X-Ray analysis of compacted and sintered UHMWPE reactor powders

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Abstract. X-ray diffraction analysis of solid-state compaction/sintering-induced changes in crystalline structure of lab-scale (M332) and commercial UHMWPE (X600) reactor powders has been carried out. The profile fitting programs TOPAS-5 and Peakfit 4.1 have been used to deconvolute the overlapping peaks. The linear FWHM of (110) and (002) X-ray peaks have been taken for calculation of the transverse \(D_{110}\) and longitudinal \(D_{002}\) crystallite sizes with the help of Sherrer method. The growth of crystallite sizes in cold compacted powders with sintering has been detected in both directions. Besides, the sintering has resulted in the generation of the planar a-texture, more pronounced in the lab-scale UHMWPE samples. As known, orientation hardening of the sintered reactor powders is an alternative route to UHMWPE high performance fibers distinct from the common gel-technology. It has been found that the highly oriented thin film threads produced from highly textured sintered material demonstrated the extremely high tensile strength up to 3.0 GPa, close to that of gel-fibers (3.5GPa) [1] while X600 less textured powders has shown low compactability and drawability.

1. Introduction

UHMWPE is a unique material due to its exceptional physical and mechanical properties, such as low friction, highly abrasive resistance, chemical inertness and the record specific strength, in particular. It determines the wide range of its applications, from bullet-proof jackets to artificial joints, implants, membranes, fishing nets and sportive goods. The gel-technology for production of UHMWPE high performance fibres, much needed in both engineering and science, was developed [2-5]. However, processing of low concentration UHMWPE solution via gel-technology is expensive and environmentally harmful because of recuperation of the large solvent volume. Then, in current times, the alternative solvent-free route to high performance fibres adopted from powder metallurgy is intensively developed. The so called “dry” technique involves the cold
compaction of the “never processed” UHMWPE reactor powders and sintering followed by orientation drawing, the sintering temperature being lower than that of melting (Tm). This technique was materialized on lab-scale in a number of the scientific groups [6-8]. The small-scale production of high-performance UHMWPE film-threads under trademark Tensylon was started not so long ago. However the tensile strength of these films threads is slightly lower (2.5 GPa) than that of the most strong gel-fibers Dyneema and Spectra produced by leading firms DSM (the Netherlands) and Honeywell (USA), correspondingly (3-3.6 GPa) [1].

As known, not all the reactor powders can be successfully processed to high performance fibers via solvent-free method. It is widely believed that the main factor controlling their drawability is the density of entanglements which catastrophically increases provided that sintering is carried out at T > Tm. But the structural changes inevitably occur even on sintering at T < Tm, which also can influence the effectiveness of the orientation hardening. In the present work the changes in crystalline structure of two different UHMWPE reactor powders upon sintering are investigated with the help of X-ray technique and the influence on their drawability and mechanical characteristics of the end-products is studied.

2. Experimental method and materials

The objects of investigations were UHMWPE compacted and sintered films produced from two different UHMWPE reactor powders M332 and X600. The synthesis of M332 reactor powder (\(M_w = 2.5 \times 10^6\)) was performed at the Institute of Physical-Organic Chemistry of the National Academy of Sciences of Republic Belorussia, Minsk, in a slurry process in n-heptane at 60°C on colloidal size particles of catalyst system (a high-performance titanium chloride catalyst modified with an organic magnesium compound). Almost nothing is known about commercial X600 reactor powder (China) except its \(M_w = 6.0 \times 10^6\) because of confidentiality.

According to the principle of powder metallurgy, reactor powders were compacted and then sintered. Powder compaction was performed by compression in hydrostatic conditions in a Carver hydraulic press (model 3912) at room temperature at a pressure of 95 MPa for 15 minutes. The tablets of 1 mm thick and 20 mm in diameter were produced from about 210 mg of the powder.

The sintering of compacted tablets was performed by compression of the compacted tablets between two aluminium foils at a temperature of 130 °C under a pressure of 95 MPa for 30 minutes. During sintering the pressure was falling down to 46 MPa because increasing the area of the sintering sample. The obtained films of near 150 μm thick were cut into narrow strips of 1 mm wide and subjected to multi-stage high temperature zone drawing, the temperature in the process increasing stepwise from 110°C to 140°C. The film threads drawn to different draw ratios were tested on calibrated Instron 1120 equipment.

Characterization

Wide angle X-ray diffraction (WAXS) data from compacted and sintered samples were collected in Bragg-Brentano mode on a D2 Phaser, Bruker (Cu Ka radiation, \(\lambda = 1.54 \text{ Å}\)) operating at 30 kV and 10 mA using an PSD detector. Signal accumulation time for each step was 4 sec in an angle range from 10 to 30 degrees (the region of 110 and 200 orthorhombic and three monoclinic peaks, if any), 40 sec for a range from 30 to 60 degrees (the range of 220 orthorhombic peak) and 60 sec from 60 to 80 degrees (the range of 002 orthorhombic peak). The analysis of X-ray diffraction profiles was performed by the programs TOPAS-5 and Peakfit 4.1. In the first case the fitting was performed when the X-ray peaks are approximated by a complicate combination of 8 different functions. In the latter, Pearson VII was used. The broadening of the reflections of higher orders was analyzed using Sherrer method [9], which takes into account a dependence of X-ray peak shape on crystallite sizes and crystalline distortions. The fitted 110 and 220 diffractions were used to calculate the transvers crystallite sizes (\(D_{(110)}\)) and the crystallite distortions (g-factor)) by Sherrer formula: \(D_{(hkl)} = \frac{0.89 \lambda}{(\text{FWHM} \cdot \cos \theta)}\), where 0, 89 is the form-factor, \(\lambda\) is the X-ray (Cu Ka) wavelength (1.54 Å), the FWHM
(Full Width Half Maximum) is the linear half-width of correspondent X-ray peak, and \( \theta \) is the Bragg angle. The 002 diffraction was used to calculate the longitudinal crystallite sizes (\( D_{002} \)).

3. Results
The typical X-ray scattering from compacted reactor powders are shown in Figure 1.

![Figure 1](image1.png)

*Figure 1.* Deconvolution of WAXS M332 compacted powder by Peakfit (at left) and by TOPAS (at right)

It is well seen that besides from the usual 110 and 200 PE orthorhombic peaks the three peaks from monoclinic crystalline phase are easily recognized. Since monoclinic phase is only stable under stress one should conclude that compaction results in developing stress in the compacted powder. The appearance of monoclinic phase in the UHMWPE powders when compacted was earlier observed in our experiments [10] and also by other authors. The estimates of monoclinic phase content differ a lot [11-1]. The mess in the results is caused by both methodological causes as well as meta-stability of monoclinic phase. Besides, there is an uncertainty in deconvolution of the overlapped peaks in the range of 19.6° because both monoclinic 010 peak and amorphous halo contribute to this region. Put then aside the monoclinic phase to concern with orthorhombic crystallites, all the more so it disappeared after sintering in both M332 and X600 films (see Figure 2).

![Figure 2](image2.png)

*Figure 2.* WAXS of sintered X600 film (at the left) and M332 (at the right).
First what immediately springs to eyes is that abnormal relationship between intensity of 110 and 200 orthorhombic reflexes ($I_{200}/I_{110}$). It is 1.13 for X600 sintered film, and 1.53 for M332 film instead of table value 0.7. This evidences the generation of plane “a”-texture in the compacted samples upon sintering. The role of this structural transformation will be discussed later on. Along with the observed phenomena sintering the compacted sample is accompanied by growth of transverse and longitudinal crystallite sizes.

![Figure 3. Changes in transverse ($D_{110}$) and longitudinal ($D_{002}$) crystallite sizes on sintering calculated for M332 and X600 on the base of TOPAS and PeakFit fitting (M332: 2.1 and 1.1.; X600: 2.2 and 1.2, correspondingly).](image)

The larger crystallite sizes $D_{110}$ obtained for M332 with PeakFit than those with TOPAS are obvious because in the first case the broadening of higher order (220) were taken into account while TOPAS only gave the estimate on the broadening of the first order 110 peak. For all other cases when the crystallite sizes were calculated for the first order reflection, TOPAS data were larger than those obtained with the help of Peakfit. Anyway, despite the significant scatter in the crystallite sizes estimated one can emphasize a certain tendency in the presented data: the sintering actually results in growth of crystallite sizes. The size $D_{110}$ in M332 samples grow faster than in X600.

Thus with the help of X-ray study a difference in crystalline structure behavior was manifested. The difference in drawability and ultimate mechanical characteristics of the samples investigated were also discovered. The results of the mechanical testing of the film threads of various draw ratios produced from the sintered films obtained from UHMWPE powders are given in Figure 4.

![Figure 4. Dependence of tensile strength of oriented film threads from X600 (1) and M332 (2) on draw ratio.](image)
It is seen that both sintered films could be drawn to very high orientation elongation however, they have different rate hardening. Despite X600 film thread could be drawn even more (DR=73) than M332 film threads (DR=63) the former has lower tensile strength while the tensile strength of the latter reach very high values (3.3 GPa) comparable to the best gel-fibers.

4. Discussion
What is the reason of so different structure-mechanical response of UHMWPE on one and the same processing? First, we believe that the best results obtained for M332 ultimately oriented threads is due to distinct a-texture convenient for re-arrangement of fold crystal into the highly oriented fibrils. At the same time, to receive an additional information on the powder investigated we studied the initial powder with the help of scanning electron microscopy. The morphology of X600 and M332 reactor powders appeared to be catastrophically different (see Figure 5).

![SEM of X600 UHMWPE reactor powder (at the left) and that of M332(at the right)](image)

**Figure 5** SEM of X600 UHMWPE reactor powder (at the left) and that of M332(at the right)

The morfology of X600 is two fold. It consists of a lot of fibrillar entities and small nodulus of obviously lamellar structure. The existence of fibrillar bundle evidences high rate of synthesis because these fibrils could be formed during desintegration of catalists under the tension of fast growing polymer mass. As distinct from X600, M332 reactor powder has characteristic homogeneous morphology that comprises lamellar nodulus of 0.5-1μm size. One can propose that the fibrillar bundles prevent to fully re-arrangement of initial morphology to a-texture more convenient to effective orientation hardening.

5. Conclusions
It is shown that the “dry” route to high performance UHMWPE fibers can be successfully realized, and highly oriented super strong film threads can be obtained, provided that the initial reactor powder can be re-formed by compaction/sintering into the “a”-textured film convenient for effective orientation hardening. X-ray analysis that follows after changes in crystalline structure upon sintering gives a valuable information on the structural transformations.

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7. References
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