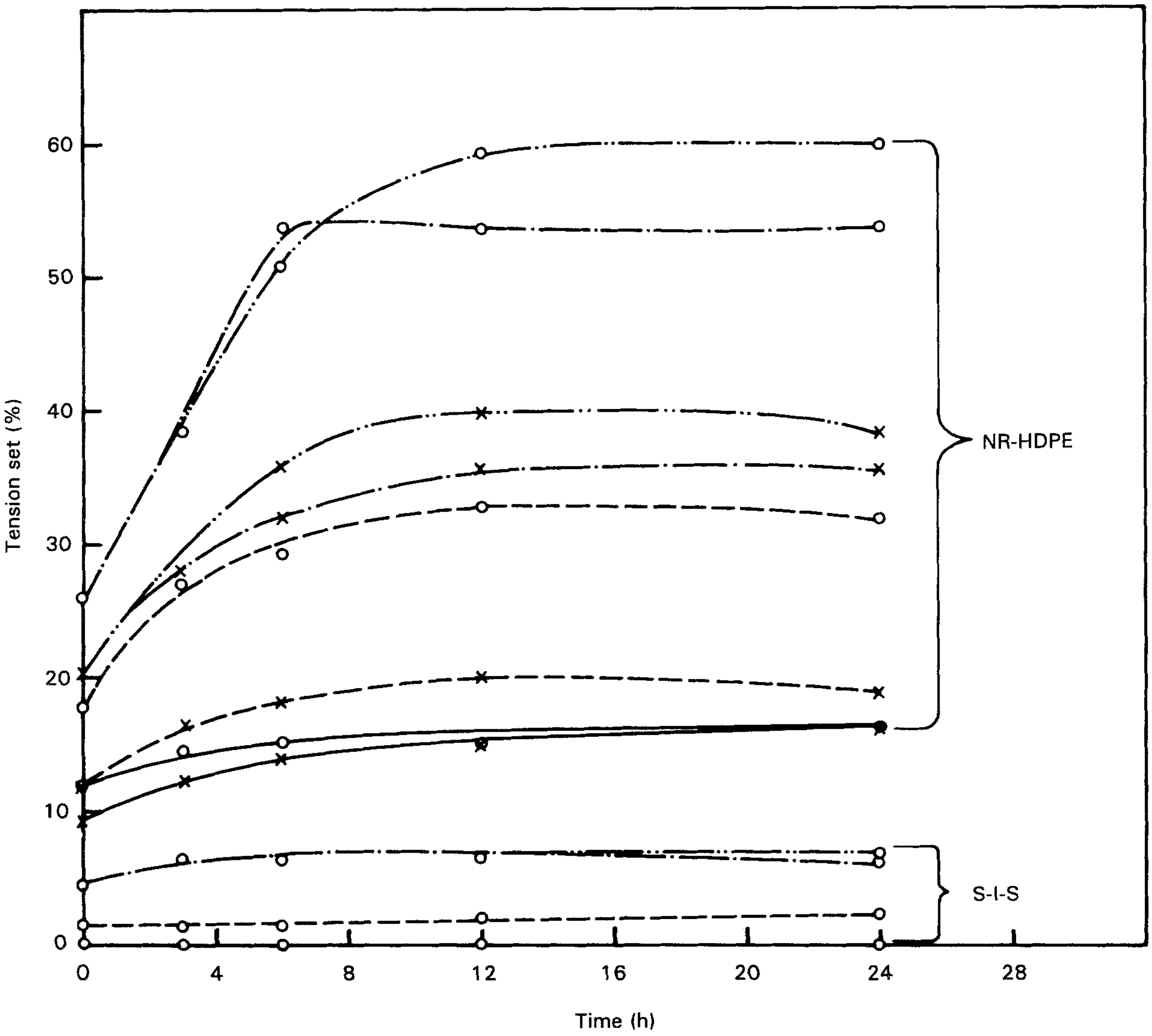


Figure 6 Plot of percentage set of composites against time for both NR–HDPE and S–I–S system. ○, L; ×, T composites. (——) NH-0; (– – –) NH-5; (–·–) NH-10; (–··–) NH-20.

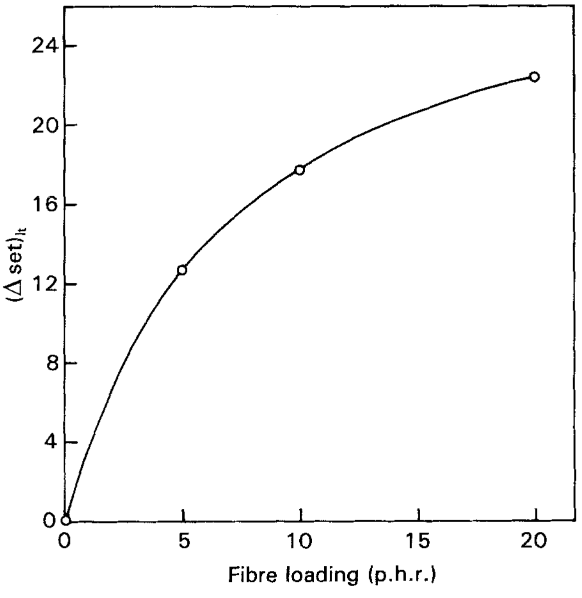


Figure 7 Plot of percentage permanent set difference $(\Delta\ \text{set})_{\text{lt}}$ against fibre loading for NR–HDPE system.

composites it is very low and independent of time. For the NR–HDPE system, the set values for L composites are more than those for T composites, indicating the presence of anisotropy in tensile set. There is, however, no anisotropy in set for S–I–S composites. The permanent set difference between L and T composites, i.e. $(\Delta\ \text{set})_{\text{lt}}$ for the NR–HDPE system increases with fibre loading as shown in Fig. 7. The inherent reasons for this anisotropy in tensile set are essentially the same as those for hysteresis loss anisotropy as discussed above.

4. Conclusions

1. The NR–HDPE system shows considerably higher hysteresis loss and tensile set anisotropy as compared to the S–I–S system.
2. The S–I–S system shows negligible anisotropy of both types.
3. For the NR–HDPE system, the hysteresis loss anisotropy is a function of both percentage strain and

fibre loading, and an empirical relationship between Δw_{lt} and V_{f} has been developed.

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Received 7 September 1992
and accepted 16 December 1993