JOURNAL OF MATERIALS SCIENCE **27** (1992) 2413–2419

Characterization of roll-drawn polypropylene using shear wave birefringence

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Ultrasonic shear waves have been used to estimate the degree of anisotropy present within roll-drawn polypropylene samples, using shear wave birefringence. These measurements have been correlated with the physical properties that result from the draw ratio used during manufacture. It is shown that the technique has promise as a monitoring tool for this material.

1. Introduction

Oriented polymers are being investigated increasingly as possible materials for structural applications. Of particular interest is the increase in elastic modulus and tensile strength as a result of drawing [1]. This process induces a degree of anisotropy into the structure of the previously isotropic material, giving it increased strength in the direction of drawing. There are a variety of methods for producing molecular orientation, including rolling, drawing and a combination of both [2–4]. Several analytical techniques have been developed for the measurement of the resulting molecular orientation [5], examples being X-ray diffraction and optical birefringence, where a thin film of the sample is required. The present work was directed towards the development of a method for estimating the degree of orientation of roll-drawn polymers, using the as-rolled sheet through its total thickness, without the need for taking a thin section of the sample.

There did not seem to be a technique available that could quickly and accurately give a nondestructive measurement of the degree of anisotropy present, which is often not known for a particular material if the production parameters are not strictly controlled. An ultrasonic method has thus been investigated, which uses shear wave propagation as a measure of anisotropy. Ultrasonic shear wave studies have been used in previous work to investigate the fibre orientation in fibre-reinforced polymer composites [6, 7], but do not seem to have been applied to roll-drawn polymers.

Of particular interest in this work was the study of roll-drawn polypropylene, which was fabricated using the technique described by Capaccio and Ward [8], and Burke *et al.* [9]. In this method, a rectangular slab, or billet, of polypropylene is heated to a temperature near 145 °C, and then drawn by passing it through a set of four rollers (Fig. 1), the first being heated to the billet temperature. The second set of rollers rotates at a faster speed than the feed-in-rollers, producing a positive draw component and thereby drawing out the material. A third and fourth set of rollers, rotating at a speed equal to the second, serve to maintain tension on the polypropylene as it cools down, so that relaxation of the drawn structure is minimized. Control over the degree of drawing is achieved by setting the feed-in roller gap, the speed differential between the first and second sets of rollers, and the draw temperature.

With the roller gap too low, it has been found that friction-heating causes localized melting in the sheet. Capaccio and Ward [8] noted that a higher temperature does not necessarily produce a greater strength and modulus in the sheet produced. These observations indicate that optimal processing conditions are achieved by skilful balancing of the processing parameters in relation to each other.

One manufacturing parameter that can be used for a correlation between processing conditions and physical properties is the draw ratio (DR), which is defined as the strain in the draw direction of the polymer. In

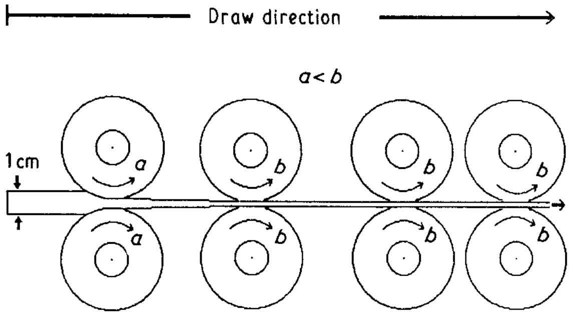

Figure 1 Schematic diagram of the roll-drawing process.

the present work, the DR is calculated by taking the ratio of the cross-sectional areas perpendicular to the draw direction before and after drawing (Fig. 2). This ratio gives an indication of the degree of mechanical deformation, which, in turn, will be linked to the extent of alignment of polymer chains caused by roll-drawing.

The undeformed material, unoriented polypropylene in our case, may be described by a model incorporating spherulites [10]. Each spherulite is composed of crystalline lamellae which grow radially outward from a nucleus, in a helical structure. There is a large amount of non-crystalline material between these lamellae, which are ~ 10 nm thick. Sections of molecules not incorporated in crystalline structure exit the lamella, which have randomly arranged molecule ends leaving it. These may re-enter at some point further along their length, or may enter the structure of another lamella, thus tying the two together; the latter type have been called tie molecules. The region in the spherulites not occupied by crystalline lamellae is called the amorphous region and is made up of the non-folded, randomly-arranged sections of tie molecules, molecules that are entirely non-crystalline, and the non-folded sections of molecules which eventually re-enter a single lamella.

Under deformation such as that caused by roll-drawing, the initially isotropic material exhibits molecular alignment in a preferred direction. This is due to many factors [1, 10], such as rotated and deformed lamellae, and the disintegration of spherulites. This results in the formation of a microfibrillar structure, with polymer chains aligned preferentially in the drawing direction. The material is now anisotropic, and its elastic behaviour will have a directional dependence. It is this anisotropy that causes shear wave birefringence, and it is this property which allows the measurements described in this paper to be performed.

In the following sections, the ultrasonic shear wave technique will be described. Experimental results will then be presented, which link the ultrasonic measurements to manufacturing conditions and other physical properties.

2. Shear wave birefringence

In the bulk of an isotropic solid, two types of elastic waves can propagate: longitudinal waves, where the particle motion is in the direction of travel, and shear (or transverse) waves, which exhibit particle motion perpendicular to this direction. In all solids, the longitudinal wave travels at a higher velocity. The shear wave, because of its transverse nature, can be polarized, but the velocity of propagation is independent of the direction of polarization.

In an anisotropic solid, the situation becomes more complicated, although longitudinal and shear waves still exist. It has been shown [11] that the wave modes possible in an anisotropic medium arise from solution of the appropriate wave equation. The three eigenvectors obtained from this equation as a solution [11] correspond to three elastic (or acoustic) waves, propagating in a single direction in the solid body (defined by *k*, the wave number vector), and polarized in three different directions. The magnitudes of the eigenvectors correspond to the different speeds of propagation of the three waves. The directions of polarization of the three waves are found to be mutually perpendicular.

In general each wave is not purely transverse or longitudinal; however, in a given crystal lattice along certain directions of propagation, there are one longitudinal and two transverse waves. The longitudinal wave has a faster phase velocity than the shear waves.

The significance of this phenomenon is as follows: it has been shown that, in general, three different waves will exist in an anisotropic medium, for propagation along a given direction in the solid. Two of these, known as *quasi*-shear waves, are transverse waves polarized in mutually perpendicular directions. They travel at different velocities (i.e., they have different wave numbers). These waves travel at a slower velocity than the longitudinal mode (Fig. 3). The above is true for any material exhibiting anisotropy. However, the relative velocities of the two *quasi*-shear waves will be sensitive to the structure of the solid in the direction of travel. This velocity difference is the origin of shear wave birefringence, in that there will be a phase difference between the two orthogonally-polarized components, generated by a suitable source and arriving subsequently at a detector. It is this phase difference that will be used as a measure of anisotropy.

For an isotropic solid, there is no difference in the wave velocities of the two transverse components. A shear wave travelling in any direction through the material has the same velocity and, as stated above, this is independent of the plane of polarization.

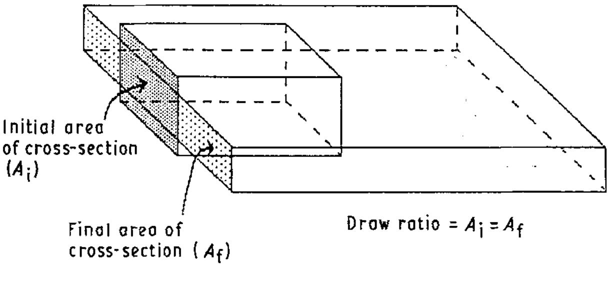

Figure 2 Diagram illustrating the definition of draw ratio.

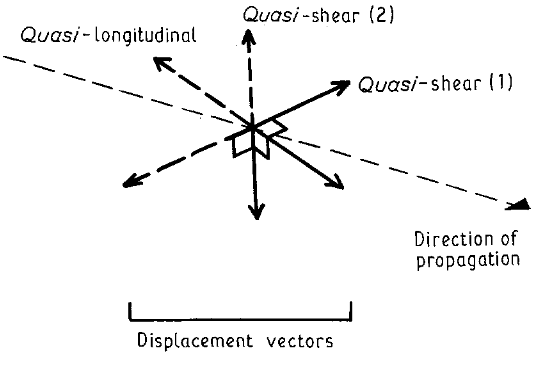

Figure 3 Characteristics of the three ultrasonic modes that propagate in a bulk anisotropic solid: a *quasi*-longitudinal wave, and two *quasi*-shear waves.

It is thus apparent that a transition from an isotropic to an anisotropic material, caused, for instance, by deformation, will lead to the existence of two shear-wave components, polarized orthogonally and travelling at different velocities. This velocity difference is material dependant. Hence, changes in the anisotropy of the material causes a change in the stiffness properties, and hence a variation in the velocity difference of the two shear waves. It is this velocity variation (i.e., the variation in shear wave birefringence) that will be used in this work to investigate changes in structure of polypropylene due to the roll-drawing process.

3. Experimental procedure

A series of roll-drawn polypropylene samples were available, which had been prepared under carefully controlled conditions with a known DR. The DR of the samples ranged from 2.4–18.24, the upper value being close to that defined by Burke *et al.* [9] as the highest DR achieved conveniently for bulk polypropylene.

Oriented polypropylene discs were prepared, 66 mm in diameter and with thicknesses varying between 0.7 and 3.7 mm, according to the degree of roll-drawing. Each disc was clamped between the two brass annuli of a sample-holder and held in by three screws placed to form an equilateral triangle, in order to spread the pressure evenly. Before mounting in the holder, a gentle curvature was easily discernible in several of the samples, although most of them were fairly flat. When clamped in the holder, they were found to stay flat, with a variation of within 75 mm across their surfaces.

The birefringence was measured using an ultrasonic transducer in the pulse-echo mode, in which the same piezoelectric transducer acts as both source and receiver, as shown schematically in Fig. 4. The transducer was a commercial Panametrics 20 MHz shear probe, fitted with a quartz delay line, excited by a high voltage pulse from a Panametrics 5052 pulser/receiver.

Shear waves polarized in a known direction entered the polypropylene from the quartz delay line, after passing through a thin honey couplant layer. The anisotropy of the polypropylene then split the energy into the two *quasi*-shear modes, polarized in orthogonal directions. These directions were parallel and perpendicular to the direction of drawing. Hence, with the polarization direction of the transducer at an intermediate angle, the shear energy was naturally split into the two *quasi*-shear components. These travelled with different velocities through the sample (Fig. 4), and were almost totally reflected from the back wall (a polypropylene/air interface). The shear components travelled back to the transducer, which now acted as a detector, and two distinct pulses were observed, separated by some time difference, Δt, which was caused by the birefringence. The Panametrics 5052 pulser/receiver amplified the signals, which were then displayed on a Tektronix 2430A digital oscilloscope. The waveforms could be transferred to an IBM PS/2 microcomputer for storage and analysis. An example of a typical received waveform is shown in Fig. 5. The fast and slow *quasi*-shear wave components are clearly visible, separated by a time difference,

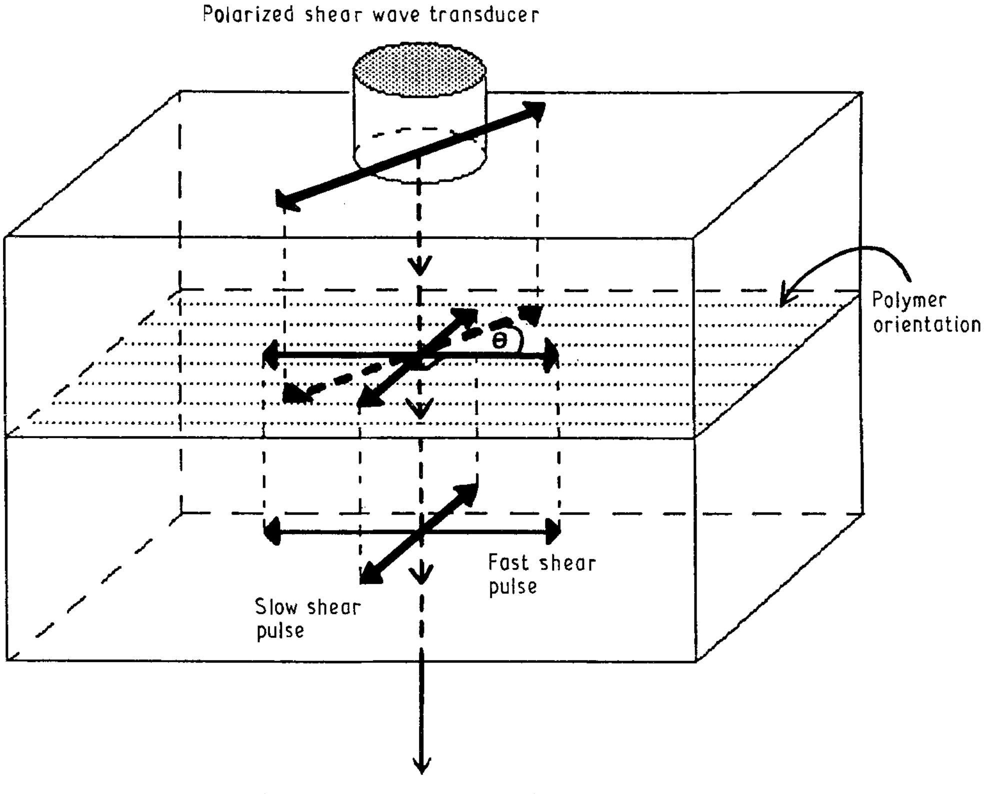

Figure 4 Propagation of shear energy through an oriented polymer sheet, showing the piezoelectric transducer used for generation and detection, and the two ultrasonic shear wave components.

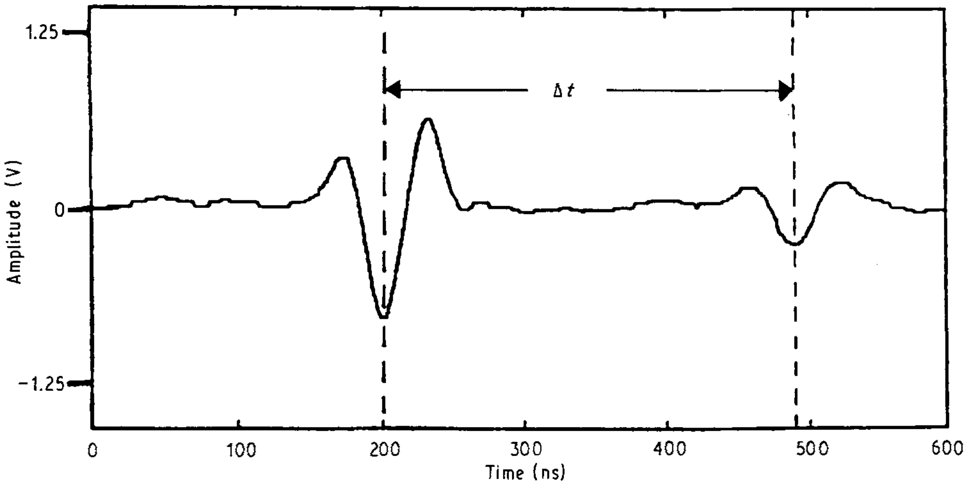

Figure 5 Typical ultrasonic waveform detected by a 20 MHz shear transducer on a roll-drawn polypropylene sheet.

Δt, which was typically of the order of 200–500 ns for oriented samples of various thickness in the range of 0.5–4 mm.

Rotation of the shear wave transducer caused the relative heights of the fast and slow shear wave signals to change, due to the angle θ subtended between the transducer polarization direction and the orientation direction (Fig. 4). For ease of measurement of θ, it was found best to rotate the transducer, and hence its direction of sensitivity, so that both components had comparable amplitudes. Δt could then be determined by a simple cursor measurement on the oscilloscope screen.

Because of the indeterminate nature of the exact thickness of couplant connecting the transducer to the sample, the absolute velocity of any pulse through the material may be obtained only if two or more echoes are received by the oscilloscope. The number of echoes distinguishable on a trace is determined by the energy of the transmitted pulse, the degree of attenuation in the sample material, and the sensitivity of the transducer receiver circuit. For almost all the polypropylene samples measured, only one received pulse was visible on the trace. So, only the difference in time-of-arrival between the fast and slow shear waves could be determined, and not their absolute velocities.

The ultrasonic birefringence, B, may be estimated from the measurements in several ways. In our case, the difference in time of arrival of Fig. 5 corresponds to a distance of travel of two sample thicknesses ($2h$). Hence

$$\Delta t = 2h\left[\frac{1}{v_s} - \frac{1}{v_f}\right] \tag{1}$$

where v_s and v_f are the slow and fast *quasi*-shear wave velocities, respectively. If the birefringence, B, is defined as

$$B = \left[\frac{1}{v_s} - \frac{1}{v_f}\right] \tag{2}$$

we get

$$B = \frac{\Delta t}{2h} \tag{3}$$

Δt is measured directly from the oscilloscope waveform, using digital cursors, and a measurement of sample thickness, h, leads directly to an ultrasonic birefringence measurement.

4. Results and discussion

4.1. Ultrasonic shear wave data

A series of measurements of shear wave birefringence have been performed in a set of polypropylene samples, with known draw ratios. These two variables have also been compared to other physical properties, and as will be shown the data leads to some conclusions concerning the structure of the roll-drawn polymer.

Consider first the correlation of birefringence, B, with draw ratio (DR), the results being presented in Fig. 6. As the draw ratio increases from a low value, the birefringence increases steadily, up to a draw ratio of approximately 10. Beyond this value, little increase in birefringence is observed, and a plateau region is evident. This indicates that some form of structural saturation effect had been reached, i.e. there was a marked initial birefringence, up to a draw ratio of 10. At higher values of draw ratio, little additional orientation had been achieved.

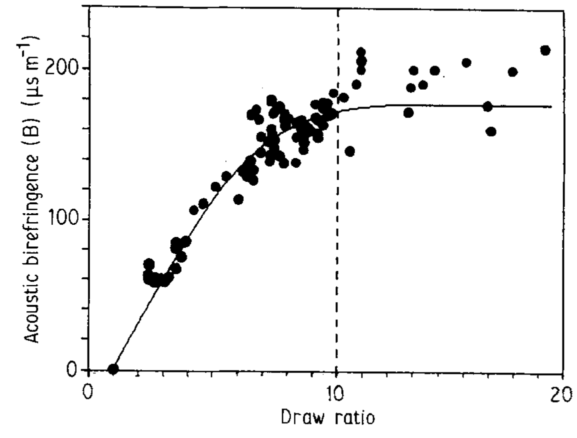

Figure 6 Correlation of ultrasonic birefringence B with draw ratio (DR), for a series of roll-drawn polypropylene samples.

The nature of this saturation may be explained by the following model for roll-drawn polypropylene structure: assuming a polypropylene sample that is sufficiently thick initially, the polymer would be expected to undergo more deformation at the surface than near the centre of the sheet. This is because the forces are applied at the sheet surfaces. As the sheet is roll-drawn, the tensile forces on the polypropylene are greatest near the contact surface with the rollers. According to the accepted model, outlined in the Introduction, microfibrillar structure is formed only after deformation of the spherulites, and therefore it would form first in the regions with the most stress applied, i.e. near the two surfaces of the sheet. A microfibrillar structure forms at the surfaces of the polymer, to a characteristic skin depth at the surface. The depth to which the deformation of the polypropylene penetrates, and hence the thickness of the highly-oriented skin is determined by the drawing conditions—temperature, gap thickness between rollers, weight of rollers, drawing speed. At low enough DRs, it is possible, that the spherulites may suffer negligible deformation at the centre of the polymer sheet. The model is thus a three-layered structure: the outer, highly-oriented, microfibrillar skin, the inner, unoriented, spherulitic core, and a transition zone in the region between the outer skin and the core, as shown schematically in Fig. 7.

As the sheet is stretched to greater DRs, more of the inner, deformed spherulitic material is incorporated into the skins near the surface, and the total thickness of the sheet decreases; this results in greater tensile forces being exerted on the central, spherulitic core, until the entire core has been incorporated into the microfibrillar structure. At this stage, the two outer skins meet, no longer separated by the less dense spherulitic material. The DR at which this occurs is affected by the drawing conditions. Because the polypropylene is then made up entirely of microfibrillar structure, further drawing would be expected to result in a much slower decrease in thickness of the sheet, if any. In addition, the birefringence would be expected to saturate, as was observed in Fig. 6.

Evidence which bears out the process outlined above is seen in the distribution of sample thickness of polypropylene with DR, which is presented in Fig. 8. Beyond a DR of about 10, the total thickness of the sheet remains fairly constant at about 0.9 mm as the DR is increased, thus indicating that the two microfibrillar skins have met. The thickness of the skin is, therefore, inferred to be approximately 0.45 mm—half the amout identified here as the final, stable, sheet thickness. The composition of the outer skin layer is postulated to be as highly drawn as the material will permit, and to have the microfibrillar structure given in the polymer literature [1]. In the region beyond a DR of 10, the sheet is able to continue to deform at constant thickness by decreasing its width.

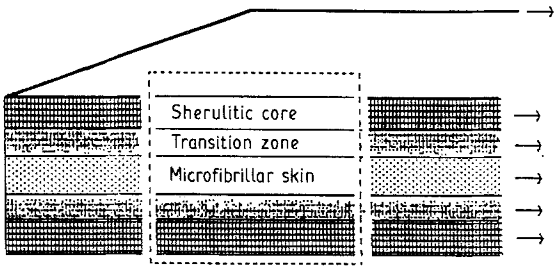

Figure 7 A model for the structure of the roll-drawn polypropylene samples used in the present study.

More information concerning structural deformation during roll-drawing may also be obtained from the acoustic data as shown in Fig. 9. Here, the time difference, Δt, remains approximately constant as the sample thickness decreases (from approximately 4 to 2 mm), but then at higher DRs Δt decreases, commencing at a thickness of $\sim$ 1.6 mm. This data suggests that any polypropylene further than 0.8 mm (half of 1.6 mm) from the surface is not oriented enough by the roll-drawing to register any effect on the Δt value obtained with the shear transducer, and is thus composed of unoriented spherulites. The 0.8 mm includes both a microfibrillar skin, and an inner layer of partially-oriented spherulitic material in the transition zone (Fig. 7).

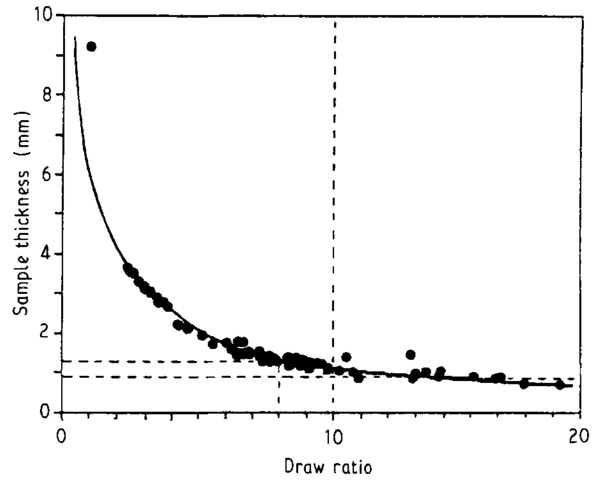

Figure 8 Correlation of sample thickness with draw ratio for a series of roll-drawn polypropylene samples.

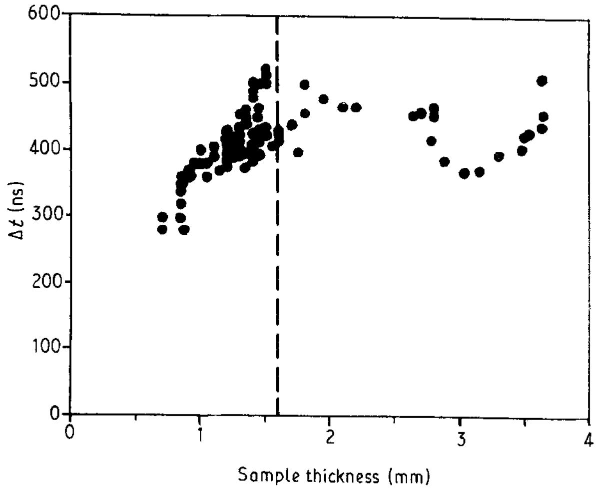

Figure 9 Correlation of the time difference, Δt, defined in Fig. 5 with the sample thickness, for the roll-drawn polypropylene samples.

The above observations are compatible with those of Peterlin [12], who reported that the sorption of linear polyethylene decreased as the DR increased up to a value of 8 or 9, beyond which the sorption remained constant. In the same paper, it was noted that infrared data showed little increase in amorphous chain orientation beyond a DR of 10. Although these studies were in polyethylene, they suggest a similar mechanism is present. In addition, the outer skin layer of highly-oriented polymer postulated in the present work may be related to the previous work of Keller and Pope [5]. They report a single-textured layer with a thickness of 0.5 mm on either side of a sheet of rolled low density polyethylene. This value corresponds closely with that presented of 0.45 mm for the thickness of the postulated outer, microfibrillar, layer of roll-drawn polypropylene sheet.

To further substantiate the above observations, the samples of polypropylene were analysed using a standard ASTM D-4093 optical birefringence test on thin sections. In this method, the phase difference (retardation) between the light-waves parallel and perpendicular to the draw direction is measured by introducing an equal and opposite retardation with a compensator. The polypropylene was prepared using a microtome model 820, made by the American Optical Company. Samples of 30, 40 and 50 μm were cut in a plane perpendicular to the draw-direction of the polypropylene and mounted on a clear glass microscope slide with a cover-slip.

The results are shown in Fig. 10, in which an increasing optical birefringence is evident with DR up to a DR of about 10. For DR values greater than about 10, a plateau region is evident in the graph at a constant OB value of about 32×10^{-3}, a result that has also been obtained in previous studies on polypropylene [13]. These measurements, saturating at a DR of 10, are in agreement with those of shear wave birefringence above. Note however, the main difference in the two techniques: the optical method relies on the preparation of a thin section, whereas the ultrasonic birefringence approach can treat the sample without additional preparation in a nondestructive manner.

4.2. Correlation with modulus and strength measurements

The polypropylene samples were also tested for their tensile properties, the aim being to compare such measurements with both the DR and ultrasonic birefringence, *B*, data described in the previous section.

For the tensile measurements, standard tensile testing samples (ASTM type 2) were cut from the polypropylene discs and centred in the region of the discs where the transducers were applied, so that, as closely as possible, an identical portion of polymer was used in both cases for tensile testing and birefringence measurements. The long axis of the sample was cut parallel to the principal orientation direction and clamped into the holders on the Instron machine. The sensitivity of the modulus measured to the angle of inclination between the tensile force and the orientation direction of the polypropylene was expected to be high; hence, trouble was taken to align the samples carefully.

A tensile test of standard type "D638" was carried out, in which 1.25 cm extensometer was used to determine the changing length of a portion of the sample as the load was increased up to fracture, at a crosshead speed of 0.25 cm min^{-1}. Crosshead speed is the rate of elongation of the polypropylene in the Instron machine. In cases where the sample extended beyond 1.25 cm, the extension beyond the range of the extensometer was inferred from the distance travelled by the clamps on either end of the sample, registered within the mechanism of the Instron machine. The load and length were recorded digitally and printed out on a graph after the test was completed. Fig. 11 shows a typical example of the results from such a tensile test. Note that all stress values calculated are the so-called engineering stress, where the load is divided by the initial cross-sectional area of the sample to obtain the stress; no provision is made for the reduction in cross-sectional area that takes place as the sample is stretched. The ultimate tensile strength (UTS) was

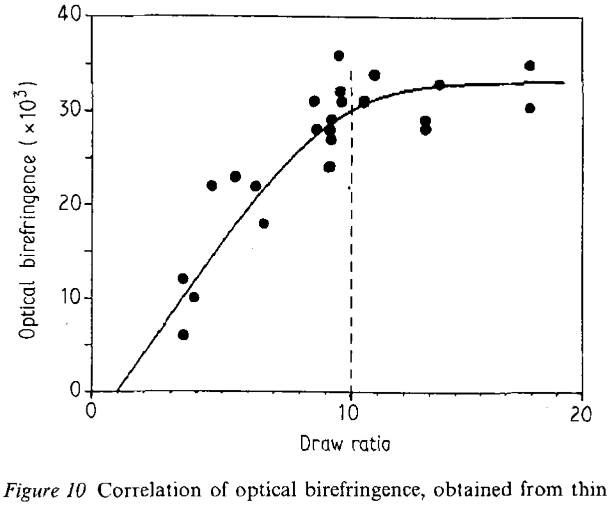

Figure 10 Correlation of optical birefringence, obtained from thin sections, with draw ratio (DR), for the roll-drawn polypropylene samples.

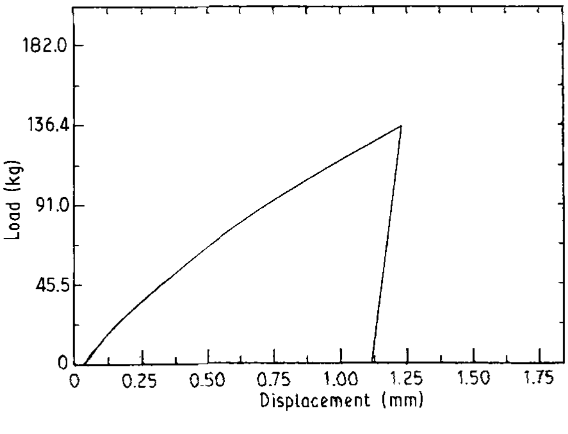

Figure 11 Typical plot of load against displacement during tensile testing of a roll-drawn polypropylene sample.

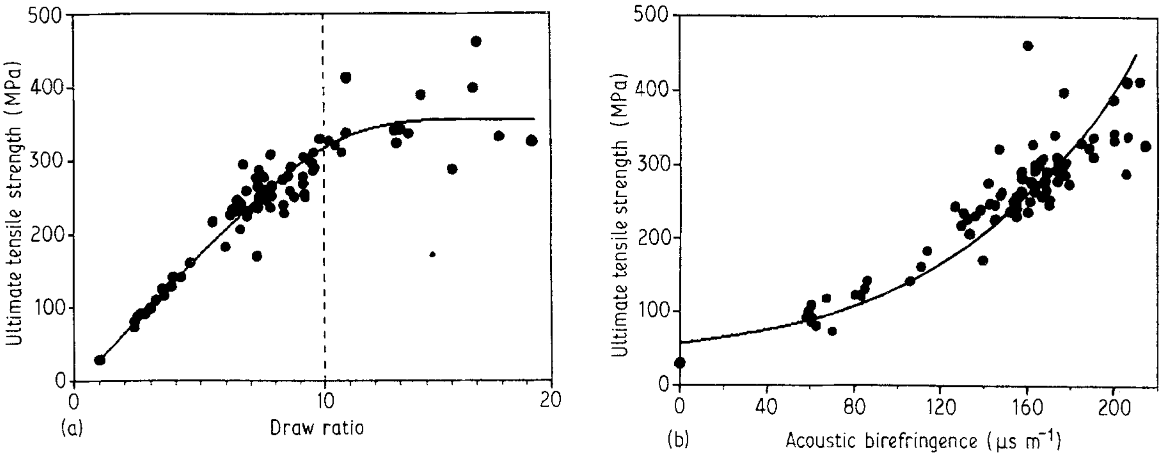

Figure 12 Correlation of ultimate tensile strength with: (a) draw ratio, and (b) shear wave birefringence, for the roll-drawn polypropylene samples.

taken to be the stress at the first discontinuous point on the stress/strain curve, indicating where the sample first fractured.

The correlation of UTS with DR is shown in Fig. 12a. There is a pronounced increase in UTS with DR, up to a value of 10, at which point the curve levels out. This behaviour is similar to that of the shear wave birefringence data as a function of DR, presented earlier in Fig. 6. It would thus appear that the factors affecting shear wave birefringence (degree of anisotropy) also cause the UTS value to change in a similar manner. It is thus interesting to plot UTS against shear wave birefringence, as presented in Fig. 12b, where an estimated fit to the data has been included. This suggests that shear wave birefringence would be a good method for estimating the strength of a particular roll-drawn polypropylene sample, even in situations where the draw ratio is not known, by using a calibration graph such as that shown in Fig. 12b.

5. Conclusions

It has been demonstrated that shear wave birefringence can be used as a monitoring tool for the orientation induced by the roll-drawing of polypropylene. The measurements of birefringence as a function of draw ratio have shown that the orientation seems to saturate at a draw ratio of approximately 10. This has been explained using a model of a microfibrillar skin, induced by rolling, together with a transition zone and an undeformed central core at thicker sections. The birefringence measurements have been compared to the tensile properties of the samples, and it has been demonstrated that the method has promise as a method for estimating such properties in a previously uncharacterized sample.

Acknowledgements

The authors would like to thank Professor R. T. Woodhams, of the University of Toronto, for assistance in preparation of samples, and Alcan International Ltd, Kingston Research Labs., for other technical assistance.

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Received 8 January
and accepted 22 April 1991