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THERMAL AND MECHANICAL BEHAVIOR OF POLYETHYLENE FILM OBTAINED BY ORIENTATIONAL CRYSTALLIZATION

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The thermal and mechanical behaviour was measured in the U. S. for a polyethylene that had been prepared and highly drawn in the U. S. S. R. The melting point and percent crystallinity were evaluated in this studies as a function of heating rate and recrystallization. The Young's modulus and tensile stress to break in the orientation direction were 4.1 and 0.15 GPa, respectively. The tensile strain to break was about 8 %.

For many reasons, such as clarity and strength, there is a continuing interest in the preparation of unusual morphologies of the world's largest production polymer, polyethylene. For example, transparent, highly-oriented and highly-crystalline strands of high-density polyethylene have been produced in an Instron capillary rheometer under the combined effects of pressure and deformation below the polyethylene melting point [1–3]. The melting behavior of this ultradrawn polyethylene has been investigated in detail [4–6].

Transparent polyethylene filaments [7] and films [8] of high modulus have also been prepared by hot drawing. The polyethylene was drawn between rollers in the melt state to an extension ratio over 10 in a controlled oven and at hot roller temperatures. The present work details the thermal, annealing and mechanical characteristics of this interesting morphology of polyethylene prepared in the Institute of Macromolecular Compounds in Leningrad.

The sample was a "technical" film obtained not in the ultimate conditions described in [7, 8] when an extended chain crystal "carcass" necessarily appears as a result of orientational crystallization. Samples of more pronounced properties have been prepared in the same laboratory.

Thermal studies

Thermal behavior was determined with a Perkin–Elmer Differential scanning calorimeter (DSC) Model 1-B. Precise sample weights of 1–3 mg were used. Calorimetry was calibrated using an indium standard. The degree of polyethylene crystallinity was calculated from the area under the melting peaks. The heat of

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fusion for polyethylene and indium used for calculation was 69.2 and 6.75 cal/g, respectively. All DSC values were corrected for instrumental thermal lag [9]. A series of fusion curves on separate samples provided melting points as a function of heating rate. The fusion curves are broad, especially at low heating rate, < 10°/min. This breadth reflects a wide distribution of crystallite sizes and perfections [10]. The apparent melting point increased with heating rate (Fig. 1) but the superheating effect is lower than that reported by Southern *et al.* [4], for an ultra-oriented polyethylene. The melting point was taken as the projection of the peak maximum onto the base line. The melting point was 126.5° at a heating rate of 10°/min.; lower, by about 10° than reported for high density polyethylene [11]. The film samples were annealed at a temperature as high as 150° for 5 minutes in the DSC pan to insure complete fusion, followed by cooling at 10°/min to 50 – 60°. These samples were scanned again and the melting point plotted *vs.* heating rate as shown in Fig. 1. The melting point was found to decrease with annealing and the melting point *vs.* heating rate was found to be nearly parallel to that of the unannealed samples. This small apparent superheatability is in part due to instrument response. The parallel plots imply the absence of extended chain crystals, as detected by superheating, in the original drawn morphology.

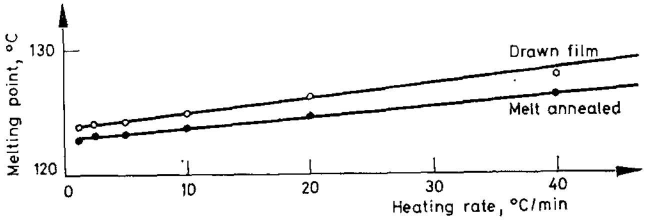

Fig. 1. Effect of heating rate on the melting points on drawn films and melt annealed polyethylene

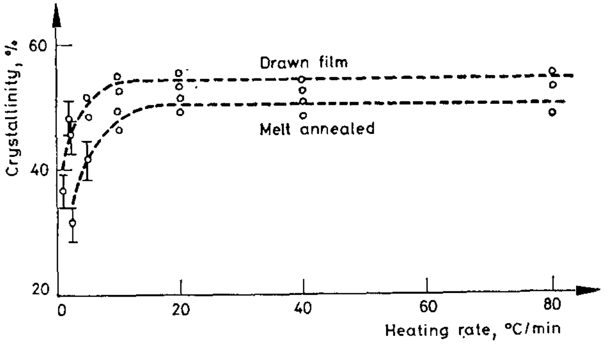

Fig. 2. Effect of heating rate on the percent crystallinity for drawn films and melt annealed polyethylene

It is also of interest to note the effect of heating rate on the area of the fusion curves which is proportional to the percent crystallinity. Separate runs were made at different heating rates as plotted in Fig. 2. It can be seen that heating rates from 10 to 80°/min. have practically no effect on the percent crystallinity, as measured by DSC.

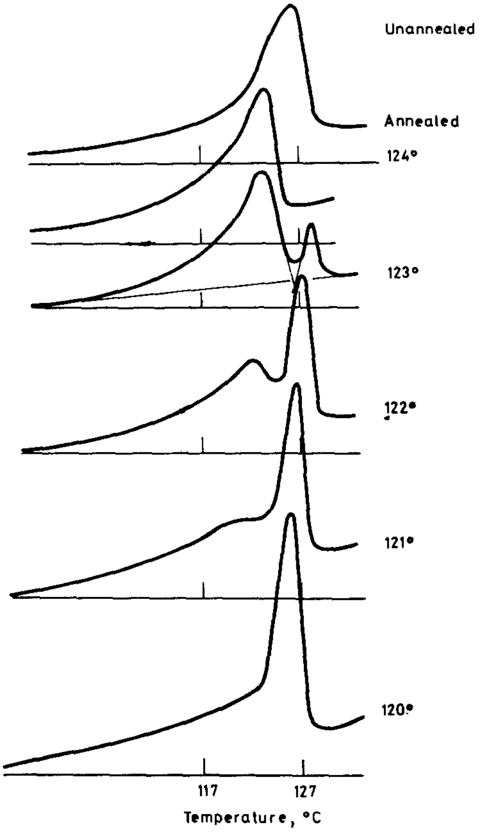

Fig. 3. DSC fusion curves for a drawn polyethylene film annealed for 1.5 minutes

At lower heating rates, however, the area under the fusion curves decreases. The reason for this is unknown, but it may be instrumental. The same procedure was repeated with samples annealed at 150° for 5 minutes. The crystallinity was found to decrease on annealing by about 5% and the crystallinity variation was similar to the case of the unannealed samples. At low heating rate the fusion curves are broad with long tail on the lower temperature side. This may lead to errors in area measurements. However, the crystallinity definitely decreases with annealing.

An attempt was made to resolve some features of these crystalline structures by annealing the polymer at various temperatures and times. Samples were heated in the DSC pans at different temperatures, cooled quickly to 50° below the temperature at which annealing begins and then scanned at a heating rate of 10°/min. Figure 3 illustrates the fusion curves of samples annealed for 15 minutes at a series of temperatures. The annealing time was calculated after thermal equilibrium when the recorder pen comes to rest. Figure 3 shows splitting of the fusion curves into two components which indicates two endotherm melting points. The peak melting point at 126–127° is the melting point of the original sample. According to Southern, *et al.* [4], the melting point defined from the fusion peak approximates the temperature at which the majority of crystallites melt rather than the temperature at which the final crystallites melt. When the polymer is annealed at 124° for only one and one-half minutes, the DSC curve shows no splitting but rather shifting of the peak by about 4° to lower temperature. On lowering the annealing temperature to 123°, the DSC curve shows clearly two endotherms, one peak at ~ 128° and the other at ~ 124°. At lower annealing temperature the area under the peak at higher temperature was found to increase and the peak shifts slightly to lower temperature reaching finally the melting point of the original samples when annealed at 120°. However, the curve obtained after annealing at 120° differed from the curve of the original sample. It shows slight separation of two components, one sharp narrow peak plus a diffuse area. The melting peak at lower temperature may be associated with a morphology of lower order. Moreover, the crystalline texture remaining at high temperature close to the melting point is in a state that the larger, more perfect crystals of higher thermodynamical stability remain, while the other portion of the sample is in the melt state. Multiple endotherm peaks of polyethylene have been described during fusion of unfractionated, branched and linear polyethylenes [12, 13], for polyethylene copolymers [14], and for polyethylene crystallized under high [15] or normal pressure [16, 17].

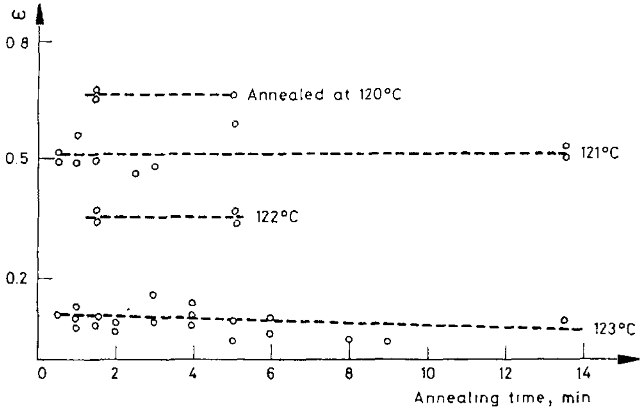

Fig. 4. Effect of temperature and time on the annealing properties of polyethylene films

To investigate the effect of annealing time on the relative areas of the two peaks, the area under the endotherm trace having the peak melting point ~ 128° was divided by the area under the whole curve, and this ratio (w) was plotted against time as shown in Fig. 4. For purpose of area integration, the two peaks of the DSC trace were approximately separated as shown in Fig. 4. Within the precision of 5%, the sum of the two areas under the individual curves equaled the total area of the fusion curve. w is considered to be the weight fraction of the most stable crystals. Figure 4 shows that w does not depend on the annealing time for the temperatures and intervals used. The data obtained by Mead, *et al.* [11], for the ultra-oriented PE fibers showed time dependence of this ratio in the first 2–3 minutes of annealing and then the ratio attained constant value after a certain time. This was attributed to the nature of the fiber with surface and core morphologies. In the present work, the thin film had good contact with the DSC pan and the gradual change of w with time will need only a few seconds to attain the constant value. In addition, the time of annealing is recorded after reaching a state of thermal equilibrium (about 1.5 minutes are needed).

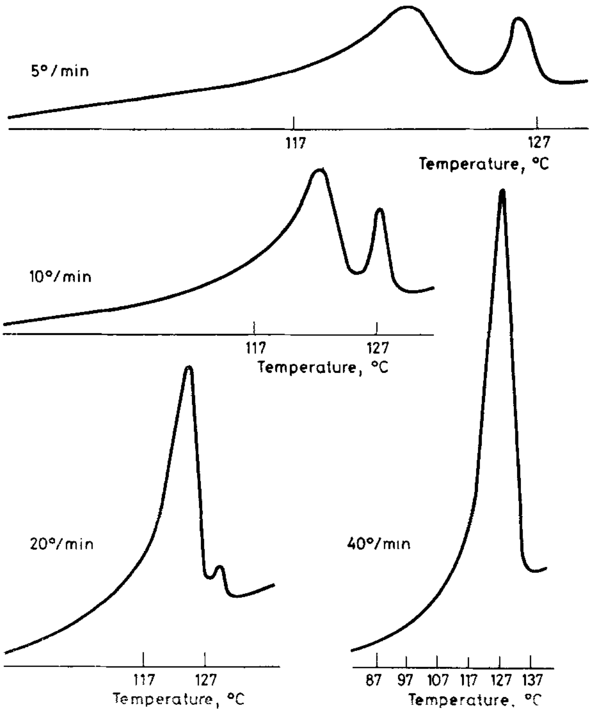

Fig. 5. DSC fusion curves of polyethylene annealed at 123° for 1.5 minutes at different rates of heating

The splitting behavior of the DSC melting curves of this type of PE differs from the behavior reported for PE crystallized from the melt [16]. The heating rate was found to affect the shape of the DSC trace as shown in Fig. 5. At 5°/min.

heating rate the splitting is pronounced and on increasing the rate the ratio of the two peaks decreases until the second peak completely disappears when reaching 40°/min.

Discussion and conclusions

This thermal analysis of polyethylene on first and second heating reveals features of the polymer composition and of the properties after extensive draw.

The results after second heating, i.e. after melt annealing, may be compared with values published on related polyethylenes in order to assess the original polyethylene composition, *viz.* molecular weight and branching, as revealed through the crystals formed under controlled conditions. The results are consistent with properties of a medium density polyethylene containing appreciable concentrations of at least short chain branches. This is clear from the heats of fusion and melting points as a function of heating rate. This is also consistent with the annealing studies below the melting point which produced crystals with maximum peak melting points of 128 ± 0.5° which is well below the maximum melting point for linear polyethylenes which exceeds 140°. The maximum annealed percent crystallinity is less than 55%, also well less than that for high density polyethylene which is over 70%.

The differences in thermal analysis for initial and annealed samples reveal characteristics of the drawing process. The draw increased both the melting point, about 2°, and the crystallinity by about 4%. The similarity of the melting point *vs.* heating rate curves for the original and annealed samples reveals the absence of chain-extended morphologies. A systematic set of annealing studies reveals the rate of change at different temperatures for conversion of the original drawn morphology.

Mechanical studies

Three samples were cut parallel to the orientation direction of the polyethylene film and were tested in uniaxial tension in the same orientation direction in an Instron tensile testing machine. Data and results for Young's modulus, tensile stress at break, and tensile strain at break are given in Table 1. The (engineering)

Table 1

Tensile properties of drawn polyethylene in orientation direction

Sample	1	2	3	Average
Young's modulus	4.6 GPa	4.1 GPA	3.6 GPA	4.1 GPA
Tensile stress	0.17 GPa	0.17 GPa	0.14 GPa	0.15 GPa
Tensile strain	9.3 %	6.8 %	8.0%	8.0%

stress/strain curve obtained was typical for that of a hard, strong polymeric material. No necking was observed nor indicated by the stress-strain curve. The sample strain was recorded directly by the crosshead movement. The values given in Table 1 are similar to those previously given for samples made in the same instrument. In Ref. 8, tensile strengths for films are given as 20 – 30 kg/mm^2 and tensile moduli up to 400 kg/mm. Percent extensions at break were down to 8%. 20 – 30 kg/mm^2 = 0.2 – 0.3 GPa; 400 kg/mm^2 · 4.0 GPa; since 1 GPa · 101 kg/mm^2.

Discussion

At first sight, the absence of chain-extended morphologies is in apparent contrast with earlier data for strands [4 – 6] and fibers (or filaments) [7 – 8]. However, differences in thermal and rheological treatment of the starting polyethylene readily explain the differences in structure and properties.

Importantly, in the absence (or rather non-discernability) of extended chain crystals, the overall morphology of the films is still peculiar as revealed by thermal and mechanical properties. A possible physical reason for the increase in tensile stress (the "industrial average" for ordinary oriented polyethylene films does not exceed 3 kg/mm^2) would be a substantial increase in the number of tie chains or, consequently, a decrease in the degree of chain folding.

From the view of at least one of the authors (S. F.), this may have a fundamental implication concerning the theory developed recently by Prigogine [18] showing that pre-transitional phenomena (also connected with heterophase fluctuations) [19] can play just the same (if not more!) important part as in the case of "ordinary" first order transitions.

Particularly, in the technological conditions of film preparation, neither critical extensions nor longitudinal gradients necessary for bifurcation [18, 20] and a transition to a preferential growth of extended chain crystals [21] were attained. However, the system was already "prepared" for the bifurcation which is readily provoked in more ultimate condition of melt pre-extension [7].

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RÉSUMÉ — On a effectué, aux Etats Unis, l'étude du comportement thermique et mécanique d'un polyéthylène préparé et fortement étiré en URSS. Le point de fusion et le pourcentage de cristallinité ont été évalués en fonction de la vitesse de chauffage et de la recristallisation. Les valeurs respectives du module d'Young et de la limite de rupture dans la direction d'orientation s'élèvent respectivement à 4.1 et 0.15 GPa. L'allongement à la rupture est d'environ 8%.

ZUSAMMENFASSUNG — Das thermische und mechanische Verhalten eines in der UdssR hergestellten und stark gezogenen Polyäthylens wurde in den U. S. A. gemessen. Schmelzpunkt und Prozentsatz der Kristallinität wurden als Funktion der Aufheizgeschwindigkeit und Rekristallisation in den Untersuchungen ausgewertet. Der Young-sche Modulus und die Zugspannung zum Reissen in der Orientierungsrichtung betrugen 4.1, bzw. 0.15 GPa. Die Dehnung bis zum Bruch betrug etwa 8%.

Резюме — В США было проведено изучение термического и механического поведения полиэтилена, полученного и высоко вытянутого в СССР. Точка плавления и плоцент кристалличности были оценены как функция скорости нагрева и рекристаллизации. Модуль Янга и растягивающее усилие к разрыву в ориентационном направлении составляли соответственно 4.1 и 0.15 ГПа. Деформация растяжения на разрыв составляла около 8%.