

# Ultra-high modulus polyethylene. 1 Effect of drawing temperature.

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Drawing behaviour and the properties of ultra-drawn high density polyethylene have been investigated as a function of the drawing temperature. An optimum temperature has been found for each type of polyethylene, at which the best drawing behaviour is found. It appears that the temperature range for effective drawing (leading to a high draw ratio and high Young's modulus) depends on the molecular weight and its distribution. The temperature range of the effective drawing is shifted towards higher temperatures for polyethylene exhibiting broader molecular weight distribution and higher weight-average molecular weight. Ultra-high modulus and transparent samples have been obtained by drawing high density polyethylene with broad molecular weight distribution ( $\bar{M}_w/\bar{M}_n \sim 20$  and  $\bar{M}_w \sim 200\,000$ ) at higher drawing temperatures. It has been found that in the range of drawing temperatures 80–105°C the modulus of this polyethylene is higher for samples drawn at higher temperatures. Transparent samples with draw ratios of 35–40 and with Young's moduli of 600–650 kbar (at room temperature) have been obtained by drawing the polyethylene at 100°–105°C. We conclude that the high molecular fraction in the polyethylene, forming tie molecules in the drawn material, is responsible for the high modulus, while the low molecular weight fraction facilitates alignment of the long chains and retards the internal voiding (whitening) to a very high draw ratio during drawing at the higher temperatures.

## INTRODUCTION

During the last few years linear polyethylene (LPE) has become a subject of interest as a polymer which at high degrees of molecular deformation and orientation exhibits unusually high values of Young's modulus measured along the axis of molecular orientation. The theoretically<sup>1</sup> and experimentally<sup>2</sup> estimated upper limit of the modulus of an anisotropic LPE with fully aligned chain macromolecules is above 2000 kbar, which is comparable with the moduli of inorganic fibers and is even higher than that of steel.

A high degree of molecular orientation can be achieved by the so-called ultra-high drawing technique where solid, semicrystalline films are drawn to a very high extent. Although the technique of drawing up to 40 $\times$  has been applied earlier for structural investigations<sup>3–6</sup> rather than to achieve high moduli, Capaccio and Ward<sup>7–14</sup> used it to achieve very high values of Young's modulus. They have reported a unique correlation between the modulus and the draw ratio. The relationship between the modulus and the draw ratio appeared to be independent of initial morphology of the drawn material (initial thermal treatment) and the molecular weight distribution of the polymers used in their investigations, although the material characteristics were critical for the draw ratio achievable at fixed time of drawing and drawing temperatures<sup>7,9,13,15</sup>. At the drawing temperature of 75°C the highest draw ratios and the highest moduli have been achieved for LPE with low weight average molecular weight ( $\bar{M}_w < 300\,000$ ) and narrow molecular weight distribution.

At this temperature the draw ratios achieved at fixed time of drawing were sensitive to the morphology of the initial material, and the best results were obtained for LPE slowly cooled from 160° to 110°C and then quenched in cold water. The highest moduli reported for the ultra-drawn LPE were close to 700 kbar (1 kbar =  $10^8 \text{ Nm}^{-2}$ ) at draw ratios of the order of 30. Later investigations<sup>14</sup> showed that high and ultra-high molecular weight LPE ( $\bar{M}_w \approx 300\,000$  and 3 500 000, respectively) can be drawn effectively to a high extent, but in this case higher drawing temperatures are required. The LPEs were drawn by the authors<sup>14</sup> at 115°C and 135°C, respectively. On the other hand the effect of the initial thermal treatment (immediate quenching in cold water from 160°C or slow cooling to 110°C followed by quenching) was less pronounced with increasing weight average molecular weight and practically disappeared for LPE with  $\bar{M}_w > 300\,000$ . The authors<sup>14</sup> claim that the highest moduli achieved by high temperature drawing of high molecular weight LPE are lower (about 500 kbar) than those of low molecular weight drawn at 75°C. The effect of drawing temperature seems to be substantial in this field and one can expect that further investigations of the effect can provide more information concerning the mechanism and nature of ultradrawing of semicrystalline polyethylene films.

Recently we have obtained some results on the effect by drawing LPE over a wide range of temperatures. It appears that drawing temperature affects not only the draw ratio at failure but also melting points, degree of crystallinity and Young's moduli of ultra-drawn LPE. The temperature range over which LPE can be effectively drawn to a very high extent depends on the molecular weight and its distribution.

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Table 1 Material characteristic of the used LPE: densities, degrees of crystallinity (from the density) and melting points are listed for compression moulded, isotropic films

Polymer	Melt index	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Density (g/cm <sup>3</sup> )	Crystallinity (%)	Melting point, °C
Alathon 7030	2.8	22 000	93 700	4.3	0.9606	75.8	134.0
LP 51.1	0.3	11 000	208 000	18.9	0.9618	76.5	133.5

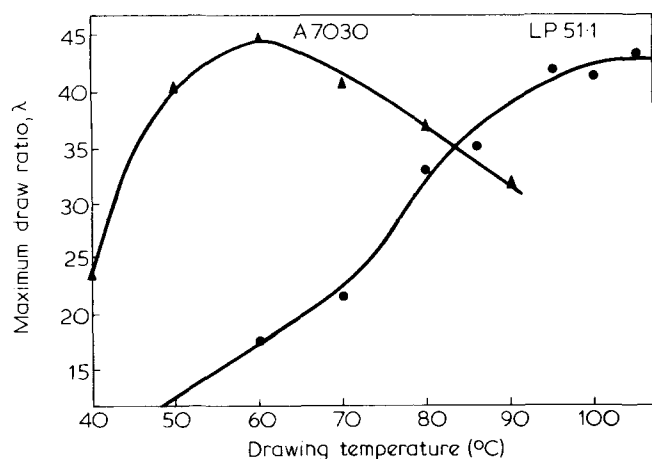


Figure 1 Maximum draw ratio achievable vs. drawing temperature for: Alathon 7030 and the LP 51.1

## EXPERIMENTAL

Two grades of LPE were used in this study: Dow Chemical LP 51.1 and du Pont Alathon 7030. The samples were prepared in the form of isotropic films 0.08–0.1 cm thick by the compression molding of pellets (Alathon 7030) or powder (LP 51.1). Some material characteristics, densities, degree of crystallinity estimated from density and melting points of the prepared films are listed in Table 1.

The following molding procedure recommended by Capaccio and Ward<sup>7,13</sup> was used. The pellets or powder were sandwiched between two metal plates and melted in a hot press at 160°C under slight pressure of 1 kg/cm<sup>2</sup> for 2–3 min to allow a complete melting. Next the polymer was annealed at 160°C for 2 min after increasing the pressure up to 25 kg/cm<sup>2</sup> and subsequently slowly cooled to 110°C with the cooling rate  $\sim 7^\circ\text{C}/\text{min}$ . The above procedure has been shown to give the optimum morphology of LPE films to achieve the best drawing behaviour<sup>7,15</sup>. Samples for drawing were cut out in the form of dumbbells of 1 cm and 0.5 cm gauge length and width respectively. The dumbbell samples were drawn with an Instron tensile testing machine at a crosshead speed of 5 cm/min within an environmental high temperature chamber at various constant air temperatures from 40° to 105°C. The draw ratio and the draw ratio distribution were found by measuring the distances between ink marks which were put on the samples at one millimeter intervals before drawing.

The modulus of elasticity of the drawn material along the axis of drawing was determined by testing the samples at room temperature with the Instron Tensile Tester using a crosshead speed of 0.05 cm/min. The test was performed on samples 5 cm long and exhibiting satisfactory uniform draw ratio (in most cases deviation of the draw ratio was  $< \pm 2$ ). The moduli were calculated from the tangents of the stress–strain curves taken at the points corresponding to a strain of 0.1%.

Melting points were taken as the peak temperatures on the DSC endotherms obtained with a Perkin–Elmer DSC 1B at a scan speed of 5°C/min, with the run starting at 100°C. Degree of crystallinity was calculated from the heat of fusion measured by the DSC method using a value of 69.2 cal/g as the heat of fusion of the perfect extended chain crystal<sup>16</sup>. Densities of isotropic and drawn LPE samples were measured at room temperature in a density gradient column made using toluene and chlorobenzene. The mass fraction of crystalline polyethylene ( $\alpha_m$ ) was determined from the densities ( $\rho$ ) using the formula

$$\alpha_m = [(\rho - \rho_a)/(\rho_c - \rho_a)] \rho_c/\rho$$

assuming the values of  $\rho_a = 0.855 \text{ g/cm}^3$  and  $\rho_c = 1.000 \text{ g/cm}^3$  for the densities of the amorphous and crystalline phase respectively<sup>12</sup>.

## RESULTS AND DISCUSSION

The maximum draw ratios achievable before failure as a function of temperature of both types of polyethylene were investigated and the results are presented in Figure 1. The achievable draw ratio shows a single maximum for each polymer; at 60°C for the Alathon 7030 and at around 100°C for the LP 51.1. Both polymers show maximum draw ratios above 40, but there is a significant difference in the temperature range at which such draw ratios can be achieved between the two polymers. For example, at the drawing temperature of 60°C, at which the Alathon can be drawn to its highest degree of elongation (40x), the Dow Chemical LP 51.1 fails at elongations even below 20x. But at higher drawing temperatures, the LP 51.1 can be drawn to draw ratios up to 40 (at temperatures about 100°C), while the drawing behaviour of the Alathon 7030 becomes poorer. There is a qualitative difference in the performance of both polyethylenes in the range of drawing temperatures between 60 and 100°C. We believe the striking difference results from the differences in molecular weight and its distribution, as characterized by the number ( $\bar{M}_n$ ) and weight ( $\bar{M}_w$ ) average molecular weights (Table 1). Alathon 7030 shows narrower molecular weight distribution ( $\bar{M}_w/\bar{M}_n = 4.3$ ) with  $\bar{M}_w = 93\,700$  corresponding to shorter chains than those of Dow Chemical LP 51.1 with  $\bar{M}_w = 208\,000$  and  $\bar{M}_w/\bar{M}_n = 18.9$ .

Longer chains, especially in the case of the LP 51.1, passing through a number of crystalline regions in the solid polyethylene form a higher number of interlamellar bridges and inter-chain entanglements. This leads to a better defined network-like structure with crystalline regions playing the role of cross links. The differences in the structure as related to the differences in the molecular weight distributions cause the shift of the range of the effective drawing temperatures towards the higher temperatures in the case of the LP 51.1. The single maxima on the curves shown in Figure 1 appear as a result of two competitive effects: (1) internal void formation being more prevalent at lower drawing temperatures and (2) lowering of t

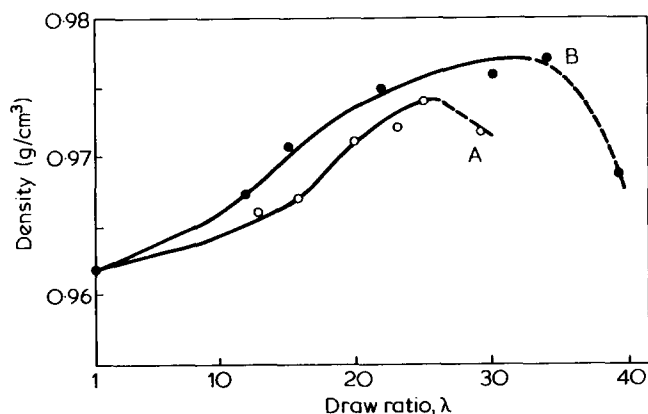


Figure 2 Density vs. draw ratio for the LP 51.1 drawn at: A, 90° and B, 100°C

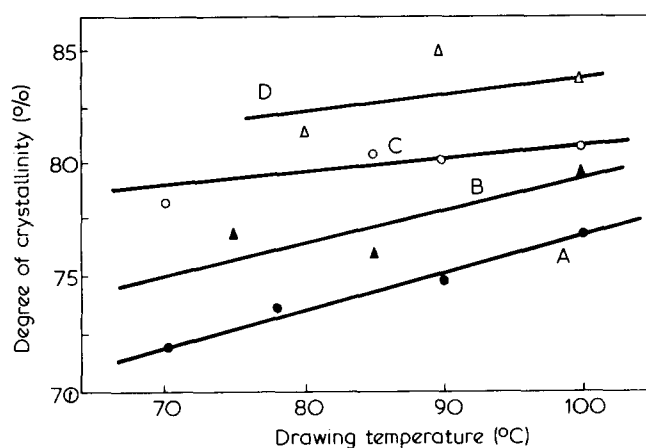


Figure 3 Degree of crystallinity from d.s.c. measurements vs. drawing temperature at fixed draw ratio: A,  $\lambda = 15$ , B, 20; C, 25 and D, 30 for the drawn LP 51.1

interchain friction forces leading to a lower degree of molecular alignment at higher temperatures, and accompanied by a more pronounced relaxation of molecular deformation and orientation. There was also a visual difference between those two polymers drawn to draw ratios  $\lambda > 15$ . The drawn Alathon 7030 was always opaque at all drawing temperatures, the opacity being the result of a content of internal voids in the material. However, in the case of LP 51.1 drawn at the temperatures around 90–100°C, very high draw ratios ( $\sim 30$ ) have been achieved before the material became opaque. More detailed information concerning the temperature dependence of cracking and voiding in the drawn LPE will be published soon<sup>17</sup>.

The relatively low content of the voids in the LP 51.1 drawn at higher temperatures allowed us to measure the density of the drawn material by using the density gradient column method. Figure 2 shows an increase in the density with increasing draw ratio (to draw ratios  $\sim 30$ ) followed by an apparent decrease which we related to intensive internal voiding at very high draw ratios. The highest densities of the LP 51.1 drawn at 100°C were about 0.977 g/cm<sup>3</sup>. The highest mass fractions of the crystalline material,  $\alpha_m$ , in the drawn and transparent LP 51.1 were 84 and 86% at drawing temperatures 90° and 100°C and, at draw ratios 25 and 35 respectively, in comparison with 75% for the initial isotropic polyethylene. Figure 2 shows higher densities of the polyethylene drawn at 100°C than those of the material drawn at 90°C at the same draw ratios. The results of our d.s.c.

measurements confirm. The degree of crystallinity estimated from the heat of fusion by the d.s.c. method increases at fixed elongation with increasing drawing temperature. Figure 3 presents the results at draw ratios  $\lambda = 15, 20, 25$  and 30. The samples with draw ratios below 20, drawn at 100°C exhibit about a 5% higher degree of crystallinity than those drawn at 70°C. For higher draw ratios,  $\lambda > 20$ , the difference in crystallinity is 2–3%. The d.s.c. data confirm all the previous conclusion that crystallinity increases with increasing draw ratios at constant drawing temperature (compare Figure 2).

Melting points were measured using the d.s.c. and the melting point increment vs. draw ratio is shown in Figure 4 for the Alathon 7030 drawn at 60°C and for the LP 51.1 drawn at 100°C. The melting point increases monotonically with increasing draw ratio for both polyethylenes. A similar observation has been reported by Capaccio and Ward<sup>7</sup>. The melting temperatures of the samples drawn to a very high extent ( $\lambda > 30$ ) are higher by  $\sim 7^\circ\text{C}$  than those of the initial isotropic polyethylene. We have also investigated the melting point increment vs. drawing temperature at several fixed draw ratios for the Alathon 7030 and the LP 51.1. In the case of the Alathon 7030 the measurements were performed for samples with  $\lambda = 15, 25, 35$  and 40 and the results are plotted in Figure 5a covering the temperature range of drawing of 40–90°C. The melting point of the Alathon increases slightly with increasing drawing temperature, except for the samples with low draw ratio,  $\lambda = 15$ , and the highest increase observed for highly drawn samples ( $\lambda \geq 25$ ) was  $\sim 1.5^\circ\text{C}$  in this range of drawing temperature. The melting temperatures of the samples with  $\lambda = 15$  are scattered along a horizontal line with the range of  $\pm 0.5^\circ\text{C}$  indicating that the melting point is approximately independent of the drawing temperature at the low draw ratio. An increase of the melting temperature with increasing temperature of drawing seems to be more pronounced in the case of higher draw ratios. The results obtained for the Dow Chemical LP 51.1 are plotted in Figure 5b, covering drawing temperatures of 70–100°C, and at fixed draw ratios of 20, 25 and 30. In this case the curves in Figure 5b show single maxima of the melting point at the drawing temperatures around 80–90°C, indicating a high degree of molecular orientation and/or a less defective structure of the crystalline regions formed during drawing at those temperatures. The increase of the melting point with increasing drawing temperature observed for the Alathon 7030 and LP 51.1 in the d

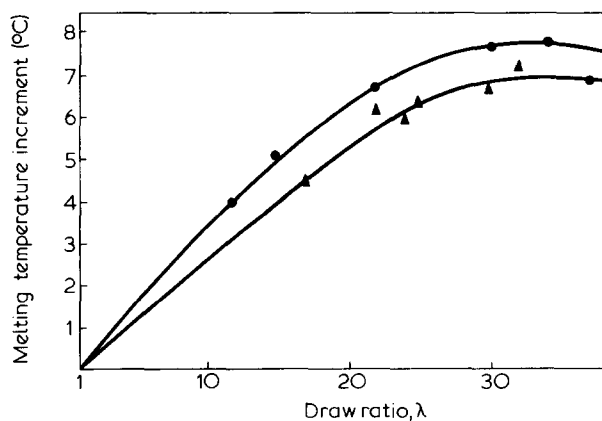


Figure 4 Melting temperature increment vs. draw ratio for the Alathon 7030 drawn at 60°C (▲) and for the LP 51.1 drawn at 100°C (●)

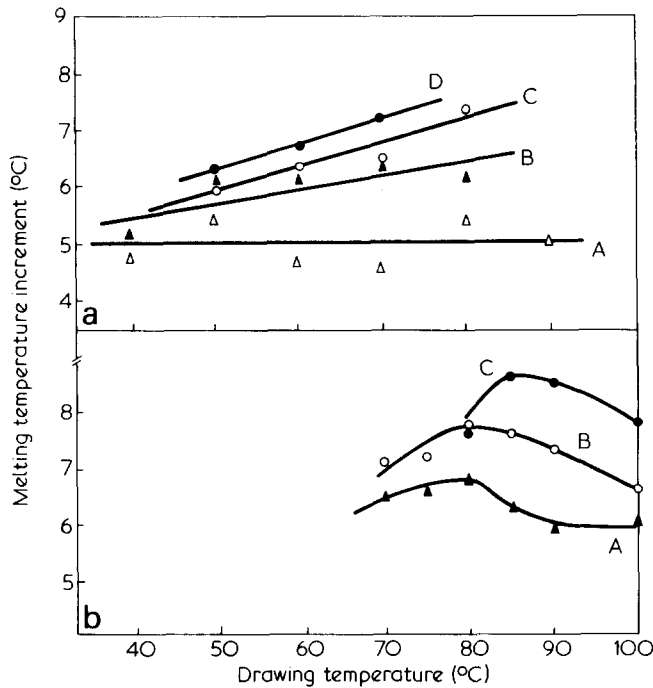


Figure 5 Melting temperature increment at fixed draw ratio vs. drawing temperature. (a) Alathon 7030, A,  $\lambda = 15$ ; B, 25; C, 35; D, 40; (b) LP 51.1, A,  $\lambda = 20$ ; B, 25; C, 30

ing temperature range below 80°C (Figure 5a and b) can be attributed to higher mobility of the chain macromolecules at higher temperatures and a better rearrangement of the chains leading to a less defective structure of the highly oriented crystalline regions. The content of internal voids also appears to be lower in the material drawn at higher temperatures<sup>17</sup>. However with further increase of the drawing temperature, relaxation of the molecular deformation appears as a competitive process and results in the appearance of the maximum (around 80–90°C) on the melting point increment vs. drawing temperature curve in Figure 5b. The more pronounced relaxation at higher temperatures affects the molecular deformation and orientation so that the melting point is lower even at the same degree of macroscopic elongation. The drop in the melting temperature is of order of 1°C in the range of drawing temperature between the optimum and 100°C. It is quite obvious that the relaxation of the molecular deformation concerns mostly low and medium molecular weight fraction of the material, while the longest chains can be still effectively deformed and oriented by the drawing at higher temperatures, forming the tie molecules presumably being responsible for a high modulus. In the case of Alathon 7030 the maximum was not observed because of the lower drawing temperatures required for an effective drawing.

It has been concluded by Capaccio and Ward<sup>7</sup> that the Young's modulus increases monotonically with increasing draw ratio. Our investigations generally support this conclusion, but we have observed that the relationship is affected by the drawing temperature. We measured the Young's modulus of the LP 51.1 drawn at different temperatures as a function of draw ratio and it appeared that the drawing temperatures considerably affect the final moduli, especially in the range of high draw ratio,  $\lambda > 20$ . Young's moduli vs. draw ratios of the LP 51.1 drawn at temperatures  $T_d = 80, 90, 100$  and 105°C are plotted in Figure 6. The dash line in Figure 6 shows the modulus for the Alathon 7030 drawn at

60°C at which the highest draw ratios have been achieved (Figure 1), and the highest values of the modulus are about 300 kbar. The moduli of the LP 51.1 (solid lines in Figure 6) drawn at 80°C are slightly higher with maximum value of about 350 kbar at draw ratio  $\sim 28$ . A substantial increase in the modulus can be achieved by increasing the drawing temperature, especially in the temperature range between 90° and 100°C, where an increase in the modulus from 400 to 600 kbar was affected by increasing the drawing temperature by only 10°C. The highest modulus 650 kbar was obtained at drawing temperature of 105°C and at draw ratio  $\lambda \approx 35$ . The curves in Figure 6 show single maxima of the Young's modulus at very high draw ratios. The appearance of the maximum in the modulus vs. draw ratio plots can be attributed to an internal voiding process being more intensive at very high extensions and causing the lowering of the modulus of the ultra-drawn polyethylene. We presume that the higher values of the Young's modulus of the LP 51.1 appear at higher drawing temperatures because better alignment of the longer chains can be achieved at higher temperatures. At higher temperatures more intensive flow of the low and medium molecular weight fraction of the drawn material (being highly crystalline) facilitates a better orientation of the longer chains (with much longer relaxation times) which finally form well-oriented tie molecules. These connect the oriented crystalline regions and such extended chains increase the extentional modulus of the drawn material. Better flow at higher drawing temperatures of the low and medium molecular weight components of a matrix containing long chains postpones internal voiding to very high draw ratios, and transparent ultra-high modulus polyethylene with very high draw ratio can thus be obtained. Lack of correlation between melting point (decrease) and Young's modulus (increase) vs. drawing temperature in the range of high drawing temperatures causes us to conclude that the highly crystalline lower molecular weight portion of the polyethylene does not affect the modulus to the extent that the high molecular weight fraction does.

## CONCLUSIONS

The temperature range for drawing LPE to very high draw ratios depends on the molecular weight and the molecular weight distribution of the LPE. The material with broader molecular weight distribution and higher weight average

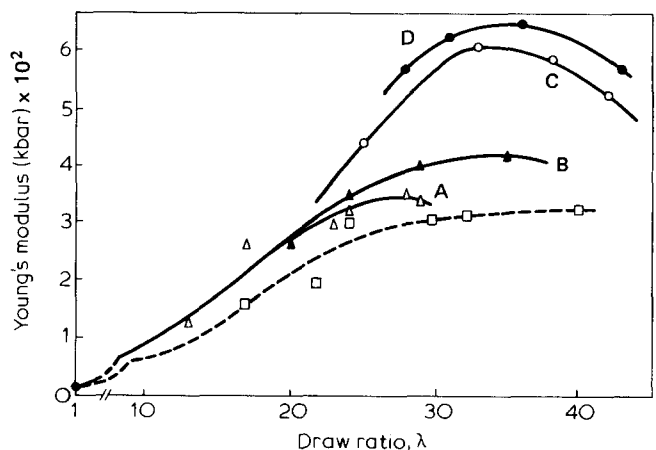


Figure 6 Young's modulus vs. draw ratio for the Alathon 7030 (---) drawn at 60°C, and for the LP 51.1 (—) drawn at 100°C; A, 80°C; B, 90°C; C, 100°C; D, 105°C

molecular weight,  $\bar{M}_w$ , requires a higher drawing temperature to achieve a high draw ratio, and thus a high modulus of elasticity.

An increase in the density and in the degree of crystallinity has been observed with increasing the draw ratio in an isothermal drawing process. It appeared that the density and the heat of fusion measured at fixed draw ratios are higher for the LPE drawn at higher temperatures.

Melting points increase with increasing drawing temperatures (up to 90°C) at fixed draw ratios with the increase being more pronounced for the LPE drawn to higher draw ratios. The highest values of the melting point increment have been obtained for the samples drawn at 80–90°C. For higher drawing temperatures up to  $T_d = 105^\circ\text{C}$  for samples which can be drawn at such temperatures a decrease of the melting point has been observed with increasing  $T_d$ . The decrease can be attributed to more intensive relaxation of molecular deformation and orientation and lower intersegmental friction forces, leading to a lower degree of orientation of the chains forming crystalline regions.

A substantial influence of drawing temperature on the Young's modulus has been observed, especially in the range of drawing temperatures above 90°C and at higher draw ratios,  $\lambda > 20$ . The highest values of the modulus of the LPE samples drawn at 100°C are higher than those of the samples drawn at 90°C. Highest values of the modulus ~650 kbar have been achieved by drawing the LP 51.1 at 105°C up to a draw ratio  $\lambda \cong 35$ , at which the drawn material was still transparent.

The content of high and low molecular weight LPE in the drawn material is decisive for obtaining ultra-high modulus and transparent polyethylene by drawing at higher temperatures. Lack of a correlation between the melting point and the modulus in the range of drawing temperatures above 80°C leads to the conclusion that the high molecular weight fraction in the drawn LP 51.1, forming oriented tie molecules is responsible for high modulus. The low molecular weight fraction, being highly crystalline, leads to higher de-

formation and better alignment of the longer chains by more intensive flow of the crystalline domains at higher drawing temperatures and by this means prevents internal void formation even at very high draw ratios.

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