Ultrasonic investigations of morphology and stress relaxation in drawn polypropylene

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The effects of annealing on ultrasound propagation in drawn samples of polypropylene are reported. Below 373K the attenuation is dominated by scattering associated with voids generated during the drawing process. Above 383K the void content changes significantly with an associated decrease in the ultrasonic attenuation. Shrinkage, changes in optical clarity and changes in density of the drawn samples are discussed in terms of possible modification of the polymer structure.

INTRODUCTION

The effects of drawing on the longitudinal ultrasound propagation in polypropylene have been reported previously[1]. It was observed that the attenuation and velocity changed markedly. The velocity in the direction of draw increased with draw ratio, indicative of an increase in the ultrasonic modulus due to the formation of a fibrillar structure. Similarly, a decrease in the velocity perpendicular to the draw direction is consistent with fibrils held together by relatively weak van der Waals forces. Changes in the temperature dependence of the velocity and attenuation show that the formation of a fibrillar structure changes the molecular relaxation characteristics of the polymer. It was observed (but not investigated) that the propagation parameters varied slowly with time, indicating stress relaxation in the samples.

The principal objective of the present work is to explore stress relaxation in drawn polypropylene using ultrasonic attenuation as a probe, relating the acoustic phenomena to changes in the morphology and molecular relaxation characteristics.

Materials, such as polyethylene and polypropylene, which in the undrawn form possess folded chain lamellar structures, when drawn change into micro-fibrillar structures[2-8]. The process of drawing induces large scale chain reorganization and this can lead to extensive void formation at low draw ratios[1,2]. As the lamellae of the original spherulites are deformed, amorphous regions are generated and then drawn into micro-fibrils, leaving short lengths of tie molecules between the fibrils. These ties may be subjected to very high degrees of deformation and electron micrographs have indicated that chain scission can often occur[6]. Tie molecules also provide a 'memory' in the polymer and provide one of the driving forces causing conformational rearrangement during annealing. Segments of polymer in amorphous regions are in a thermodynamically unstable state and so will tend to adopt what may be an apparently lower conformational entropic form by becoming incorporated into the crystalline regions. Thus X-ray observations show that freshly drawn polypropylene exhibits crystalline and paracrystalline phases, and the perfection of the crystalline phases increases with annealing[7,8].

EXPERIMENTAL

Polymers

Polypropylene sheets used in the study were obtained from British Industrial Plastics, the polymer having a nominal molecular weight, $\bar{M}_n = 1 \times 10^5$. The crystallinity of the polypropylene was calculated from the density to be 61%, the densities of the crystalline and amorphous phases having values[3,9] of respectively 936 and 858 kg m^{-1}. The crystalline melting point of the polymer was determined using a Perkin Elmer DSC-1 differential scanning calorimeter and found to be 455K. The sheets were drawn uniaxially as described previously[1], the temperature regulation being approximately ±5K. The draw ratio was controlled by adjusting the temperature and rate of draw and in the light of previous experience a nominal draw ratio of 9 was chosen for this study. The draw speed was $0.7 \pm 0.3 \times 10^{-4}$ m s^{-1} and a total draw time of approximately 10 min was used in each case. Freshly drawn samples were quenched to about 263K with solid CO_2, the stress being maintained during this operation. The drawn sample was subsequently stored at 203K until annealed. A summary of the conditions used in preparing the samples is given in *Table 1.*

Ultrasonic measurements

Ultrasonic measurements were carried out at 5 MHz using a pulsed sound immersion method[20], distilled water being used as the coupling medium. The direction of

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Table 1 Characteristics of polymers used in the time-dependent studies

Code	Draw temperature T_d (K)	Draw ratio	Optical properties
A	348 ± 5	9	O
B	393 ± 5	10	T
C	359 ± 3	10	O
D	416 ± 7	8	T
E	359 ± 3	9	O
F	359 ± 3	9	O
G	356 ± 3	9	O
H	356 ± 3	9	O
I	352 ± 3	10	O
J	357 ± 3	9	O
K	357 ± 3	9	O
L	357 ± 3	9	O
M	357 ± 3	9	O
N	357 ± 3	9	O

O – opaque
T – transparent

propagation was maintained perpendicular to the draw direction.

Density measurements

A flotation method was used to determine the density[11], the binary medium being prepared from various ratios of isopentane and chloroform.

Annealing procedure

The samples were annealed at temperatures in the range 298 to 398K for defined periods. The temperature control of the annealing chamber was approximately ±1K. Annealing for short periods, i.e. less than 10 min, was carried out by dipping the sample into a water bath at the desired temperature. Longer periods of annealing wer performed in an air bath. Shrinkage of the sample was determined at 298K using a travelling microscope; the distance between fiducial marks was typically 2×10^{-2} m and the precision of the measurement was $\pm 2 \times 10^{-5}$ m. Measurements of acoustic attenuation and density were all made at 298K. Typically, measurement of attenuation and shrinkage each required 5 minutes and that of density approximately 15 minutes. It was assumed that no stress relaxation occurred either during the measurements at 298K or during storage at 230K; the data obtained support the validity of this assumption.

RESULTS AND DISCUSSION

Effect of draw temperature

Studies of the mechanical properties of drawn polypropylene have indicated that the physical properties are sensitive to both the molecular weight of the sample and the draw temperature[12]. These measurements of the acoustic attenuation show that there is a strong correlation between the temperature of drawing and the longitudinal attenuation coefficient (*Figure 1*). Samples drawn below 373K were opaque with relatively low densities and high attenuation coefficients, whereas those drawn above 383K were almost transparent with high densities and lower attenuation coefficients.

Electron microscopic investigation of the opaque samples (*Figure 2*) indicated that they contain a large number of voids occurring as narrow gaps between fibrils, and having typical dimensions, $1 \times 1 \times 10$ μm^3. These voids are different from those described by Peterlin[6], which were associated with disordered zones generated during draw and incorporated into the fibril structure. The voids in our opaque samples appear to be a consequence of the low cohesive forces between fibrils. Transparent samples (*Figure 2c*) have appreciably fewer of these void structures. Thus, increasing the draw temperature decreases the internal strain, and allows local stress relaxation.

Heats of fusion determined by d.s.c. on drawn and undrawn samples indicate that there are no major overall changes in the percentage crystallinity during draw, although the nature of the crystalline regions may change somewhat[6], and part of the amorphous region may become incorporated into the fibril structure.

Variation of acoustic attenuation with draw conditions

The attenuation coefficient was investigated from 100 to 420K as a function of the draw conditions (*Figure 3*). These attenuation *versus* temperature curves reflect a superposition of relaxation processes having separate molecular and morphological origins.

In undrawn polypropylene there are three kinds of molecular motion causing loss peaks designated α, β and γ[13]. The maximum in the attenuation at 340K is attributed to the β relaxation process.

The significant increase in the attenuation on drawing is attributed to the effects of morphology on the acoustic propagation. Since the attenuation decreases on formation of a transparent sample, voids in the opaque samples must be responsible for a major part of the excess attenuation. Two mechanisms can be considered, inter grain thermoelastic processes[14,15] and scattering from these voids[16,17].

(i) *Intergrain thermoelastic effects.* Opaque samples comprise regions of fibrils and air voids each having different acoustic and thermal properties. Compression of the sample due to the longitudinal ultrasonic wave causes local temperature gradients and hence a contribution to the attenuation coefficient akin to the Zener loss peaks in polycrystalline metals[14,15]. The relaxation frequency f_o for this process is given by

$$f_o = \frac{\Lambda}{\rho C_p L_c^2} \quad (1)$$

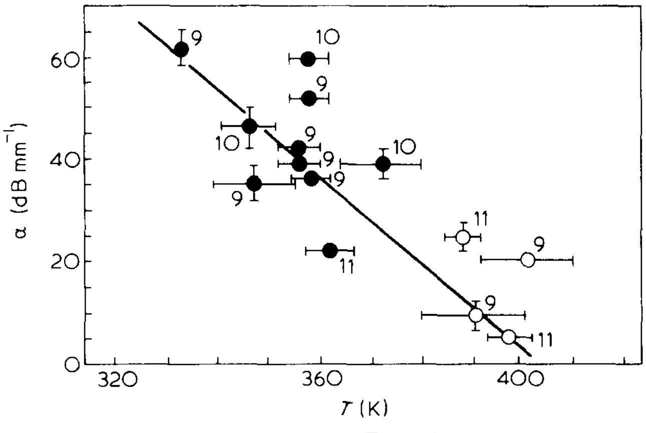

Figure 1 Effect of draw temperature T_d on the ultrasonic attenuation, α, at 5 MHz. The draw ratios of the samples are given in the figure. All attenuation measurements were made at 298K. ●, opaque samples; ○, transparent samples. Only some of these samples were employed in the time-dependent studies (*Table 1*)

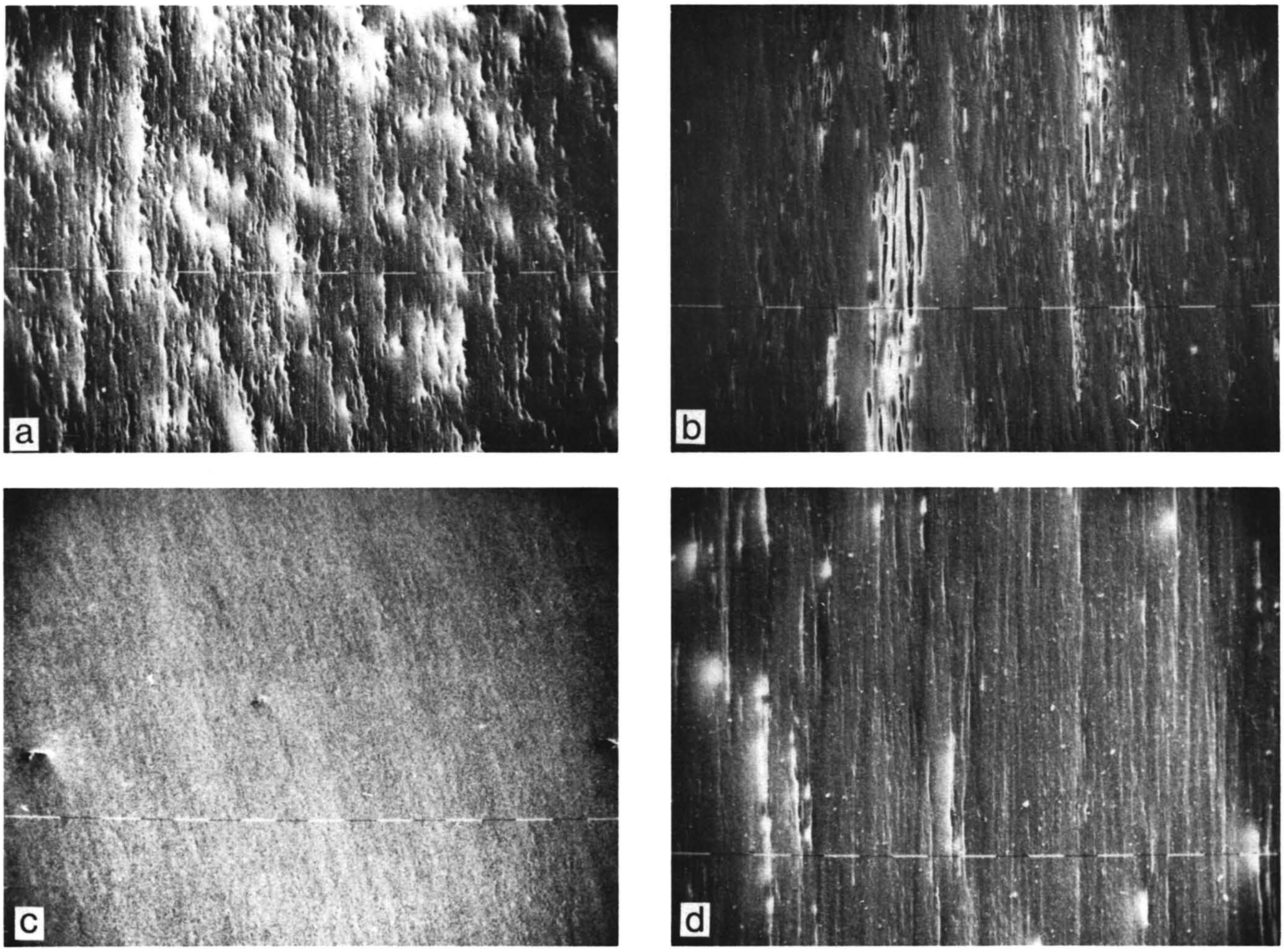

Figure 2 Scanning electron micrograph of an opaque sample, A, and a transparent sample, B (*Table 1*). Sample A (T_d = 348K): (a) the surface perpendicular to drawing direction, (b) the surface parallel to drawing direction. Sample B (T_d = 393K): (c) the surface perpendicular to drawing direction, (d) the surface parallel to drawing direction. Marker = 10 μm

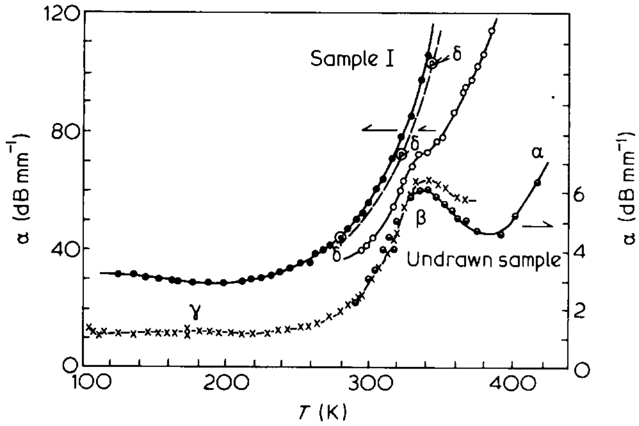

Figure 3 Temperature dependence of attenuation at 5 MHz for a drawn opaque sample (Sample I of *Table 1*) and an undrawn sample. ●, Sample I; ○, Sample I annealed at 373K for 5800 min; X, undrawn sample; ○, undrawn sample annealed at 373K for 4000 min. The broken line is calculated from equation (3) using the interpolated velocity data on drawn polypropylene

where Λ, ρ, C_p and L_c are the thermal conductivity, density, heat capacity at constant pressure and the size of the grain, respectively. In the present case, the 'grain' is an air void of size 1 μm. Substitution of approximate values in equation (1) indicates that the associated acoustic relaxation would be expected to occur at 1.9 kHz and must therefore contribute a negligible amount to attenuation at 5 MHz.

(ii) *Scattering by voids.* From the known velocity of propagation[1] the wavelength of the sound wave at room temperature is approximately 500 μm, i.e. much larger than the void dimensions. The Rayleigh condition therefore applies. Okano has predicted[16] the ultrasonic attenuation caused by viscoelastic spheres suspended in a viscoelastic medium

$$\alpha_s = \frac{8\pi^4 f^4 a^3}{v^4}\left[\frac{1}{3}\left(\frac{K_1 - K_0}{K_1}\right)^2 + \left(\frac{\rho_1 - \rho_0}{2\rho_1 + \rho_0}\right)^2\right]\varphi \qquad (2)$$

where a, K, ρ and φ denote the radius of the sphere, bulk modulus, density and volume fraction of the spheres, respectively. Suffixes 1 and 0 denote the spheres and medium respectively.

In the present case some insight can be gained by letting the 'spheres' correspond to air voids and the surrounding polymer constitute the 'medium'. From the sound velocities in air[18] and drawn polymer[1], and a value of φ equal to 0.1 it is found that α_s is equal to approximately 5×10^3 dB mm^{-1} for $a = 1$ μm. This value is roughly two orders of

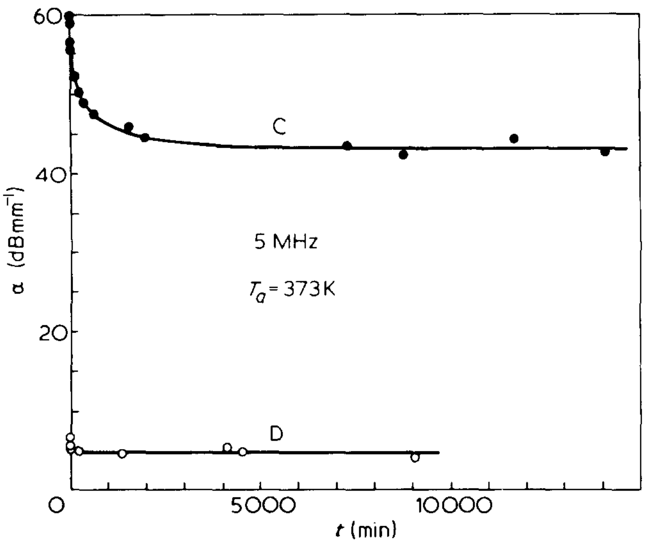

Figure 4 Variation of attenuation with annealing time at 373K for Sample C (●) and Sample D (○). All attenuation temperatures of 298K

magnitude larger than that observed. However, the uncertainties in this amplitude calculation are much greater than in the frequency calculation for thermoelastic effects, and the discrepancy may be attributed to errors in the volume fraction, shape and size of the voids. It is possible to examine the self consistency of this idea by fitting the equation at one temperature, and observing the accuracy of prediction at other temperatures. Assuming that the effective radius of a void is less than 1 μm, the temperature dependence of the attenuation can be found from

$$\alpha \simeq A/v^4 \qquad (3)$$

Fitting the value of A to the measured attenuation in sample I at 298K, and using the known dependence of velocity, v, on temperature[1] gives the broken curve of *Figure 3*. This is in close agreement with the observed values, covering a range of attenuation from 40 to 100 dB mm^{-1}. This evidence supports the hypothesis that the excess absorption between drawn and undrawn samples is due to scattering by voids.

Annealing behaviour

Comparison of the effect on opaque and transparent samples of annealing at 373K (*Figure 4*) indicates that in the case of the latter the attenuation changes little with annealing time, whereas in the former large effects are observed on a time scale of some 2000 min. Investigation of the opaque samples drawn at 359K and annealed at 313, 343 and 373K are shown in *Figure 5*. The measurements were carried out for 14000 min and an equilibrium value of the attenuation from a completely annealed sample was obtained by further annealing for 4000 min at 373K. The final equilibrium values are indicated by an arrow. Two features of the curves in *Figure 5* are worth noting. First, the time dependence of attenuation does not depend strongly on temperature, and secondly the initial and equilibrium values of the attenuation differ from sample to sample even though the drawing conditions were essentially the same. It is probable that these latter effects arise from fluctuations in the void content from sample to sample.

In an attempt to rationalize the data, normalized curves were constructed (*Figure 6*). Here the α_t, α_0 and α_∞ denote the attenuation at times t, zero and infinity respectively. The average activation energy determined from the temperature dependence of the time when the normalized attenuation becomes 0.5 is 40 ± 10 kJ mol^{-1}.

Time variation of density

From the above, it can be seen that the main change which occurs on annealing the drawn samples is a reduction in the void content. Annealing of the transparent samples leads to an extremely small change in density, whereas there is a large change in the opaque sample annealed at 313K. The variations with time are presented in *Figure 7*. These results suggest that the relatively small increase in density of the transparent specimen is due to crystallization in the amorphous region (in agreement with similar observations reported by Keller for polyethylene[19]). It is reasonable to assume that reduction of void content is accompanied by a decrease in the effective scattering radius of the voids. Since attenuation depends upon the cube of the radius this is consistent with the marked decrease in attenuation shown in *Figure 5*.

Time dependence of shrinkage

The shrinkage observed when the opaque sample was heated at a rate of 0.03K s^{-1}, is shown in *Figure 8*. Below 303K, the sample extended due to thermal expansion and then exhibited shrinkage above 308K. These observations are similar to those of Wyckoff[8]. The rate of shrinkage

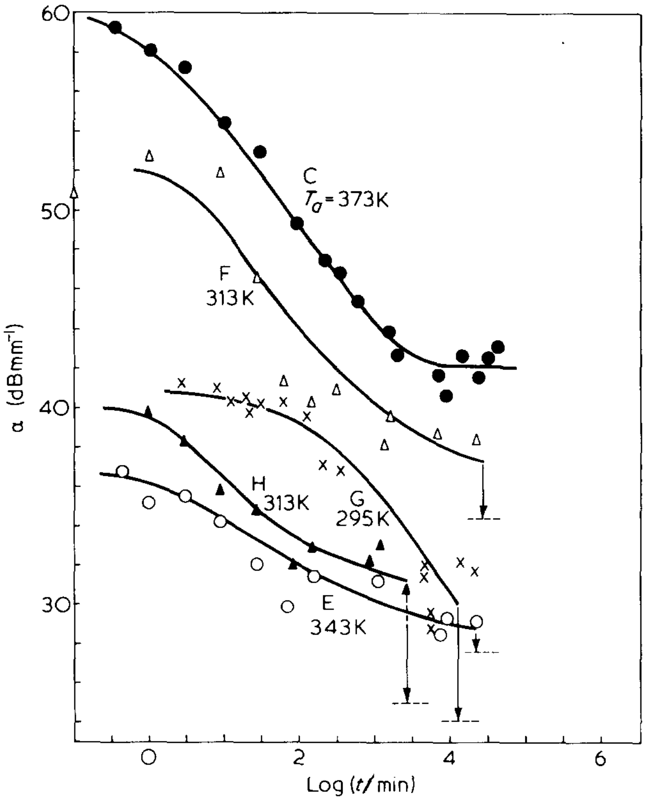

Figure 5 Variation of attenuation in opaque samples with annealing time at various temperatures for samples drawn at 359K. The sample codes and annealing temperature are as follows: ●, C, 373K; △, F, 313K; X, G, 295K; ▲, H, 313K; ○, E, 343K. The arrow indicates the equilibrium value determined after a long time period at 373K. Measurements at 298K

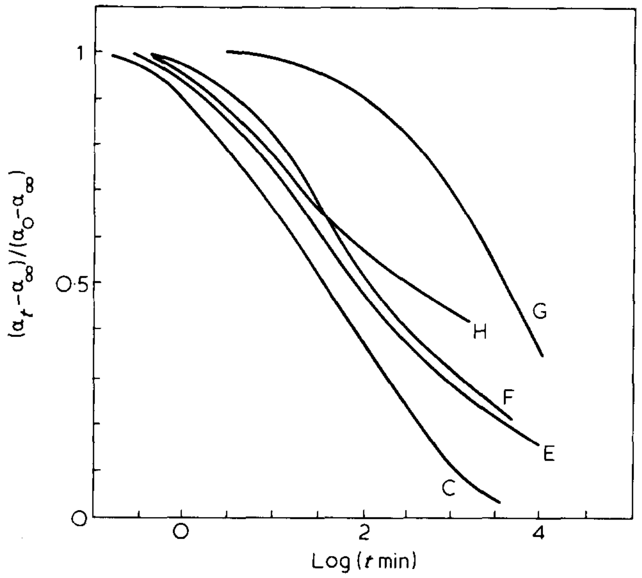

Figure 6 Normalized curves of the time dependence of attenuation. Sample code and annealing temperature: C, 373K; F, 313K; G, 295K; H, 313K; E, 343K

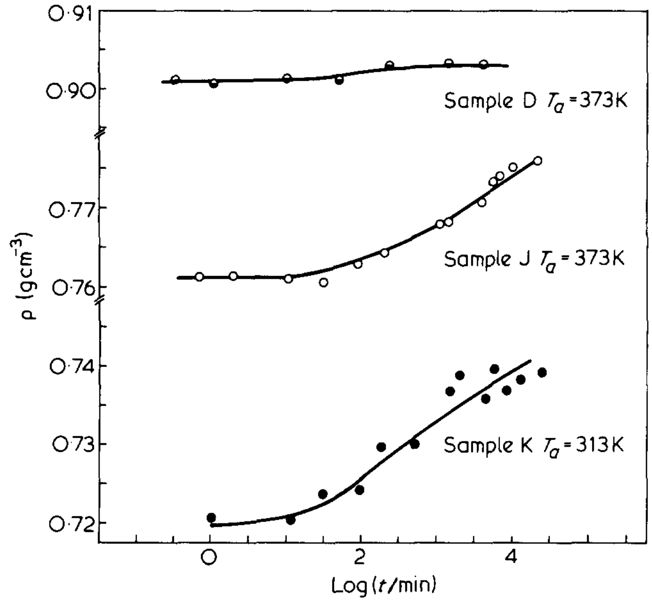

Figure 7 Dependence of density measured at 298K with annealing time for a transparent sample (D) and opaque samples (J and K). ●, D annealed at 373K; ○, J annealed at 373K; ●, K annealed at 313K

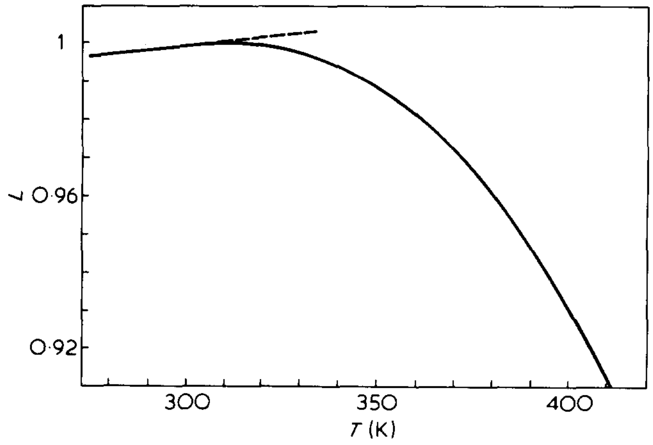

Figure 8 Shrinkage of a drawn sample (A) measured by heating the sample continuously at the rate of 0.03K s^{-1}. *L* denotes the ratio of the length of the specimen measured along the draw direction at a given temperature to that at 303K

depends strongly on the annealing temperature (*Figure 9*). After measurement of the time dependence for 9 days, the specimens annealed at 313K and 343K were further annealed at 373K for 4200 min. The arrows in *Figure 9* indicate the changes which occur during the final stage of annealing. Using a standard temperature of 343K the shrinkage curves were shifted to form a master curve (*Figure 10*). This is typical of those for relaxation involving a distribution of relaxation times.

In an attempt to probe the molecular processes responsible for the contraction, an attempt was made to correlate the shift factors obtained from *Figure 10* with the

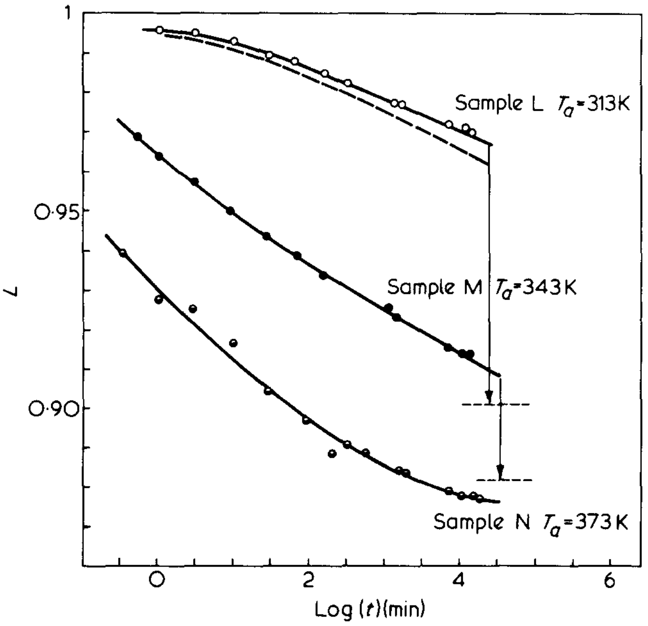

Figure 9 Time dependence of shrinkage. ○, Sample L annealed at 313K; ●, sample M annealed at 343K; ●, sample N annealed at 373K. *L* denotes the ratio of the length measured along draw direction at time *t* to that before annealing. The arrows indicate equilibrium values

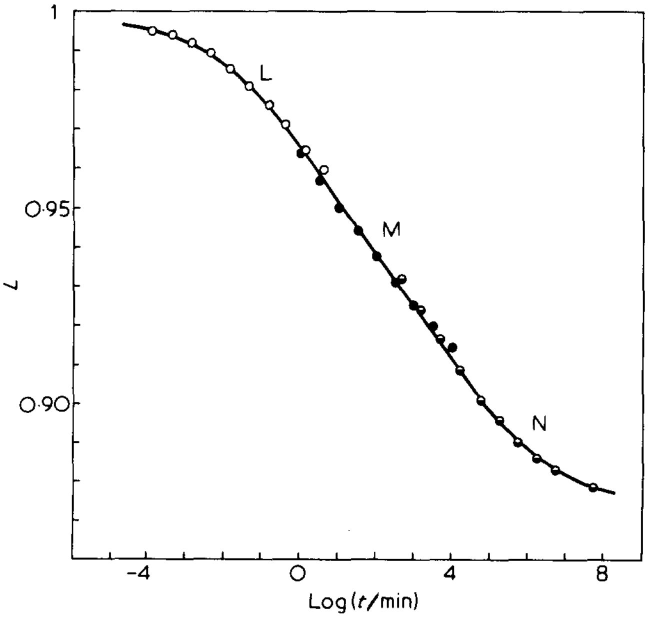

Figure 10 Master curve of shrinkage produced from the data for samples L (○), M (●) and N (●) shown in *Figure 9*. *L* denotes the ratio of the length measured at time *t* to the length before annealing

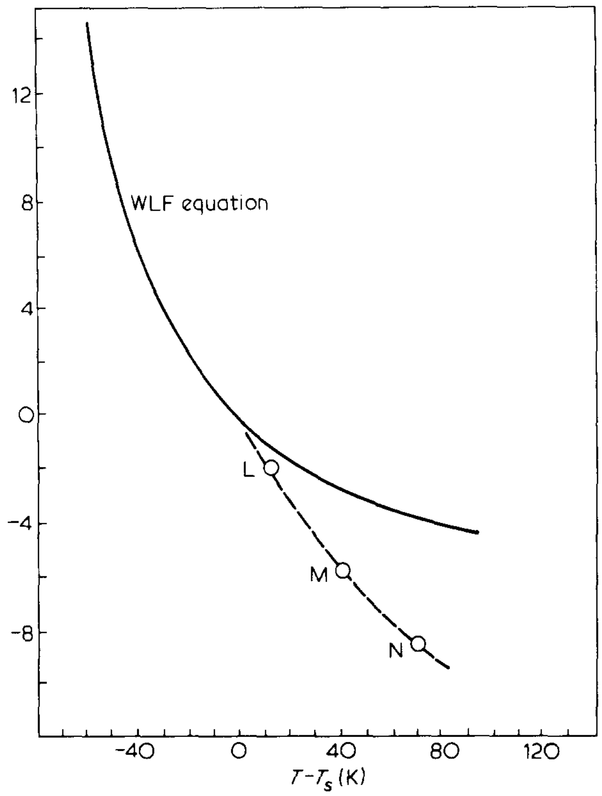

Figure 11 Temperature dependence of the shift factor for the process of shrinkage. T_S is 303K. Solid line shows the WLF equation. L—313K; M—343K; N—373K

predictions of the Williams–Landel–Ferry equation[20], using the glass transition temperature[9] of 253K (*Figure 11*). The predicted curve describes the temperature dependence of the α process and it is clear that the activation data obtained from the shrinkage study do not totally correlate with this process. An 'activation energy' derived from the temperature dependence of the shift factor was considerably higher than the activation energy for the process causing changes in attenuation. The magnitude of the shrinkage activation energy[13] is similar to that for the glass transition at low temperatures, suggesting that in this region shrinkage is associated with amorphous regions of the polymer. However, at the higher temperatures, shrinkage probably involves relative motion of fibrils with a corresponding reorganization of severely strained interfibrillar tie molecules.

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