

Scanning electron microscopy and ultrasonic studies of drawn polypropylenes

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Ultrasonic measurements and scanning electron microscope studies are reported on a series of drawn samples of polypropylene. The ultrasonic measurements were performed over the frequency range 15 to 35 MHz and over a temperature range 283 to 343K. The scanning electron microscope observations confirmed the predictions from density data that the 'void' content initially increases on drawing and then decreases. The acoustic measurements on the samples with the highest draw ratios indicated that severe restriction of the motion of the polymer occurs when the fibrous structure is formed.

INTRODUCTION

In the last ten years a considerable interest has developed in high modulus organic fibres¹⁻⁷. The high values of the modulus recently reported in polyethylene and related materials^{2,7,8} have a close correlation with the molecular organization and morphology developed in these materials on drawing^{7,8}. In a previous paper¹² the application of high frequency ultrasonic measurements (100-1000 MHz) for the investigation of morphologically related dispersion phenomena in undrawn samples was reported. In this paper low frequency (15-35 MHz) observations are reported on both drawn and undrawn samples and the effects of molecular orientation on acoustic propagation investigated.

EXPERIMENTAL

Preparation of samples

Polypropylene sheets used in this study were supplied by British Industrial Plastics and were nominally of $M_n = 1 \times 10^5$. Samples were drawn at 393K and then slowly cooled under tension over a period of 12 h to room temperature.

Ultrasonic measurements

The absorption and velocity measurements were performed using an immersion technique as described previously^{13,14}. The velocity of the compressional wave was determined using the critical angle method, the absorption data being obtained in normal incidence; allowance was made for the effects of reflection at the liquid-polymer interface¹⁵. The transverse velocity could not be measured since the critical angle for this mode of propagation is of the order of the angular aperture available from the ultrasonic source. Two orientations were chosen for the deter-

mination of the velocity, one parallel, the other perpendicular to the direction of the draw. The acoustic absorption normal to the polymer sample was found to be independent of the orientation and the mean of the parallel and perpendicular velocities was used in the calculation of $\tan \delta$. Water uptake was found to have no measurable effect on the acoustic properties of the samples studied.

Density measurements

The data reported in this paper were obtained by measuring the average physical dimensions and the mass of the sample and refer to room temperature values (293K).

Scanning electron microscopy

Scanning electron micrographs were obtained from gold replicas of the surface or microtomed sections. The polymer samples were carefully washed and ultrasonically cleaned before replication, eliminating the effects of dust and adsorbed particles on the observed morphologies.

RESULTS AND DISCUSSION

Scanning electron microscopy of drawn polypropylene

The micrographs obtained for the undrawn and drawn samples are summarized in *Figure 1*. It is evident that in the undrawn sample there exist a number of distinct spherulitic structures. This type of morphology is consistent with structures reported from previous studies on moulded samples^{16,17}. The electron micrographs demonstrate two effects: firstly that the formation of the microfibrils occurs by a process which involves the pulling of the polymer chains out of the spherulitic domains and the formation of them into the highly organized orientated fibres. There has been considerable controversy¹⁸⁻²⁴ as to the correct description of the process by which the fibres are

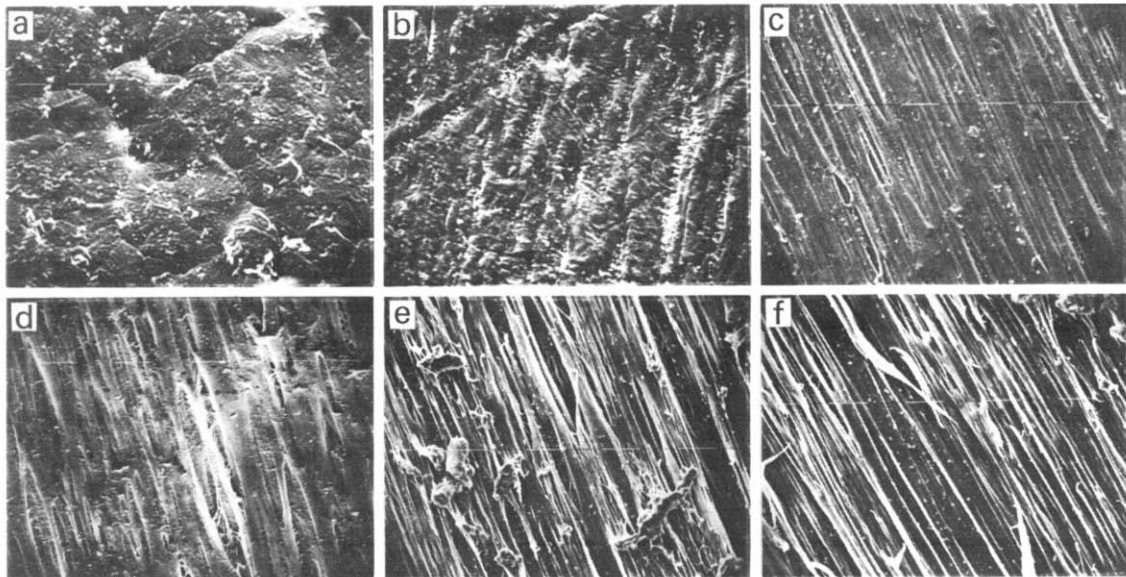


Figure 1 Scanning electron micrographs of drawn polypropylenes. (a) $[\lambda] = 1$; (b) $[\lambda] = 2.6$; (c) $[\lambda] = 6$; (d) $[\lambda] = 9$; (e) $[\lambda] = 12$; (f) $[\lambda] = 14$. Marker = 10 μm

formed. Peterlin²⁰ has proposed that fibre formation occurs via a process in which parallel lamellae stacks are pulled out of the spherulites forming a disordered zone and ultimately packing into microfibrils²⁵. The various stages in the drawing process observed in this study (Figure 1) are consistent with this type of model. At low draw ratios the formation of the fibres leads to an increase in the density of 'voids' defined on the proportion of a lower density interfacial region between the spherulites and fibre domains in sample. Above a draw ratio of 11 the now highly formed fibres interconnected by semi-amorphous bridges are slowly moulded together with a lowering of the total 'void' content. The observed changes in the sample density with draw ratio (Figure 2), are consistent with an initial increase in the 'void' content followed by a decrease, the limiting density approaching that of the crystal form. The interfibril ties evident in Figure 1d are obviously responsible for the structural stability of the polymer when formed into highly aligned microfibrils²⁰. The remains of the original spherulites from which a fibre is formed can clearly be seen in Figure 1e. Such nodular structures probably occur as a result of ties within molecules and exist even in the most highly aligned samples, where chain alignment, according to the mechanical studies, has virtually reached its limiting value. It may be anticipated that the stability of these nodular structures will be directly related to the concentration of ties in the undrawn polymer but would not be expected to influence the bulk modulus significantly.

Ultrasonic attenuation measurements

The ultrasonic attenuation data obtained over the temperature range 283 to 343K was used to compute $\tan \delta$. The variation of $\tan \delta$ as a function of temperature and draw ratio for polypropylene (Figure 3) shows a marked peak at high temperature and draw ratio. The initial increase in the value of $\tan \delta$ arises from either stochastic scattering²⁷⁻²⁹ or thermal elastic loss mechanisms³⁰⁻³⁴. From our earlier studies of the high frequency acoustic absorption in thin films of polymeric material it was established that the microspherulitic structures in polypropylene gave rise to thermal elastic loss¹². The acoustic wave as it

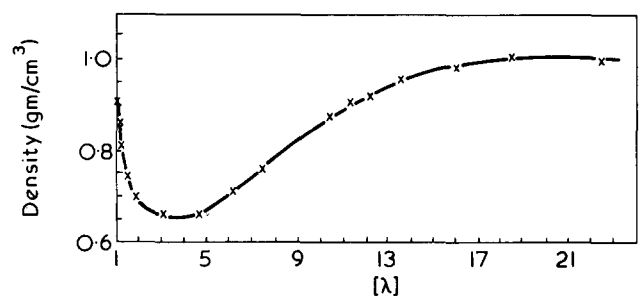


Figure 2 Effect of draw ratio on density for polypropylene

propagates through the solid interacts with the spherulites to an extent which depends on their relative orientation to the wave vector. As a result of the misalignment of neighbouring domains and a discontinuity of the elastic waves at the domain boundary, finite differences in temperature can be generated and subsequent conduction between domains can give rise to high frequency acoustic losses. It is clear that since this process involves both the ratio of the wavelength and the particle size, change of the latter should influence the losses observed at a particular frequency. Stochastic scattering¹⁵ will also be expected to contribute to the loss. However, a comparison of the characteristic wavelengths of the morphology observed in these samples (Figure 1) and theoretical computation indicates that this process is not expected to be dominant. The observed increase and then decrease in the acoustic loss in the region $\lambda = 1-8$ is consistent with the changes expected on the basis of a combination of thermal elastic and scattering losses. The frequency dependence of the acoustic attenuation (Figure 4) in the region of $\lambda = 1-8$ was found to be approximately first power with frequency support in the hypothesis that the loss arises from a thermal elastic process and weights against the stochastic scattering, which might be expected to give rise to fourth power frequency dependence. The origin of the large increase in the attenuation and $\tan \delta$ above $\lambda = 10$ is not very clear. The observed square law dependence on frequency appears to support a molecular relaxation mechanism and its amplitude appears to rule out a thermal elastic process.

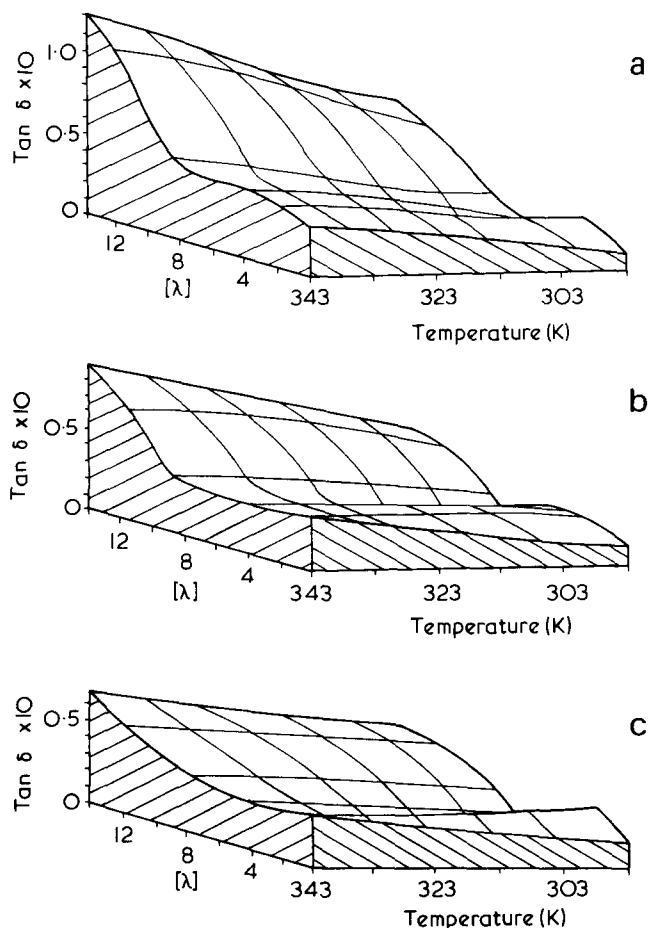


Figure 3 Plots of $\tan \delta$ for drawn polypropylene. (a) 35 MHz; (b) 25 MHz; (c) 15 MHz

Above $\lambda = 10$, the high degree of orientation and close packing of the fibres has the result of significantly modifying the dynamic spectrum of the polymer. The glass transitions of the amorphous and crystalline regions^{35,36} are respectively 258 and 388K indicating that both relaxations should occur at higher temperatures than those used in these studies when observed at 25 MHz. Studies of orientated polyethylene have indicated that part of the lower temperature losses are observed to be shifted to higher temperatures⁴⁵ as the draw ratio is increased. The shifted mechanical loss in this case was found to be highly anisotropic and ascribed to a relaxation involving shear deformation of the drawn fibres. It was not possible using the present apparatus to test whether or not the acoustic loss was anisotropic.

Acoustic velocity data

The values of the velocity parallel and perpendicular to the draw direction are anisotropic (Figure 6). It can be seen that the velocities measured across the draw direction are significantly lower than those along the fibre axis. This observation is consistent with measurements of the modulus obtained using more conventional measurements³⁸⁻⁴⁰. The shape of the curves for the high draw ratio samples are characteristic of those observed in polymers such as polystyrene⁴¹ and poly(methyl methacrylate)⁴²⁻⁴⁴, in the region of the onset of molecular motion in these polymers. The change of slope of the curve (indicated by an arrow) corresponds to a decrease in the modulus with an increasing degree of molecular motion in the polymer as the temperature is raised.

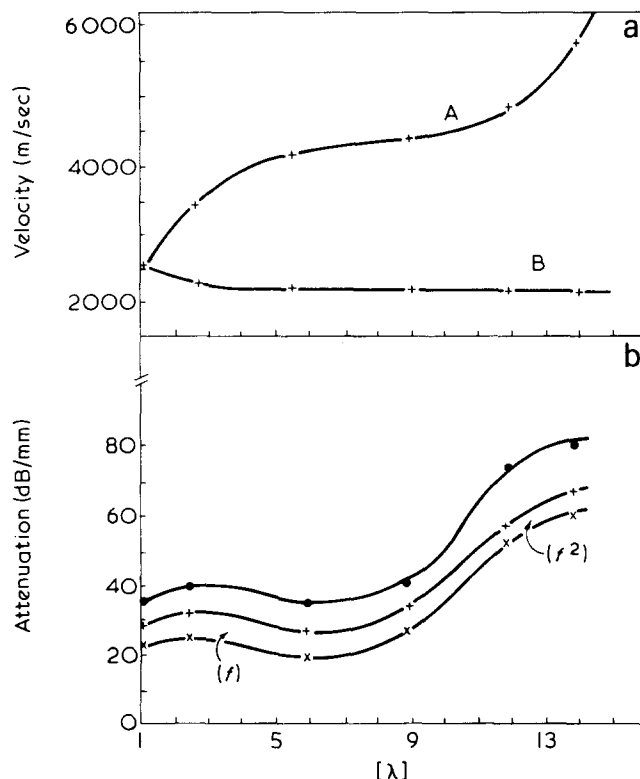


Figure 4 Acoustic velocity and attenuation data at 303K for drawn polypropylene. (a) //; (b) \perp , \bullet , 35 MHz; +, 25 MHz; X, 15 MHz

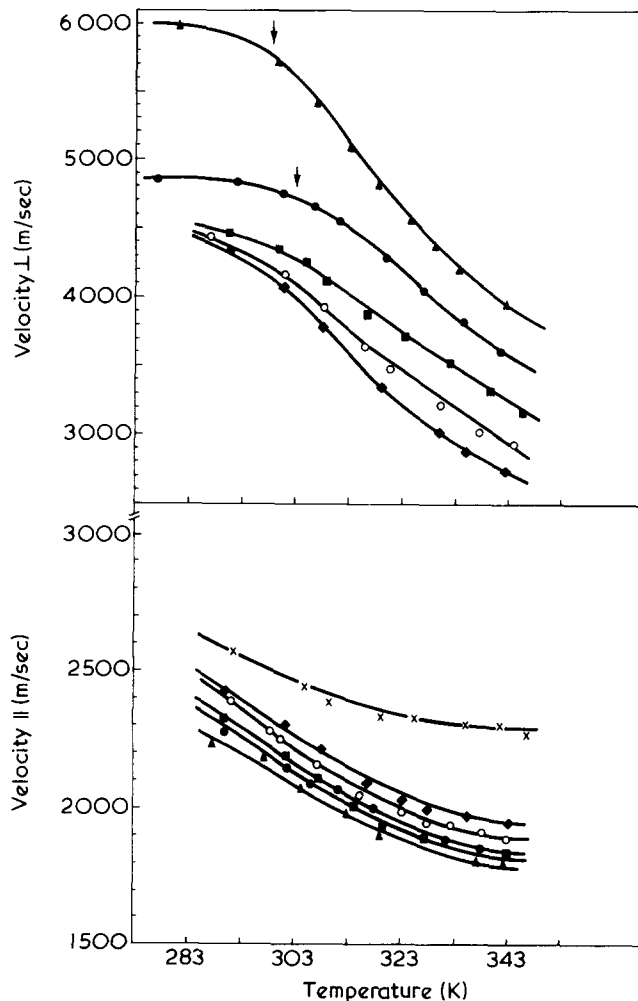


Figure 5 Velocities parallel and perpendicular to draw directions. X, Undrawn polymer; \blacklozenge , $\lambda = 2.6$; \circ , $\lambda = 6$; \blacksquare , $\lambda = 9$; \bullet , $\lambda = 12$; \blacktriangle , $\lambda = 14$

An isothermal plot of the velocity data (Figure 5) indicates that as the sample is drawn the velocity (v) firstly becomes anisotropic and then shows a marked increase above a λ value of 9. This observation is consistent with mechanical studies. The velocity (v) on the other hand decreases and then apparently shows little or no change. These observations are consistent with the sound wave sensing the modulus across the axis in the perpendicular orientation and sensing the modulus along the fibre axis in the parallel orientation. In the former situation the velocity senses predominantly the intermolecular force field whereas in the latter it senses the intramolecular force field. It should be noted that the values presented in this paper for the velocities do not correspond strictly to the moduli across and along the fibre axis since the method of critical angle observation necessarily involves a certain amount of mode conversion not allowed for in this study.

CONCLUSION

It has been established in this study that significant changes are obtained in the mobility of the polymer by drawing. The acoustic absorption, velocity and density measurements are consistent with there being an increased density of 'voids' in the low draw ratio samples associated with the progressive change of crystallites to microfibril structures. This paper reports the first observations of the anisotropy of acoustic propagation achieved by the drawing of homopolymer.

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