

Structure-Property Relationship in Heat-Set Poly(ethylene Terephthalate) Fibers. III.

Stress-Relaxation Behavior

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Synopsis

Stress-relaxation studies between room temperature and 140°C were made on oriented multifilament poly(ethylene terephthalate) (PET) yarn and on four other samples which had been prepared by heat-setting this yarn at 180 and 230°C while free to relax and when held taut at constant length. Using the time-temperature superposition principle, the data were superimposed, and the master curves of relaxation modulus were constructed for each sample; the relaxation-time spectra for these samples were computed using the Alfrey approximation. The results revealed that (i) the free-annealed samples show higher visco-elasticity than the corresponding taut-annealed samples and (ii) the relaxation-time spectra show two prominent relaxation processes on logarithmic time scale in the case of all the samples; the two relaxations being more intense in the free-annealed samples. These observations are interpreted in terms of fiber structure and morphology, which had been studied earlier; the amorphous orientation in the free-annealed samples is low, and they have a more distinct separation of the crystalline and amorphous phases. These factors facilitate molecular relaxation processes in the non-crystalline phase; the relaxations are therefore relatively more intense in these samples, and they exhibit more viscoelasticity.

INTRODUCTION

The viscoelastic properties of oriented poly(ethylene terephthalate) (PET) fibers have been studied by stress-relaxation of oriented fibers¹ and of biaxially oriented films.² While these studies have led to a phenomenological understanding of the stress-relaxation behavior in terms of the time-temperature superposition principle, there is still a clear need to identify the structural and morphological factors which govern the viscoelasticity of these systems; it was with this aim that the present studies were undertaken. Commercial drawn multifilament PET yarn was heat-set at 180°C and at 230°C in a silicone oil bath when free to relax and when held taut at constant length. These taut annealed and free annealed samples have different structures and morphologies,^{3,4} and their stress-relaxation characteristics were determined along with those of the commercial sample (called the control sample) at temperatures from ambient to 140°C. Master curves of stress-relaxation modulus were constructed using time-temperature superposition principle, and the relaxation time distribution spectra were also computed. These data were then analyzed in terms of sample morphology, and it is shown that the higher viscoelasticity of the free-annealed samples arose from their low amorphous orientation and a more

distinct phase separation between the crystalline and amorphous regions which allow relaxation processes to occur with greater ease.^{4,5}

EXPERIMENTAL

Sample Preparation. The material was a drawn (draw ratio 3.92) commercial multifilament yarn 76/36/0, i.e., 76 denier, 36 filaments, and zero twist. This sample will be referred to as control, and has been described in detail elsewhere.^{3,4} The yarn was heat-set in a silicone oil bath maintained at a fixed temperature within $\pm 2^\circ\text{C}$. The heat-setting was done at 180°C and 230°C under two conditions, viz., (i) when the yarn was free to relax (designated FA or free-annealed) and (ii) when the yarn was held taut at constant length (TA or taut-annealed) at each of the two temperatures for 5 min. The samples were taken out of the bath and allowed to reach ambient temperature; they were blotted, and then given a wash in carbon tetrachloride and finally allowed to dry in air.

Stress-Relaxation Measurements. Stress-relaxation measurements were made on an Instron Tensile Tester Model 1112 at various temperatures from ambient to 140°C . Yarn of 10 cm gauge length was extended to a present strain 0.5% within about 0.15 s, and the stress was then recorded on a chart for over 1000 s.

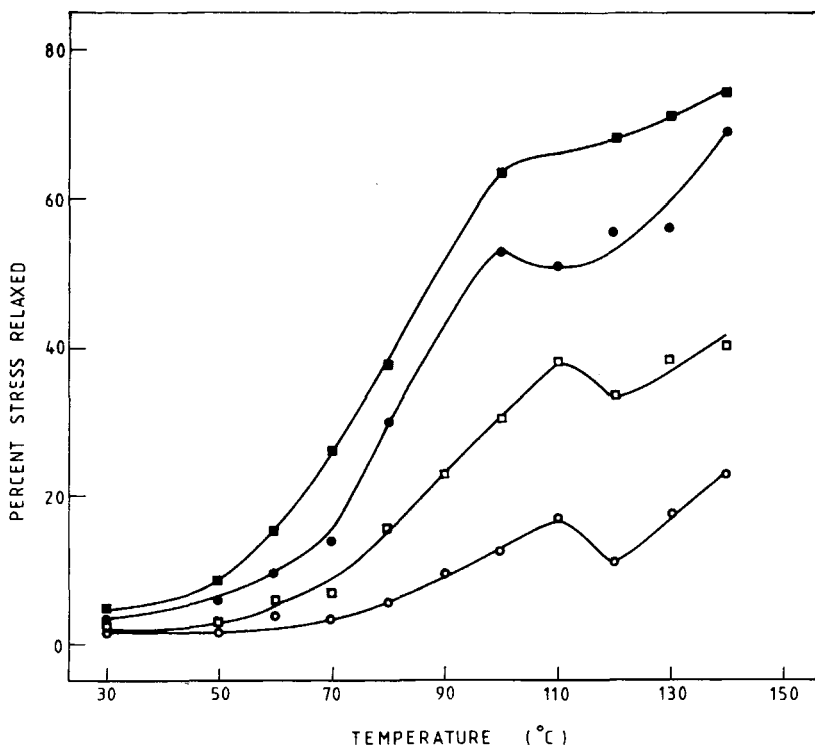


Fig. 1. Percentage stress relaxed vs. test temperature for control sample for various times (s): (■) 1000; (●) 100; (□) 10; (○) 1.

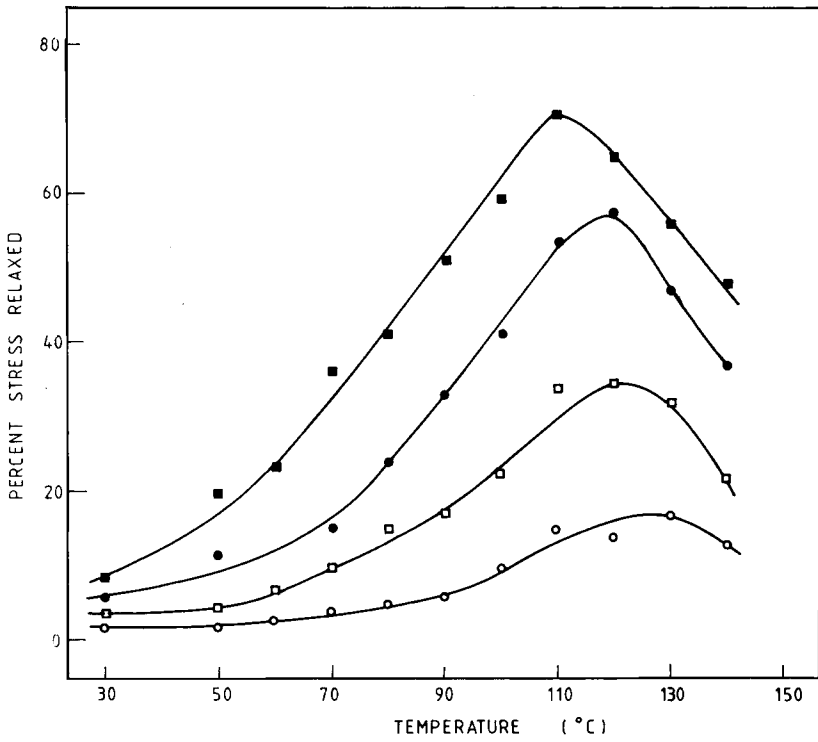


Fig. 2. Percentage stress relaxed vs. test temperature for FA-180 sample for various times (s): (■) 1000; (●) 100; (□) 10; (○) 1.

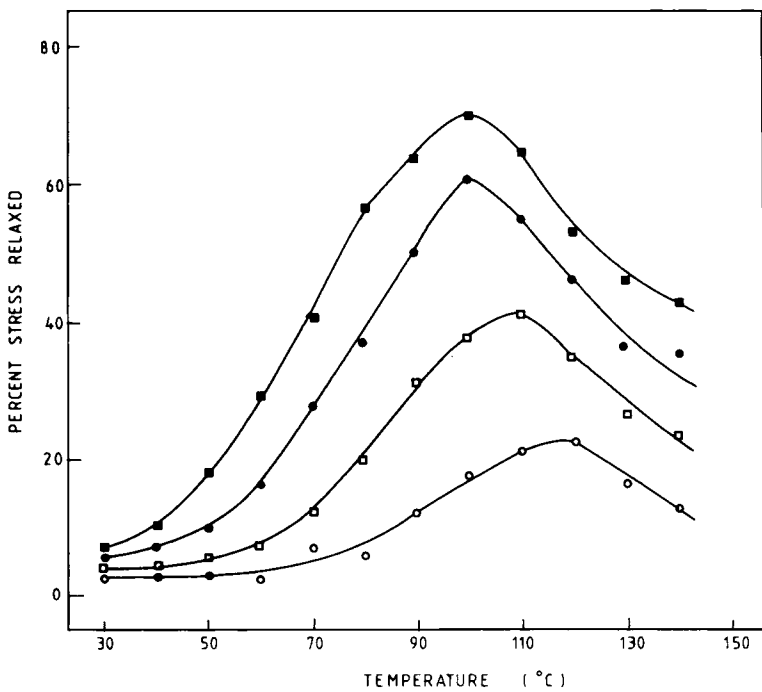


Fig. 3. Percentage stress relaxed vs. test temperature for FA-230 sample for various times (s): (■) 1000; (●) 100; (□) 10; (○) 1.

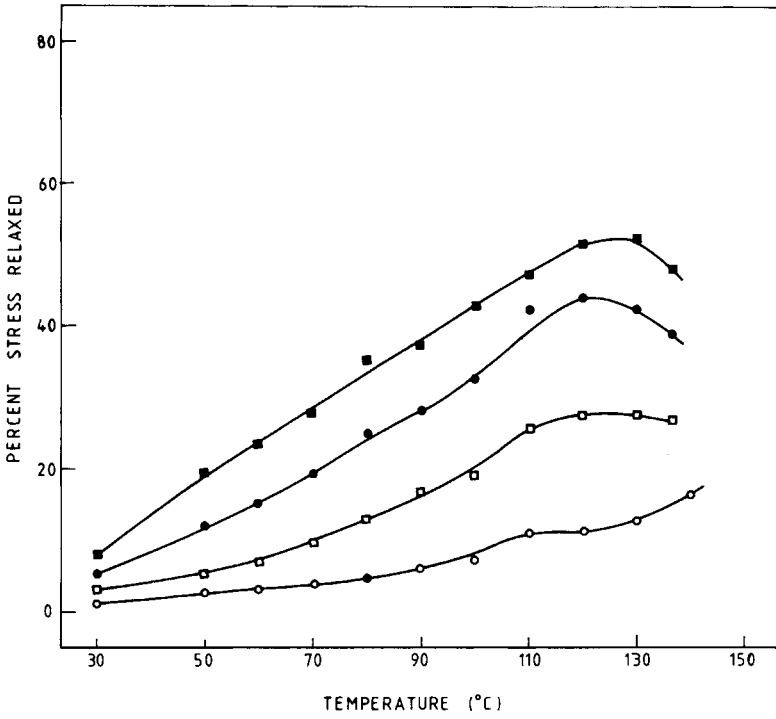


Fig. 4. Percentage stress relaxed vs. test temperature for TA-180 samples for various times (s): (■) 1000; (●) 100; (□) 10; (○) 1.

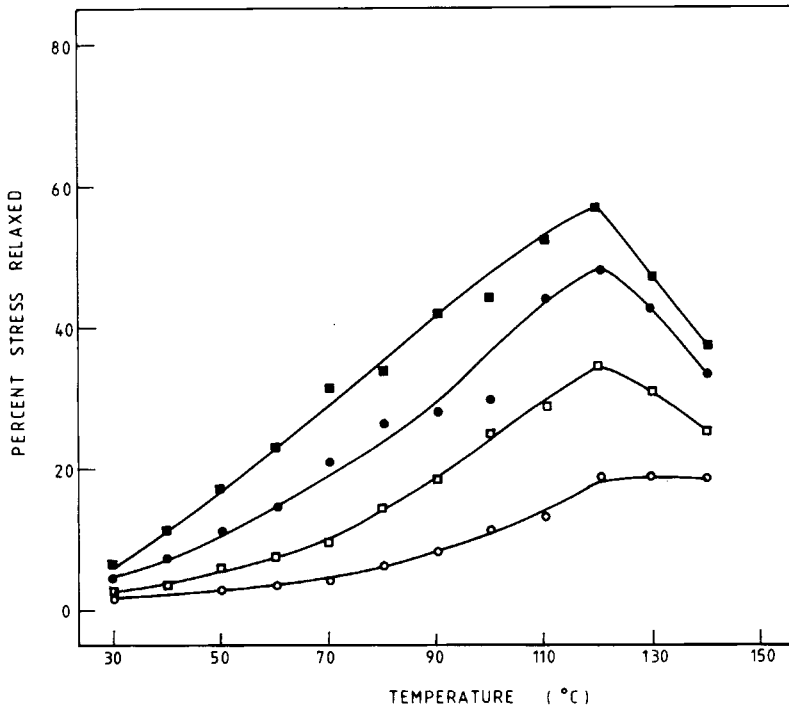


Fig. 5. Percentage stress relaxed vs. test temperature for TA-230 sample for various times (s): (■) 1000; (●) 100; (□) 10; (○) 1.

RESULTS AND DISCUSSION

The stress-relaxation data are presented in two ways. First the data for the Control, FA, and TA samples are shown in Figures 1-5, as percentage stress relaxed as a function of temperature of test at 1, 10, 100 and 1000 s. The data for 1 s and 1000 s are shown again in Figure 6 for all the samples. It is seen from Figures 1-5 that the control sample shows different behavior than the heat-set samples. In the heat-set samples, with increasing test temperature there is an increase in stress-relaxation up to 100-130°C, after which there is a decrease; well-defined maxima thus appear to be superimposed on the continuously increasing trend of the relaxed stress. It is seen from Figure 6 that the free-annealed samples always show higher stress-relaxation than the corresponding taut-annealed samples, thus indicating that the former are more viscoelastic. The control sample, however, shows low viscoelasticity at low temperatures of measurement. At high temperatures it becomes very viscoelastic. While detailed discussion of these effects will be made later in this section, it may be stated now that the stress-relaxation data for the control sample are not representative of the actual situation but represent data for this sample with the superposition of thermal history during the measurement. As pointed out elsewhere,⁶ the thermal behavior of this sample also showed extensive effects of the superposed thermal history. Such superposition of thermal effect is indeed

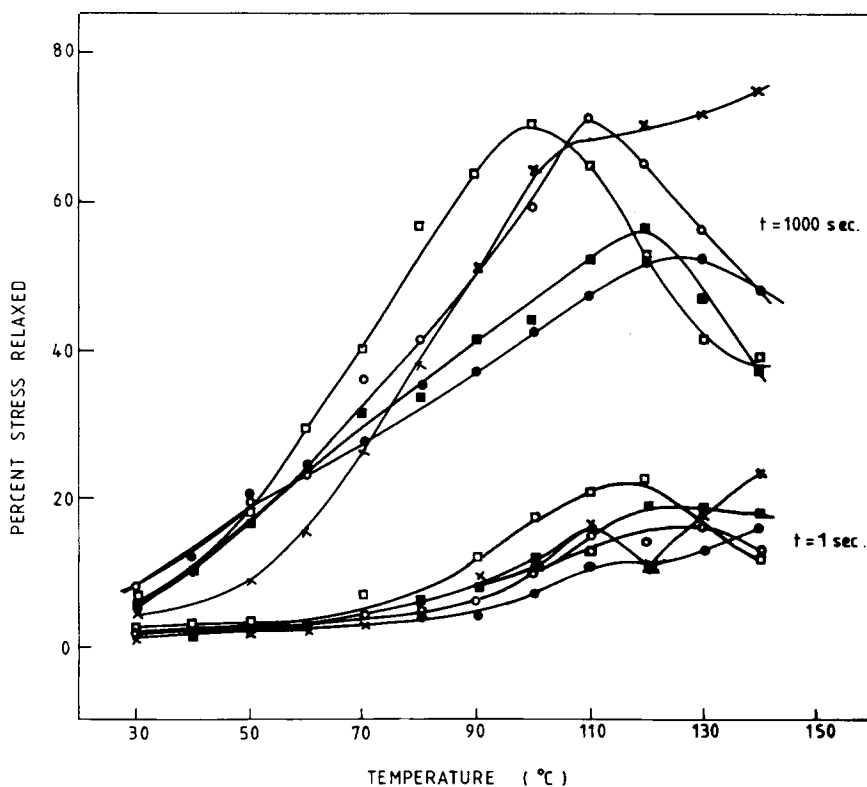


Fig. 6. Percentage stress relaxed vs. test temperature for various samples for 1 s and 1000 s: (X) control; (O) FA-180; (●) TA-180; (□) FA-230; (■) TA-230.

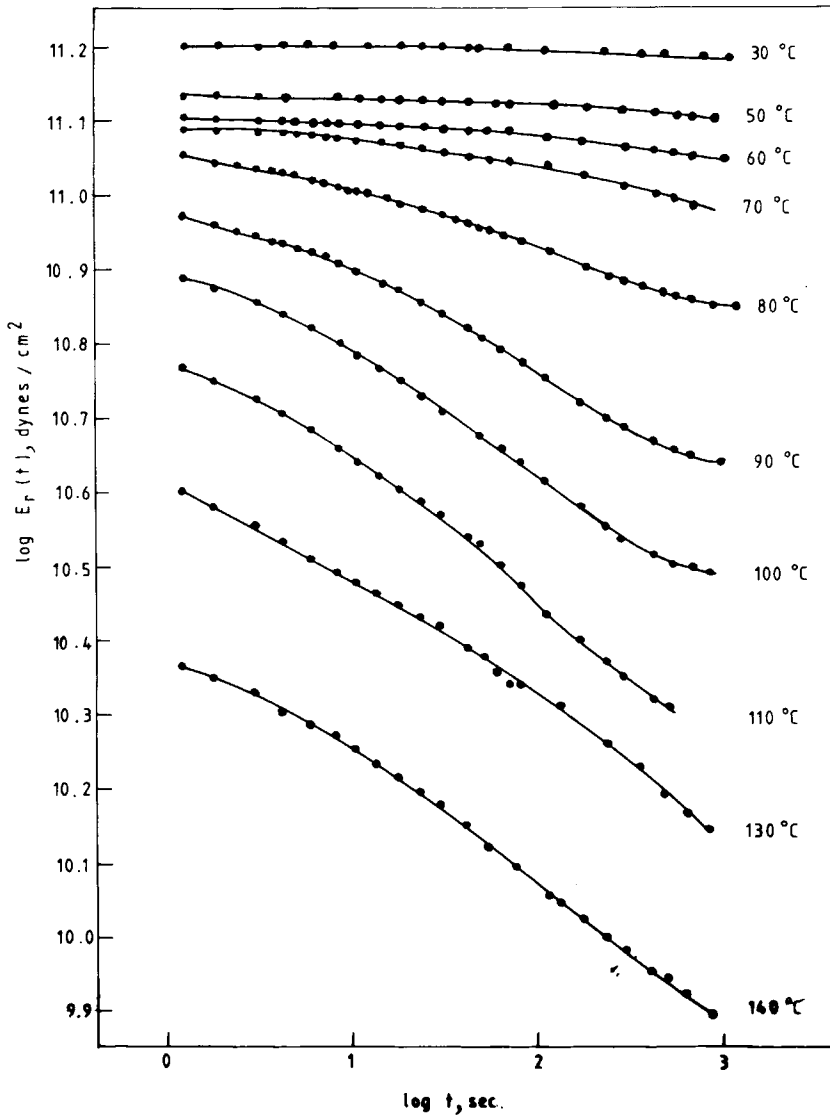


Fig. 7. The reduced modulus $[E_r(t)]$ data for control sample.

valid for the heat-set samples also, but since both the FA and TA samples have been heat-set at temperatures above the highest test temperature, viz., 140°C, the stress-relaxation data of these samples will be only slightly affected by the superposed thermal history. Thus in the case of the control sample, it may be assumed that only the low temperature data are representative of its actual behavior, and it has already been seen that at low temperatures it shows relatively low viscoelasticity, as would be expected from this sample.

It is also tempting at this stage to correlate the maxima in the percentage stress relaxed vs. test temperature curves with the glass transition temperature (T_g). The T_g data obtained from differential scanning calorimetry

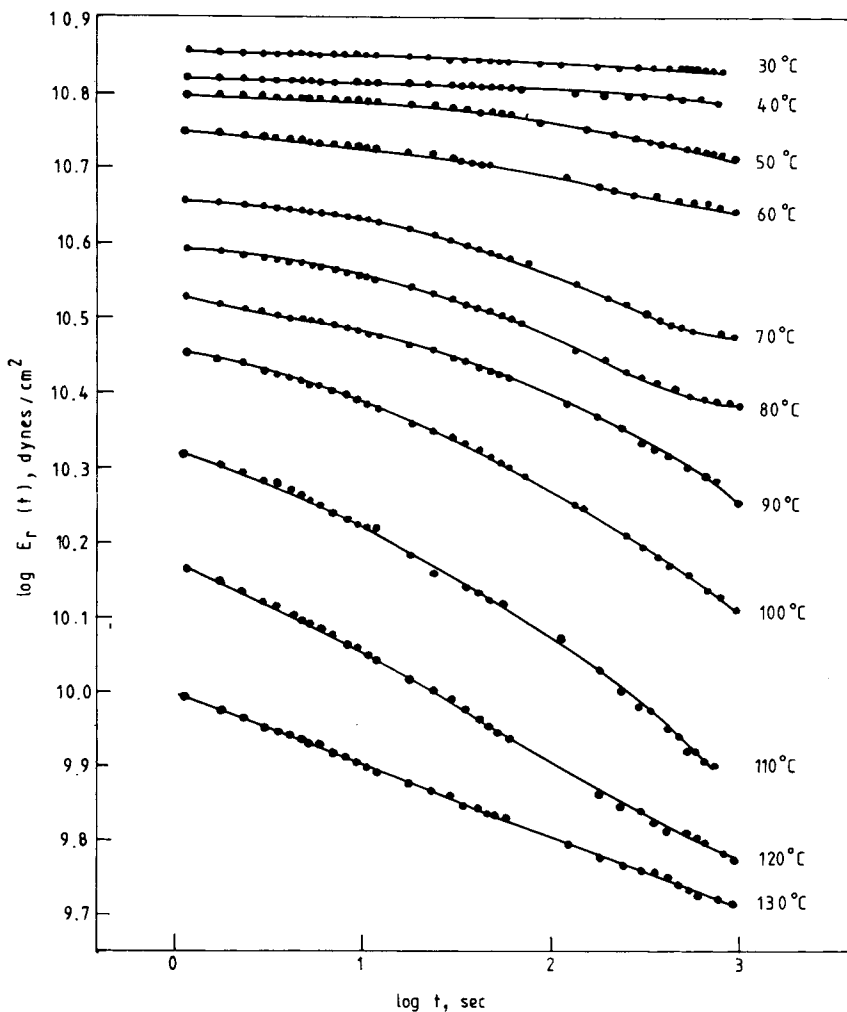


Fig. 8. The reduced modulus $[E_r(t)]$ data for FA-180 sample.

have been presented elsewhere,⁶ and, though the correspondence may not be exact, it does not appear that maximum viscoelasticity occurs at T_g . This effect is expected from usual considerations and will therefore not be discussed further.

The measured values of stress-relaxation moduli were reduced according to the procedure of Nagamatsu et al.⁷ using the following relationship and assuming that the variation of crystallinity with temperature can be neglected:

$$\log E_r(t) = \log E(t) + \log(T_s/T) \quad (1)$$

where $E_r(t)$ is the reduced relaxation modulus at time t , $E(t)$ the measured relaxation modulus at time t , T the measurement temperature, and T_s the reference temperature. Curves of $\log E_r(t)$ vs. $\log t$ for a reference temper-

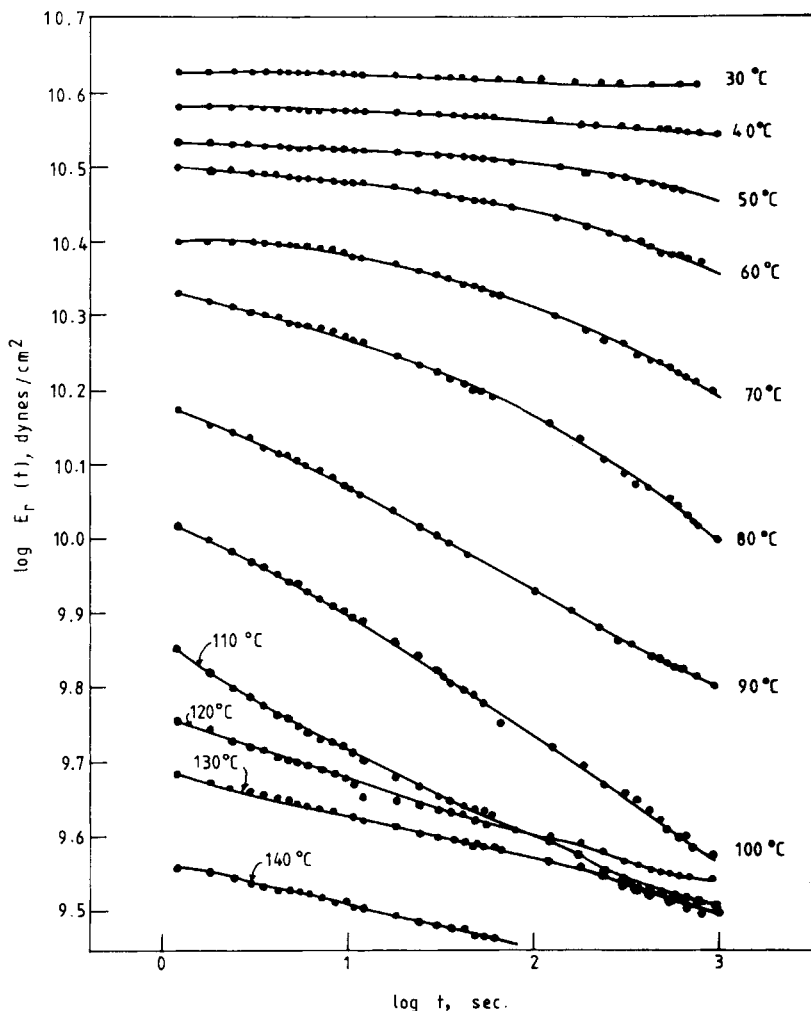


Fig. 9. The reduced modulus $[E_r(t)]$ data for FA-230 sample.

ature $T_s = 80^\circ\text{C}$ are shown in Figure 7 for the control sample and in Figures 8–11 for the 180 and 230°C heat-set samples, respectively. The curve at 80°C was selected to remain fixed on the time scale; the curves at the other temperatures were shifted parallel to the $\log t$ axis to obtain the superposed curves. Values of shift factor $\log a_T$ thus obtained are shown in Table I and are also shown in Figure 12 along with other values reported in the literature^{1,2}; it is interesting to note the closeness of these values. The master curves of the reduced stress-relaxation modulus obtained by superposition are shown in Figure 13 for all the samples. The relaxation time distribution functions, $H(\tau)$, were determined from the master curves using the Alfrey approximation⁸:

$$H(\tau) = -\log E(t) \frac{d \log E_r(t)}{d \log (t/a_T)} \quad (2)$$

The relaxation time spectra so obtained are shown in Figure 14.

The relaxation modulus master curves and the relaxation spectra show some very interesting features. Among the heat-set samples, the TA samples show higher modulus than the FA samples throughout the time range shown. Since the crystallinities of these samples are not very different,^{3,4} the lower moduli of the FA samples could be attributed to the much lower orientation of the amorphous phase and also to the distinct phase separation of the crystalline and amorphous phases in these samples.^{4,5} At low times, the low amorphous orientation will be the important factor; at longer times the effects due to the predominantly series type of coupling will be superimposed on this effect. That is why the modulus of the free-annealed samples falls steeply at higher times since relaxation processes can proceed with greater ease. As stated earlier, the data for the control sample are considerably affected by the superposed thermal history; the long time behavior which has been extracted from the high temperature stress-relaxation data

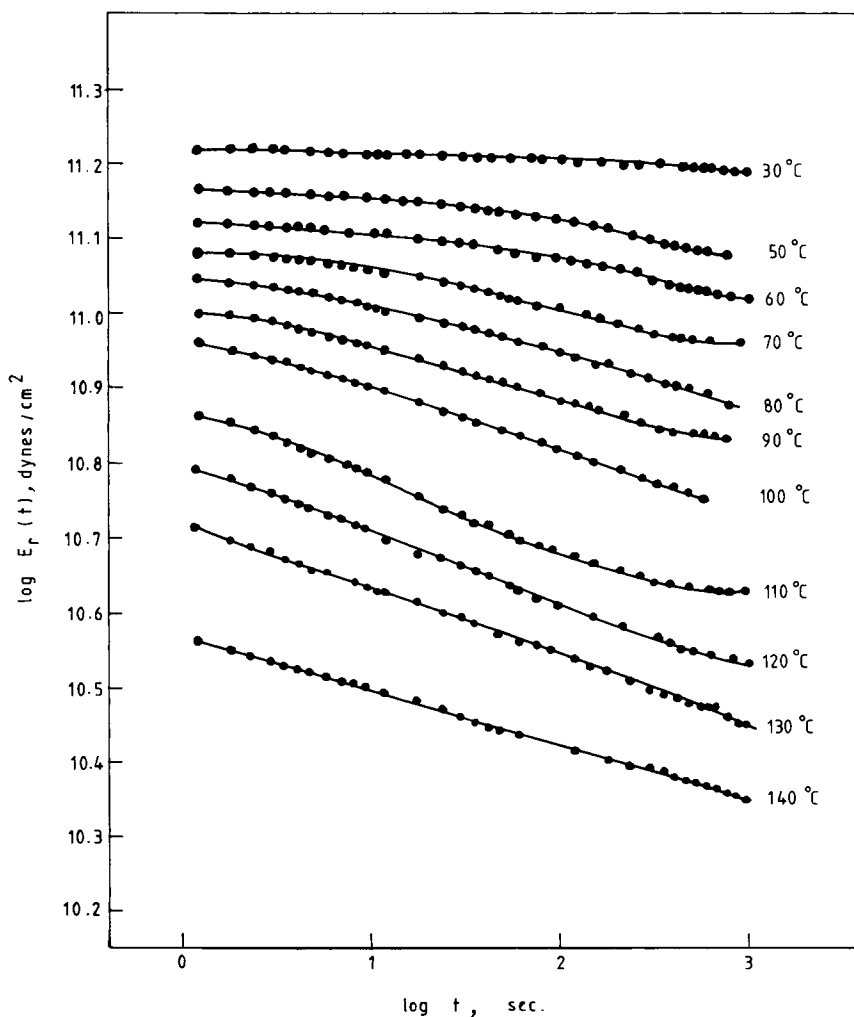


Fig. 10. The reduced modulus $[E_r(t)]$ data for TA-180 sample.

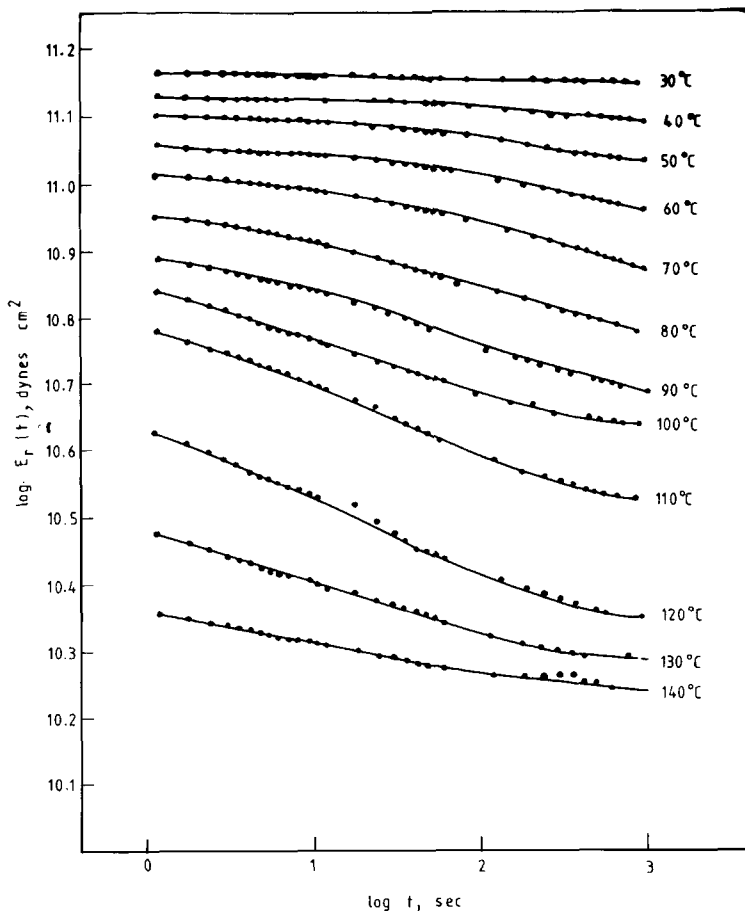


Fig. 11. The reduced modulus $[E_r(t)]$ data for TA-230 sample.

TABLE I
Values of Shift Factor, $\log a_T$, for Various Samples

Temp. (°C)	$\log a_T$					Murayama's values, PET fiber	Hawthorne's values, PET films	
	Control	TA 180	FA 180	TA 230	FA 230		Temp. (°C)	$\log a_T$
40	—	—	6.60	6.05	7.22	—	52	2.0
50	6.20	3.75	4.80	4.25	5.00	2.64	60	1.35
60	3.20	2.35	3.30	2.75	3.40	1.98	69	0.80
70	1.50	1.05	1.00	1.45	1.40	1.15	77	0.30
80	0	0	0	0	0	0	82	0
90	-1.18	0.92	-0.92	-1.22	-1.52	-0.98	87	-0.55
100	-2.08	-1.74	-1.94	-2.24	-2.84	-1.97	94	-1.30
110	-2.91	-3.06	-3.26	-3.16	—	-3.30	108	-2.55
120	—	-3.78	-4.28	-4.68	-4.16	-4.45	115	-3.25
130	-3.98	-4.65	-5.20	-5.90	-4.88	-5.42	128	-4.28
140	-5.42	-6.17	—	-7.33	—	-6.26	140	-5.38

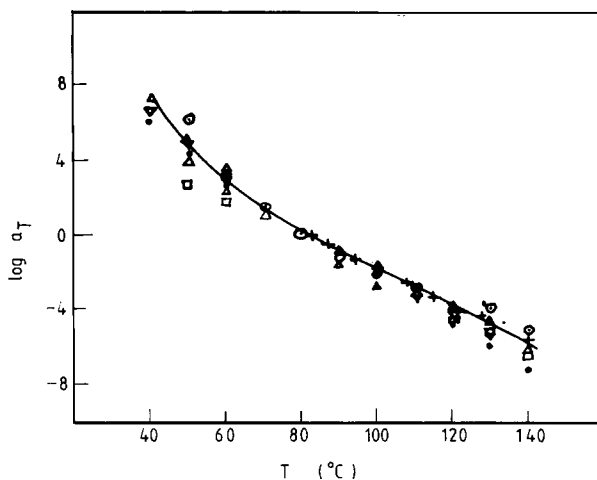


Fig. 12. Comparison of $\log a_T$ values from present studies with those from the literature: (○) control; (▽) FA-180; (△) TA-180; (▲) FA-230; (●) TA-230; (+) PET films²; (□) PET films.¹

will therefore not be representative of the original sample. At low times, the control sample shows higher relaxation modulus, as would be expected from its high amorphous orientation.^{4,5} However, it has lower crystalline content compared to the heat-set samples,^{4,5} and this may also make some contribution to its slightly lower modulus than TA 180 sample.

Considering the relaxation time spectra, it is interesting to note that two prominent relaxation processes are present in all samples, though they appear to be sharper and more pronounced in the free-annealed samples. It must be remembered that the stress-relaxation data have been obtained at 0.5% extension. Though it is not known as to what are the exact deformation mechanisms operative at this strain level, Fourier-transform infrared studies on similar films had shown⁹ that the deformation processes may be different in the two sets of samples. In the free-annealed samples, some degree of chain uncoiling sandwiched between the crystallites can occur. In the taut annealed samples the amorphous phase has relatively higher orientation and at 0.5% strain, the stress generated is higher because of its higher modulus and though a considerable portion of the energy of deformation will still be expected to be stored in the amorphous regions, it will not be expected to be in terms of a chain uncoiling process as in the FA samples. It could be, for example, through straining of the interfibrillar amorphous regions.^{9,10} After the sample has been deformed to 0.5% strain, the stress-relaxation processes are apparently much more intense in the free-annealed samples.

As pointed out by Ferry,¹¹ the shapes of the relaxation spectra are similar to those of the loss modulus curves, and the maxima represent concentrations of relaxation processes. Thus both at short times and at long times, the spectra should be reduced to very low values or vanish. Ferry has also pointed out¹² that these relaxations should not be equated to the transitions of the glass transition type because during the transition from rubberlike

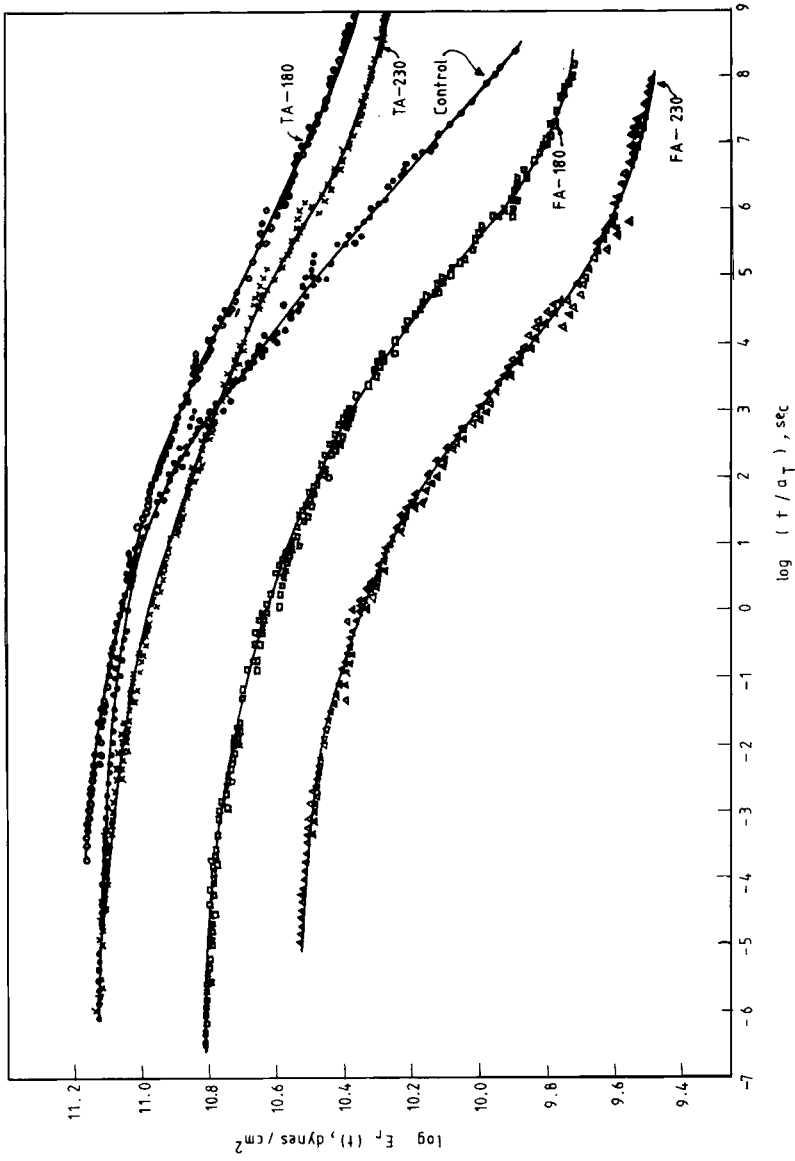


Fig. 13. Master curves of stress-relaxation Modulus for various samples.

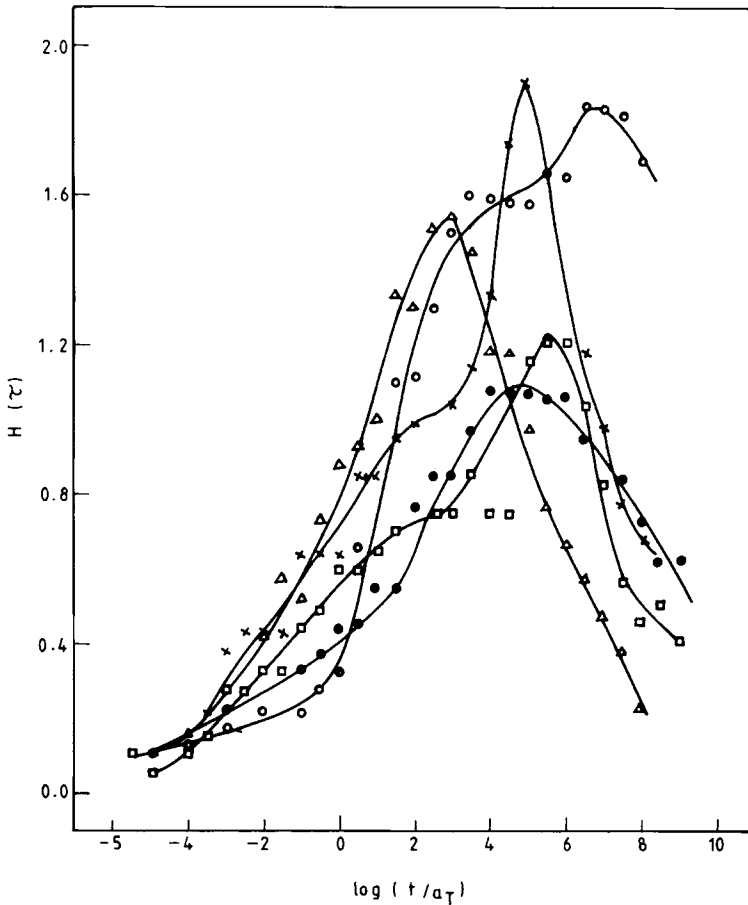


Fig. 14. Relaxation time spectra for various samples: (○) control; (●) TA-180; (×) FA-180; (□) TA-230; (△) FA-230.

state to glasslike state at a constant temperature (80°C in this case), as time or frequency is varied, no change occurs in the thermodynamic state, unlike when T_g is traversed. The spectrum for the control sample shows low relaxation intensity at short times; the high relaxation intensity at longer times is, as stated earlier, not representative of this sample.

Horizontal shift factors, $\log a_T$, are plotted against reciprocal temperature in Figure 15. The nonlinear curved shape, characteristic of the glass transition type relaxation,¹³ is apparent on those Arrhenius plots. The activation energies calculated from the two approximately linear portions of these plots of high and low temperature range are shown in Table II. In case of TA samples the distinction of these two values could not be possible owing to the lower curvature of the Arrhenius plot.

It has already been shown that the shift factors, $\log a_T$, compare reasonably well with the values obtained by other authors for similar samples.^{1,2} It would be interesting to compare the shift factors obtained from the present data with those obtained from the universal values of WLF constants,

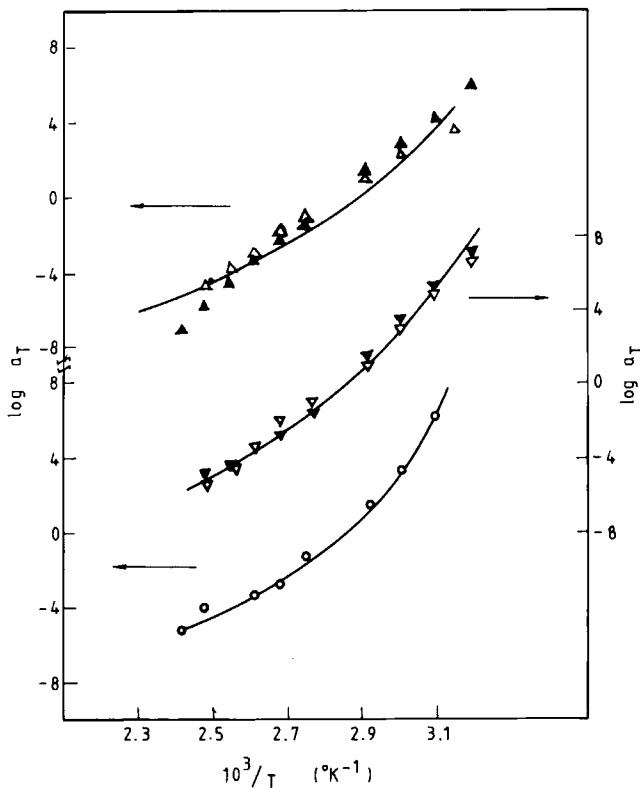


Fig. 15. Variation of $\log a_T$ with $1/T$ for various samples: (Δ) TA-180; (∇) FA-180; (\circ) control (\blacktriangle) TA-230; (\blacktriangledown) FA-230.

viz., $C_1 = 8.86$, $C_2 = 101.6$. The comparison is made in terms of $\log a_T$ vs. $(T-T_g)$ curves in Figure 16. The WLF constants were calculated for all the samples using the usual procedure¹⁴ and are listed in Table III. It is interesting to note that the free-annealed samples have a higher free volume fraction (f) and higher coefficient of thermal expansion (α_p) than the corresponding taut-annealed samples, as suggested by the relationship of the WLF constants with the free volume fraction.

TABLE II
Activation Energy for Various Samples

Sample	Activation energy ^a (kcal/mol)	
	A	B
Control	96.3	59.6
FA 180	83.9	67.3
FA 230	87.8	69.5
TA 180	62.9	62.9
TA 230	77.0	77.0

^a A = activation energy calculated from the low temperature linear portion; B = activation energy calculated from the high temperature linear portion.

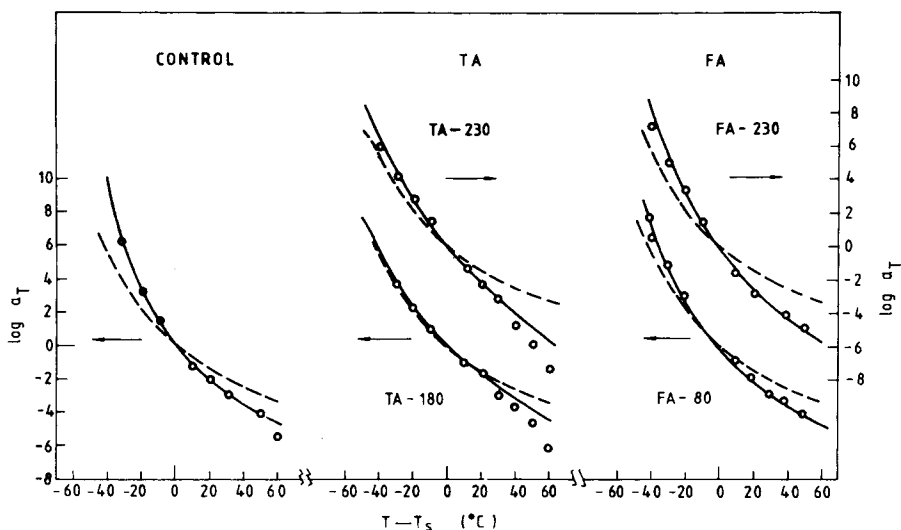


Fig. 16. Variations of $\log a_T$ with $(T-T_s)$ obtained from these data and their comparison with theoretical curves according to WLF equation: (---) using universal values of WLF constants; (—) using the presently determined values of WLF constants.

TABLE III
Values of WLF Constants for Various Samples

Samples	C_1	C_2	f_g	α_f ($\text{deg}^{-1} \times 10^{-4}$)
Control	11.1	85.5	0.039	4.57
TA 180	14.2	143.1	0.031	2.14
FA 180	12.5	103.8	0.035	3.35
TA 230	22.5	181.4	0.019	1.16
FA 230	17.2	122.0	0.025	2.10
Unoriented PET fiber ¹⁵	31.25	109.3	0.014	1.27
Universal value for amorphous polymer ¹¹	17.44	51.6	0.025	4.80

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