The nanostructuring of ultra-high-molecular-weight polyethylene in thermal and mechanical fields as revealed by DSC

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Abstract. The ultra-high-molecular-weight polyethylene reactor powders are widely used for the actively developing solvent-free method for producing high-strength high-modulus PE filaments, which includes the compaction and sintering of a powder followed by orientational hardening. To find an appropriate regime of the technological process, it is important to know how the nanostructure changes when transforming from a powder to a precursor for hardening. Nanocrystalline lamellae are characteristics of the powder structure. For the first time, the DSC technique was used to follow changes in the thickness distribution of lamellae in ultra-high-molecular-weight polyethylene reactor powder on its way to a precursor for orientation hardening. It was found that the percentage of thick (>15 nm) and thin (10 nm) lamellae in compacted samples and those sintered at temperatures lower than the melting temperature of PE (140°C) remains nearly the same. However, significant changes in the content of lamellae of different thicknesses were observed in the samples sintered at 145°C with subsequent cooling under different conditions. The influence of the lamellae thickness distribution in precursors on the mechanical characteristics of oriented filaments was discussed.

1. Introduction

Synthesis products of ultra-high-molecular-weight polyethylene (UHMWPE), the so-called reactor powders (RP), have a complicated hierarchical supramolecular structure consisting of a variety of nano-sized morphoses (crystalline lamellae, fibrils, globules, shish-kebabs) [1]. Recently [2], a solution-free method for processing UHMWPE into high-strength high-modulus filaments directly from RP has been developed. It is materialized by compaction and sintering the powder under pressure into a mechanically coherent film, which is then subjected to orientational hardening [2]. To find optimal parameters of the technological process, it is important to know what happens to the RP nanostructure at each stage of processing. One of the basic morphological units in the RP are lamellae consisting of folded nano-crystals (tens of nm), differently stacked and connected by tie molecules of various degrees of coiling [1]. The knowledge of the lamellae thickness is extremely important for finding a proper thermal and pressure regime for the technological process because their thickness influences significantly the process of the unfolding of the chains during orientational hardening.
For the first time the DSC technique is used to estimate lamellar thickness distribution in the samples investigated. DSC technique is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. DSC is used widely for examining polymeric materials to determine their thermal transitions. Important thermal transitions include the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm). Since the melting temperature of the lamellae depends on their thickness (L), one can attempt to estimate the lamellae thickness distribution from the analysis of the DSC melting curve shape. Typically, this analysis is neglected. It is carried out in this work. The heat flow is proportional to the mass fraction of lamellae melted at a certain temperature. It is converted into a thickness distribution curve (the probability of the mass percentage of lamellae of a certain thickness) using the Gibbs-Thomson equation [3]

\[ T_m = T_0 \left[ 1 - 2\sigma_c / \Delta H \times L \right] \]

Here \( T_m \) is the observed melting temperature of a lamella with thickness \( L \); \( T_0 \) is the equilibrium melting temperature of a lamella of infinite thickness; \( \sigma_c \) is the surface energy of the lamella basal surface, and \( \Delta H \) is the enthalpy of melting. It should be noted that the above equation is valid only for lamellae with lateral dimensions significantly exceeding their thickness, which is usually the case.

Then the heat of fusion in the interval \( t \) and \( t + dt \) will be equal to \((dH / dt) dt\). The same heat of fusion will be exhausted during the transition from the crystalline state to the melt of a certain number \((dn)\) of \(-\text{CH}_2-\) groups in the range corresponding to \( dt \). Then the heat of fusion can be written as \((dH / dn) dn\), which implies the equality: \((dH / dn) dn = (dH / dt) dt\). It can be rewritten as

\[ dH / dn = ((dT / dt) -1) (dT / dt) dH / dt = (dT / dn) (dH / dt) \]

where \( dT / dt \) is the heating rate which is typically constant in DSC experiments.

The following data were used to calculate the distribution of lamella thicknesses: \( T_0 = 415 \, \text{K}; \sigma_c = 87.4 \, \text{erg/cm}^2; \Delta H = 2.79 \times 10^9 \, \text{erg/cm}^3 \) [3]. Due to the thermal resistance \( R \) of the sample investigated in the calorimetric cell, the position of the peaks on the DSC curve is shifted by \( \Delta T \) (the instrumental error) which should be taken into account in the calculations to correct \( T_0 \). We estimated these values for our case at a scanning rate \( V = 2 \, \text{K/min} \): \( \Delta T = 3.0 \, \text{K} \), which gave \( T_0 = 418 \, \text{K} \).

The goal of our investigations was to study changes in the lamella thickness distribution of the UHMWPE reactor powders after compaction/sintering under various conditions and clarify the influence of lamella sizes on the orientation hardening.

2. **Samples and experiment**

The object of investigation was the lab-scale UHMWPE reactor powder \( (M \eta = 3 \times 10^6, \text{series 5224}) \) synthesized in a slurry process in toluene on a single-site metallocene catalyst (F-97) in the Institute of Macromolecular Compounds, Russian Academy of Sciences (St. Petersburg, Russia).

2.1. **Sample preparation**

Samples of three types were investigated: starting UNMWPE powder, compacted powder, and sintered compacts.

The powder was compacted under a pressure of \( P = 95 \, \text{MPa} \) at room temperature for 15 minutes in a mold with an inner diameter of 20 mm. The obtained tablets were sintered under the same pressure at 130°C for 30 minutes (standard mode). Besides, the obtained tablets were sintered at a temperature above the melting point of polyethylene. To do this, the tablets were placed in a mold heated to 130°C, and a pressure of 100 MPa was applied, then the melting temperature was increased to 145°C and held
for 30 minutes. In 30 minutes, the temperature was lowered to 130°C, and cooling was performed in
three modes: (I) the sample was quickly removed from the mold and cooled to room temperature
between two metal plates, (II) the sample was left to cool in the mold without pressure, (III) the
sample was cooled in the mold under pressure 100 MPa.

2.2. Thermal analysis
The DSC scans of reactor powders and compacted/sintered tablets/tapes were performed on a DSC-
500 thermal analyzer (OOO “Spezpribor”, Samara, Russia) in a temperature range from 270 to 450 K;
the scanning rate \( V \) was 2 K/min. The temperature scale was calibrated with respect to the melting
points of ice (273.1 K) and indium (429.7 K). The heat flow scale was calibrated with respect to the
heat capacity of sapphire. The heat of fusion \( \Delta H_m \) was calculated from the melting peak area. From the
analysis of the DSC melting curve shape, the lamellae thickness distribution was calculated (see for
the details of the approach in the Introduction). The distribution curve was decomposed into the
separate peaks corresponding to lamellae of various thicknesses with the help of the Fityk 0.9.8
program.

2.3. Scanning electron microscopy
The particles of nascent UHMWPE powder were glued to conducting tapes on a sample holder, coated
with a layer of platinum 10-15 nm thick by sputtering in the Quorum Q150T ES sputter coater
(Quorum Technologies, UK) and studied in the SUPRA 55VP (Carl Zeiss, Germany) scanning
electron microscope operated in secondary electrons mode at accelerating voltage of 5 kV.

3. Results and discussions
The lamellae of various thicknesses are well seen in a SEM micrograph of the UHMWPE reactor
powder investigated (Fig. 1 A). These are the thin plates oriented randomly so that we see the lateral
lamellar plates or their edges as it is shown by arrows. Since the lateral dimensions of the observed
lamellae significantly exceed their thicknesses, the Gibbs-Thompson equation can be indeed used for
processing the DSC curves (Fig. 1 B) and obtaining the lamellar thickness distribution (Fig. 1 C) as
described above.

![Figure 1. SEM micrograph of the UHMWPE reactor powder 5224 (A), thermogram of the powder (B)
and its lamella thickness distribution (C).](image)

As is seen, the lamella thickness distribution has a complicated shape that points to different
contents of lamellae of various thicknesses in the powder investigated.
To decompose the distribution curve into the “elementary” peaks, the Fityk 0.9.8 program was used. As an example, decomposition of the lamellar thickness distribution curve of the UHMWPE reactor powder under investigation is presented in Figure 2. One should note that this procedure is somewhat voluntary. However, a result looks plausible, and the difference between the sum and experimental curves is minimal.

Figure 2. The peaks of decomposition of lamellar thickness distribution curve of a the UHMWPE reactor powder by the Fityk 0.9.8 program corresponding to lamellae of different thicknesses and dependence of melting temperature on the lamellar thickness (dashed curve).

Thermograms of the other UHMWPE 5224 samples investigated (Figure 3) and lamella thickness distributions calculated from these thermograms (Figure 4) also demonstrate different complex shapes.

\[ \Delta C_p = 20 \text{ Jg}^{-1}\text{K}^{-1} \]

\[ \frac{dH}{dL} = 10 \text{ Jg}^{-1}\text{nm}^{-1} \]

Figure 3. Thermograms of the samples sintered at \( T = 145^\circ\text{C} (> T_m \text{ of PE}) \) in Mode I (1), Mode II (2), Mode III(3), sintered at \( T = 130^\circ\text{C} (< T_m \text{ of PE}) \) (4)) and compacted powder at \( T_{\text{room}} \) (5).

Figure 4. Lamellar thickness distribution calculated from thermograms in Figure 3.
The lamellar thickness distribution curves were processed by the Fityk 0.9.8 program, and the contents of lamellae of different thicknesses were estimated in accordance with the area of each corresponding peak of decomposition. The data obtained are presented in Table 1.

| samples             | L1, (5-7 nm) | L2, (9-11 nm) | L3, (12-14 nm) | L4, (17-21 nm) | L5, (30 nm) |
|---------------------|--------------|---------------|----------------|----------------|-------------|
| reactor powder      | 5            | 21            | 34             | 40             | -           |
| compacted powder    | 2            | 26            | 28             | 43             | -           |
| Sintering 135 °C standard | -    | 26            | 32             | 41             | -           |
| Sintering 145 °C, mode I | 5   | 27            | 32             | -              | -           |
| Sintering 145 °C, mode II | -  | -             | 64             | 30             | 5           |
| Sintering 145 °C, mode III | 5  | 25            | 35             | 35             | -           |

As follows from the data given in Table 1, the ratio between thin (2-5 nm)-(9-11 nm) medium (12-14 nm) and thick lamellae (17-21 nm) in the samples remains nearly unchanged during compaction, sintering under standard conditions (135°C) and even during sintering at temperature (145°C) higher than the melting point of PE (mode I and III). The only exception is the precursor prepared in mode II, cooled in the press from 130 °C down to room temperature without pressure. As distinct from the other samples, this one has no thin lamellae at all. It is dominated by lamellae of medium thickness (64% versus 28-35% in other samples), and a small amount of fairly thick lamellae (30nm).

As was mentioned above, the sintered films were used as precursors for drawing (orientation hardening) and obtaining the high-strength high-modulus highly oriented film threads. The idea to increase the sintering temperature above the Tm of PE at atmospheric pressure was aimed at increasing the diffusion rate of chain segments at the boundaries of powder particles and thereby increasing the strength of interparticle boundaries, which would not allow the sample to break prematurely during orientational hardening. At the same time, it was assumed that sintering at 145°C under a pressure of 100 MPa would not lead to recrystallization of the initial structure formed during the synthesis, which could worsen the deformation-mechanical properties of the material.

We believe that the observed increase in the amount of lamellae of medium thickness and the appearance of thick lamellae in precursor II were due to the increased mobility of molecules upon annealing without pressure. As known, annealing of polyethylene at a temperature lower than the melting temperature leads to regularization of molecular folds and can be accompanied by an increase in the length of the crystal core of the lamellae, which was observed earlier upon annealing of polyethylene of conventional molecular weights [4].

Initial experiments on orientational hardening of sintered samples showed that the samples sintered at 145°C could actually be drawn to higher draw ratios than the samples sintered at 135°C (70-80 versus 65, respectively). This confirms our idea about an increase in strength of the interparticle boundaries when sintering is performed at a higher temperature. In addition, the maximum achievable strength of the oriented threads obtained from precursor II proved to be much higher (3.3 GPa) than that obtained from precursors I and II (1.9 GPa). The enhanced strength of the former could be because of the more regular folded nano-crystals in lamellae. However, these data were obtained for a small number of samples, which does not allow us to draw a decisive conclusion at the moment. Much more statistical data are needed to finalize this work.

4. Conclusion
DSC is typically used to study thermodynamic properties of materials. In the case of polymers, the melting point and the degree of crystallinity are most often determined. However, the DSC method...
provides more opportunities, to estimate the sizes of nanostructural units, in particular. In this study, very valuable information was inferred from the analysis of the melting curve shapes.

Taking into account that the lamella is the main nanostructural morphological unit in the UHMWPE reactor powder, and the melting temperature of the lamellae depends on its thickness, the lamellar thickness distribution was obtained by using the Gibbs-Thomson approach. The processing of the lamellar thickness distributions for the samples investigated by the Fityk 0.9.8 program allowed us to obtain information about the contents of the lamellae of definite various thicknesses in the samples. It was found that the ratio of thin to thick lamellae after compaction and sintering the powder remained nearly the same, even after sintering compacted powder at the temperature (145°C) higher than the melting temperature of an ideal PE crystal at the atmospheric pressure (140°C).

On the one hand, this is a positive result which evidences the preservation of the original polymer structure (formed during synthesis) in the technological process of obtaining the precursors for orientation hardening. However, a change in the lamellar structure was observed in the precursor prepared according to mode II (slow cooling of the sintered samples in the press without pressure). The ratio of thin to thick lamellae in this sample has shifted towards thicker lamellae and the content of the lamellae of medium thickness doubled. Despite this, the strength properties of the oriented filaments obtained from this precursor turned out to be much better than those of the filaments film threads obtained from the precursor II, turned out to be much better than those obtained from the other precursors which retained the structure of the original powder during compaction and sintering. This suggests that some change in the lamellar structure is acceptable (the regularization of folding, in our case, as we think) and may have a positive effect. This assumption is further need to check.

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