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Characterization of roll-drawn polypropylene using optical diffractometry

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An optical diffractometer has been used to investigate the diffraction characteristics of roll-drawn polypropylene. Measurements of diffracted light intensity have been made as a function of the draw ratio used during manufacture and the ultimate tensile strength of the samples in the draw direction. It is demonstrated that the results are compatible with the expected deformation behaviour of polypropylene during manufacture.

1. Introduction

The roll-drawing of polymers such as polypropylene has been widely studied [1, 2]. The result is a material with an increased strength in the drawing direction, a result of microstructural changes induced by the drawing process itself [3]. In a typical manufacturing process [4, 5], a heated billet of polypropylene is pulled through a set of rollers. The first set of rollers is heated to the billet temperature, with a second set of rollers rotating at a greater speed to draw the polymer at the required temperature. A series of subsequent rollers then rotate at a similar speed to the second set, so as to maintain a static tension on the drawn sheet. This prevents relaxation of the structure back to its original state. The degree of drawing is controlled by three main variables: the roller gaps, the draw temperature and the speed differential between the first two sets of rollers. In general, the degree of anisotropy induced by rolling increases with the extent of drawing.

A parameter that is often used to describe the deformation induced is the draw ratio (DR). This is calculated from the ratio of the cross-sectional areas measured before and after drawing of the billet. A higher DR indicates greater deformation. Draw ratios of up to 20 are typical, but beyond this value the mechanics of drawing become more difficult.

It is thought that in the undeformed state, polymers such as polypropylene have a structure which contains crystalline lamellae and amorphous regions [6]. These are arranged within spherulites, which are believed to grow in all directions from a central nucleus via a helical structure. These spherulites vary in size from 10^{-6}–10^{-3} m, depending upon the cooling rate of undeformed material from the melt. When polypropylene is deformed, the spherulitic structure is altered, causing an overall change in the structure of the sample [7]. Under tensile stress, the spherulites change from spherical to ellipsoidal in shape, with the elongation in the direction of the force. X-ray diffraction studies show that under deformation there is a rotation of the crystals, so as to rotate the chain direction towards that of the applied force. The ease of rotation is temperature dependent, and this is why the billet is heated before the drawing process. This deformation mechanism is predominant in the equatorial fibrils.

Accompanying this deformation, the crystal lamellae in intermediate radial positions may slip past each other and rotate, thus also aligning their *c*-axes in the direction of strain. The large amount of preferential orientation in the direction of strain leads to the high level of anisotropy of drawn polypropylene. If the stresses on the polypropylene sheet are increased further, then the spherulitic structure breaks down completely and the structure changes to densely packed bundles of very long (some micrometres) and thin (10–20 nm), aligned fibres, known as microfibrils, oriented in the direction of stress. The final microfibrillar structure is then composed of alternating amorphous layers and crystalline blocks.

The present work was directed towards the development of a method for determining the extent of anisotropy present within a given sample of polypropylene, caused by the roll-drawing process. There are already several methods available for this measurement, such as the use of X-rays and neutrons, and optical birefringence [8]. In addition, some acoustic studies have been performed [9]. The most popular method at present is optical birefringence, but this has one serious drawback as a tool for industrial use in particular, in that it requires a thin slice of the material (micrometers thick) to be available. This can be inconvenient. Hence, we have investigated a different optical approach – that of optical diffraction, to achieve a similar measurement on samples several millimetres thick.

2. Experimental procedure

A schematic diagram of the apparatus is shown in Fig. 1. The sample of polypropylene was held flat against the reflecting face of a plane optical mirror. This, in turn, was attached rigidly to an optical rotation stage, so that the sample could be rotated about 360°. The optical rotation stage could be moved in a horizontal

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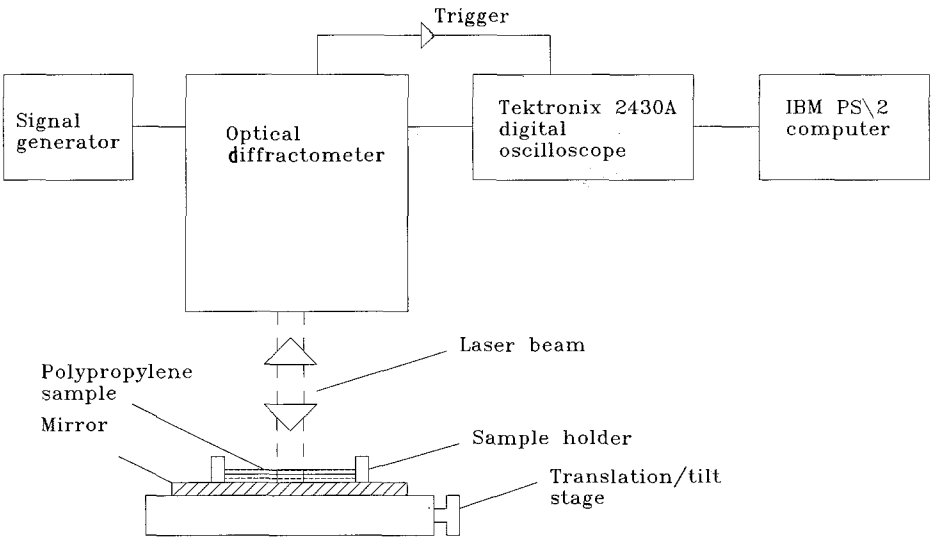

Figure 1 Schematic diagram of the sample holder, optical diffractometer and other instrumentation.

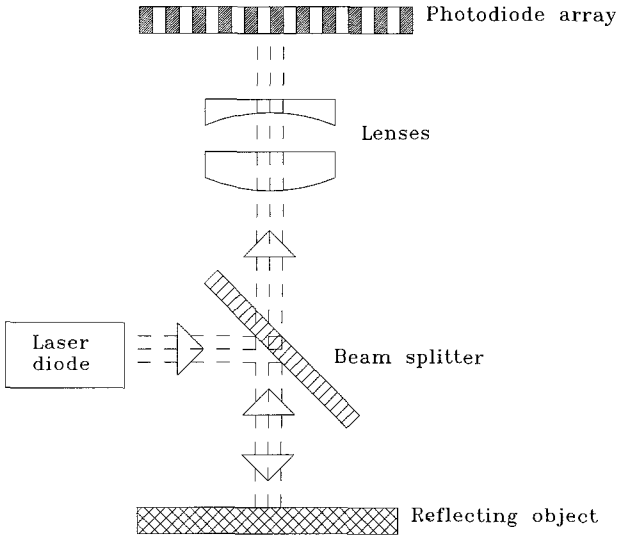

Figure 2 The internal layout of the main optical component within the diffractometer.

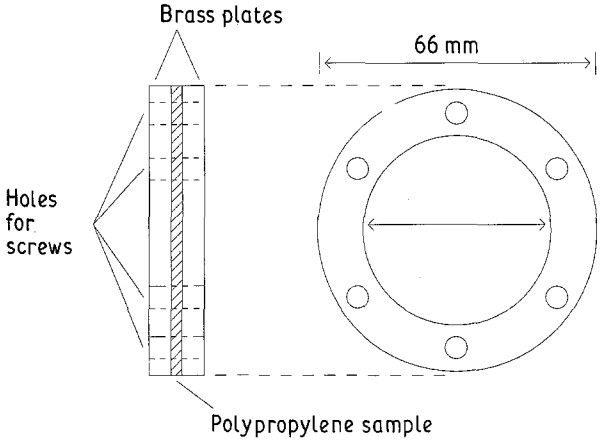

Figure 3 Brass annular sample holder.

plane using two further optical translation stages, and the height adjusted using a scissors jack. In addition, the whole assembly could be tilted using a specially designed tilt stage. Thus, the polypropylene sample could be moved accurately to any desired position and orientation.

The diffraction properties of the polypropylene samples were measured using an optical diffractometer. Such devices have been used in previous work to study surface topography and other applications, and the detailed design of the instrument used here has been described elsewhere [10]. However, the principles of operation may be explained by reference to the layout of the internal optics, shown in Fig. 2. Here, light from a laser diode (LD) is reflected via a beam splitter (BS) on to the sample of interest. Light scattered by the object of interest is then passed through the beam splitter, and directed on to a photodiode array (DA) by means of lenses L_1 and L_2. The L_1/L_2 lens combination forms what is generally referred to as a Transform lens. The image formed at the photodiode array using such a lens combination is independent of the distance from the scattering object.

The photodiode array consisted of 512 sensing elements, whose output was proportional to the light intensity at that position. Each diode was sampled in turn, using an external trigger signal. In the present experiments, the output was digitized using a Tektronix 2430 oscilloscope, and transferred to an IBM PS/2 model 30 computer for storage and analysis. The resultant display was a distribution of light intensity, which represented the farfield (Fraunhofer) diffraction pattern of the object. The experiments were designed to determine whether the light diffraction pattern was dependent upon the draw ratio of polypropylene, with the light passing through the polypropylene sample and reflected by a mirror (see Fig. 1).

To remove effects of refraction of the infrared laser beam from the laser diode due to curved faces of the polypropylene (due to the non-flat nature of roll-drawn samples), each specimen was held rigidly in a brass sample holder of 46 mm inner diameter (Fig. 3). Disc-shaped samples were cut from larger sheets for this purpose.

In practice, a given sample was mounted flat against the reflecting mirror (Fig. 1), and the tilt stage adjusted

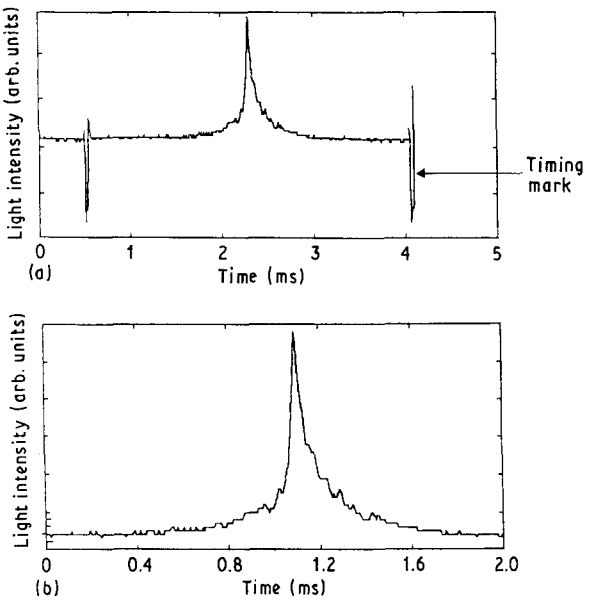

Figure 4 (a) Typical display from the digital oscilloscope, showing the diffraction pattern and the calibration timing marks. (b) Expanded view of (a).

so as to ensure reflection of light back on to the photodiode array. The time base of the oscilloscope was then set appropriately (500 ms/division was usual) to display the outputs from the photodiode array. Also displayed were timing marks, present at either end of each diffraction pattern, as shown in Fig. 4a. The diffraction pattern itself had a recognizable maximum, with a decaying intensity at either side. The horizontal scale could be expanded if desired, as shown in Fig. 4b. Note that in these patterns, the horizontal scale is in time. This is equivalent, however to distance along the photodiode array, with the distance between the timing marks being 12.7 mm.

Polypropylene samples were available in draw ratios of between 2.4 and 18.24, the latter figure representing close to the maximum draw ratio available for polypropylene. The thickness of the samples ranged from 0.77–3.5 mm. Each was cut as a disc from a larger sheet of a given draw ratio. This enabled other tests to be performed, such as conventional optical birefringence and ultimate tensile strength, for purposes of later correlation with diffraction measurements. Note that the direction of drawing was known for these samples from other tests, and for the tensile tests the material was always aligned parallel to the direction of drawing. Note also that the optical diffraction pattern measured was a function of the orientation of the draw direction with respect to that of the linear photodiode array. This was always measured with the draw direction perpendicular to the diode array, maximizing the effect observed at the detector. (The patterns of Fig. 4 were taken in this orientation.) This phenomenon is discussed further below.

The degree of anisotropy induced by the roll-drawing process caused changes in the diffraction pattern received at the photodiode. The infrared beam passed through the sample twice, and in so doing interacted with the structure, whose optical properties became

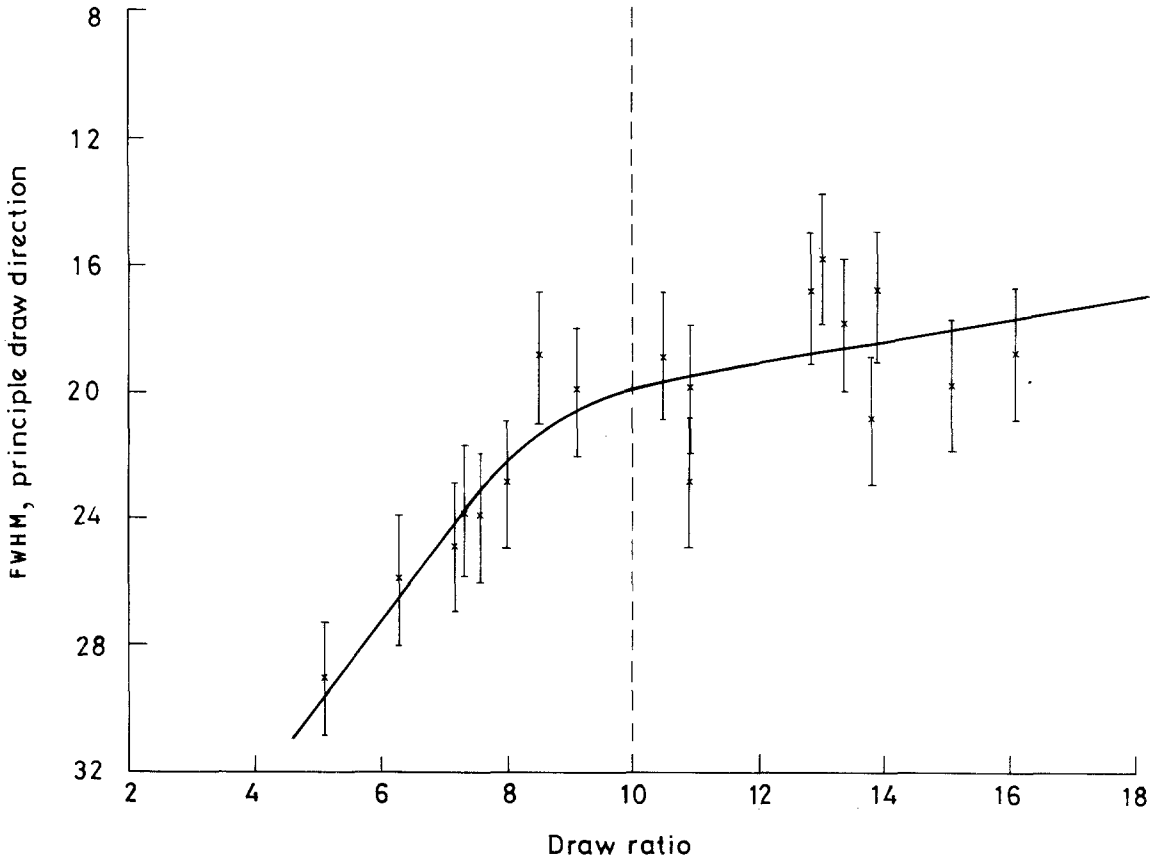

Figure 5 Plot of the full width at half maximum (FWHM) of the diffraction pattern of each polypropylene sample as a function of draw ratio. The effect is due to the principle draw direction, with the photodiode array perpendicular to this direction.

more anisotropic with increased draw ratio. The results of these measurements, and their interpretation, are presented below.

3. Results and discussion

A set of polypropylene samples was tested using the above procedure, resulting in a series of diffraction patterns as a function of draw ratio. Qualitatively, the shape of these patterns remained close to that already shown in Fig. 4. However, the width of the patterns was seen to change. To quantify this process, and to normalize the width of the maximum amplitude of each pattern, the width at half the peak amplitude was measured. This is known as the full width at half maximum (FWHM) value, and is conventionally used in optics. The FWHM is plotted against draw ratio in Fig. 5. This graph indicates that the FWHM decreased with increased draw ratio, i.e. as the material became more anisotropic, a greater degree of diffraction was observed. This might be expected, if one considers the effect of a highly ordered microfibrillar structure such as that shown schematically in Fig. 6. The sample could be considered to be comprised of a set of parallel cylindrical lenses, each of which would tend to refract light in the horizontal plane (i.e. perpendicular to the fibre orientation) but not in the direction parallel to the fibres. An increase in orientation of the polymer in a given direction would cause a narrower total diffraction pattern in a direction perpendicular to the draw direction, as was observed in practice in Fig. 5. (Note that the samples were oriented with the photodiode array and sample draw direction mutually perpendicular as stated earlier.)

The general decrease in FWHM with draw ratio can thus be understood. However, it can also be observed that the FWHM decreases rapidly with draw ratio up to a value of the latter of approximately 10, but then seems to decrease less steeply. This indic-

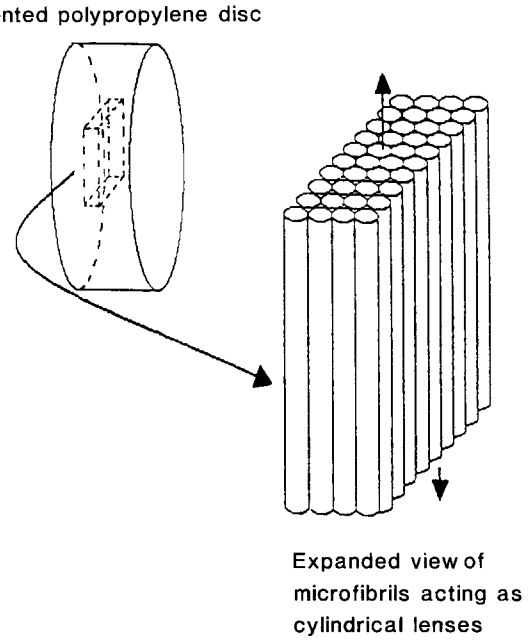

Figure 6 Schematic diagram illustrating how a highly ordered microfibrillar structure could be considered to approximate to a set of parallel cylindrical lenses.

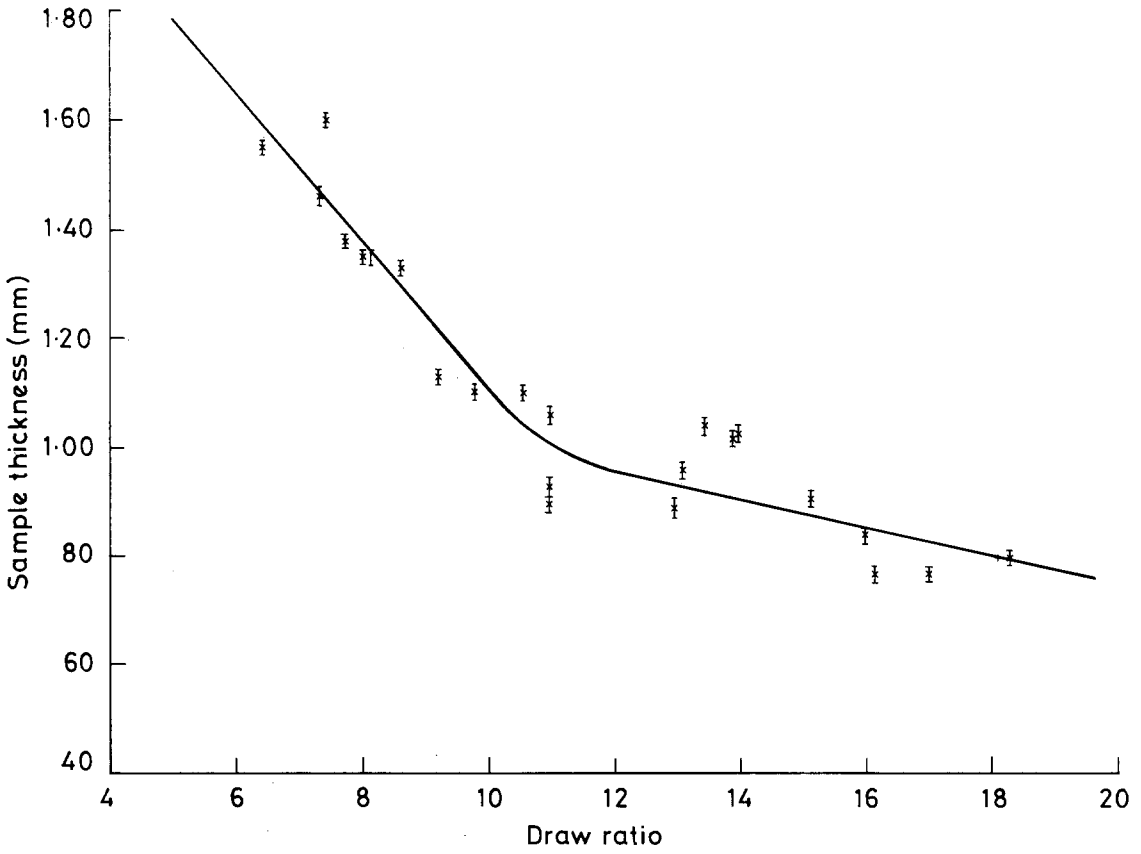

Figure 7 Correlation of sample thickness with draw ratio.

ates that marked orientation and formation of the microfibrillar structure occurs most effectively at the lower values of draw ratio, whereas beyond a value of 10 a high proportion of the sample is already highly ordered, and little increase in anisotropy was being produced at higher draw ratios. This interpretation agrees with other published work on oriented polymers [11], where similar phenomena were postulated. Further evidence is provided by the change in sample thickness with draw ratio, shown in Fig. 7. This indicates a rapid decrease up to a draw ratio of 10, beyond which the decrease is again less rapid. This tends to support the suggestion that the polymer structure rapidly undergoes a change in morphology at low draw ratios, but is highly microfibrillar and anisotropic at draw ratios above 10.

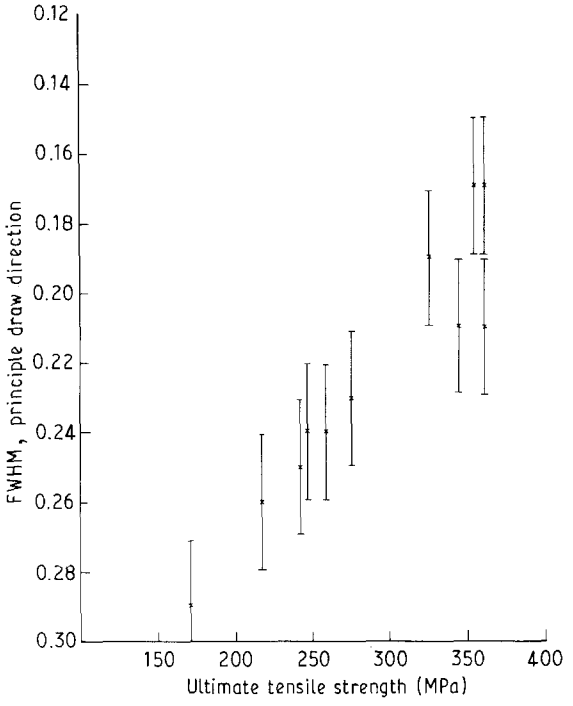

Figure 8 Plot of the ultimate tensile strength (UTS) of polypropylene samples against the full width at half maximum (FWHM) of the diffraction pattern from the optical diffractometer.

Consider now the ultimate tensile strength (UTS) of the material. This was conducted using a standard tensile test specimen, machined out of the same sheet as the circular samples used for the optical diffraction measurements [12]. As stated earlier, the measurements were taken in the draw direction. Plotting the UTS against the FWHM diffraction pattern width led to the graph of Fig. 8. There is a clear decrease in FWHM with increased UTS, and indeed the relationship is reasonably linear. Thus, it would appear that the FWHM value is a good indication of the likely strength of these materials. This is further illustrated if the UTS is plotted directly against draw ratio, as shown in Fig. 9, for the polypropylene samples. Note the similarity of the shape of this dependence with that of FWHM of the diffraction pattern versus draw ratio, presented earlier in Fig. 5. This indicates that both

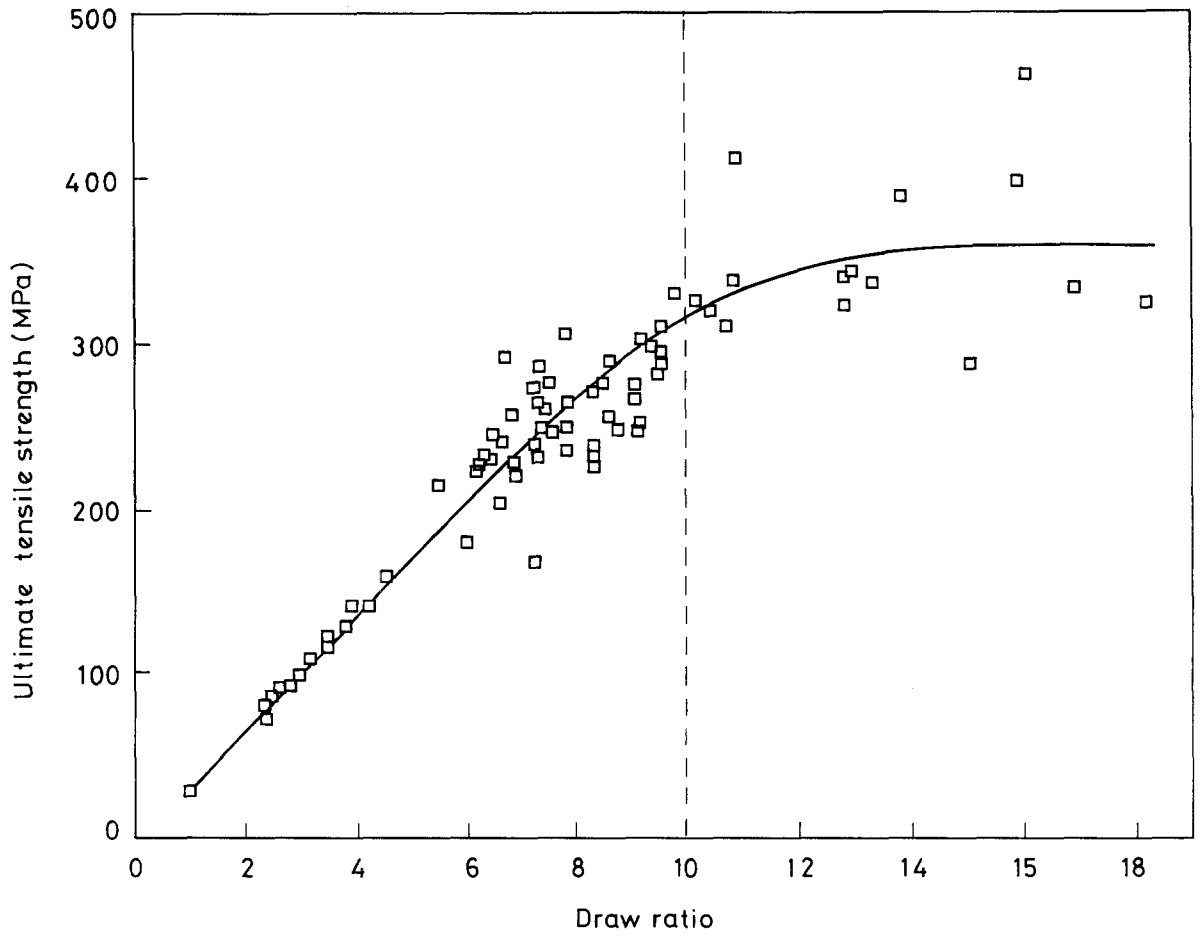

Figure 9 Plot of ultimate tensile strength (UTS) against draw ratio for the polypropylene samples.

UTS and FWHM are responding in a similar way to the change in morphology caused by the roll-drawing process, and indicates indeed that a linear relationship of FWHM with UTS might well be expected. This shows that optical diffraction could be considered a good method for predicting the strength of the material in subsequent engineering or structural applications, where the draw ratio of a given specimen may not be known.

4. Conclusions

It has been shown that the use of an optical diffractometer can lead to an estimation of the optical properties of roll-drawn polypropylene. This has been correlated with both the draw ratio used during manufacture and the ultimate tensile strength in the draw direction. It is anticipated that such a technique might find application in both the laboratory, and during production, for the estimation of the physical properties of these types of material.

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