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Citation for published version (APA):

Aerle, van, N. A. J. M., & Braam, A. W. M. (1988). A real-time drawing study of melt-crystallized ultra-high molecular weight polyethylene. Comparison with conventional X-ray results. *Makromolekulare Chemie*, 189(7), 1569-1577. <https://doi.org/10.1002/macp.1988.021890712>

DOI:

[10.1002/macp.1988.021890712](https://doi.org/10.1002/macp.1988.021890712)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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A real-time drawing study of melt-crystallized ultra-high molecular weight polyethylene. Comparison with conventional X-ray results

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(Date of receipt: January 18, 1988)

SUMMARY:

In the past morphological changes, caused by uni-axial drawing of flexible polymers have been studied mostly under conditions, quite different from the drawing conditions. This could give rise to certain artefacts, leading to mis-interpretations. Up to now very little was known about this possibility. Therefore, X-ray patterns obtained by conventional drawing studies and by real-time X-ray drawing studies are compared in this paper. It will be shown, that although some results on melt-crystallized polyethylene discussed here show indeed small differences, conventional X-ray studies can be used without any problem for qualitative studies. However, studies of deformation phenomena in elastic deformable regions as well as quantitative X-ray studies require real-time measurements.

Introduction

It has been known for a long time that the introduction of molecular orientation in polymer materials increases both the mechanical anisotropy and the crystallinity, leading to the enhancement of mechanical properties like Young's modulus and tensile strength. In the case of flexible polymers such as polyethylene, polypropylene and polyamides, orientation can be achieved in several ways^{1–3)}. In this paper the attention will be focused on molecular orientation phenomena, introduced by uniaxial drawing of melt-crystallized ultra-high molecular weight polyethylene (UHMW-PE).

To gain insight into the molecular basis of the properties resulting from the use of a uniaxial drawing technique, extensive X-ray diffraction studies were performed in the past. During these studies the deformation behaviour and the final structure were examined for tapes or fibres with several draw ratios. In most cases, however, wide angle X-ray scattering (WAXS) as well as small angle X-ray scattering (SAXS) patterns were detected under conditions, quite different from the drawing conditions. E.g., very often a polymer is drawn at elevated temperature, but studied at room temperature. Relieving the stretching force as well as cooling the sample to room temperature prior to study it, can give rise to certain artefacts caused by relaxation and/or (re)crystallization phenomena. This can lead to mis-interpretations of the X-ray results.

Discussions about the nature of structural changes caused by uniaxial drawing of flexible polymers are influenced by these potential artefacts for many years already. To exclude this possibility, real-time X-ray diffraction studies *during* the deformation process are necessary.

For this purpose a special heatable stretching device has been designed and built at DSM Research, enabling synchronous monitoring of stress, clamp displacement, oven temperature and SAXS or WAXS patterns *during* a stretching process at elevated temperatures⁴⁾. Such a stretching device necessitates the use of short X-ray exposure times, which can be obtained by combining the benefits of a very bright synchrotron source and a two-dimensional X-ray detector.

Since only very little is known about the possible introduction of artefacts via the conventional study, the drawing of melt-crystallized UHMW-PE was studied via X-ray methods in two ways to be referred to as method A and method B.

Method A: samples were drawn at elevated temperature to a desired draw ratio and studied afterwards at room temperature. This is the conventional way of investigating the drawing of polymers.

Method B: samples were studied in real-time, i.e. *during* the drawing process at elevated temperature.

By comparing the results obtained via both methods, some conclusions can be drawn concerning possible differences in X-ray patterns, caused by relaxation, re-crystallization and/or re-orientation effects.

Experimental part

As-received ultra-high molecular weight polyethylene (UHMW-PE) powder (Hostalen GUR-412, Hoechst/Ruhrchemie, weight-average molar mass $\approx 1\,700\,000$ g/mol) was compression-moulded at 180 °C for about 40 min to a thickness of approximately 0,3 mm, quenched to room temperature and subsequently cut into tapes of 100 mm $\times$ 2 mm. For *method A* tapes were drawn manually at 100 °C to the desired draw ratio, using ink-marks.

The WAXS and SAXS data for the conventional drawing study (*method A*) were obtained simultaneously with a Kiessig camera, using Ni-filtered Cu- K_α -radiation, generated by a Nonius Diffractis Generator operating at 40 kV and 26 mA. The sample to film distances were 67 mm and 400 mm for WAXS and SAXS, respectively. For quantitative results, the photographically recorded X-ray patterns were densitometerized with an Enraf Nonius micro-densitometer model 1⁵⁾.

The real-time drawing study (*method B*) was performed with a home-built stretching device, described in ref. ⁴⁾. The PE-tapes were drawn at 100 °C with a drawing velocity $\dot{\epsilon}$ of 0,0044 s⁻¹. The X-ray patterns were monitored, using the synchrotron facilities at DESY-Hamburg. The X-rays, generated at 5,260 GeV^{*)} and 25–30 mA, were monochromatized to a wavelength of 1,61 $\pm$ 0,02 Å. Combining the intense radiation with a Westinghouse two-dimensional Vidicon X-ray detector made it possible to record a WAXS or SAXS pattern every 10 s. The sample to detector distance was chosen to be about 9 cm and 205 cm for the WAXS and SAXS experiments, respectively. The resulting isointensity contour plots were obtained in a straightforward manner without any special background correction.

^{*)} In SI units 1 eV $\approx 1,60219 \cdot 10^{-19}$ J.

Results and discussion

In Fig. 1 a typical stress-strain curve is shown, monitored synchronously with real-time X-ray patterns (method B). The absence of a distinct yield stress clearly indicates a homogeneous deformation behaviour, i.e. without necking.

Fig. 1. Stress-strain curve of melt-crystallized ultra-high molecular weight polyethylene (UHMW-PE), drawn at 100°C using a drawing velocity $\dot{\epsilon}$ of $0,0044 \text{ s}^{-1}$

Wide angle X-ray scattering

In Fig. 2 the WAXS patterns obtained by both methods are compared. Due to a limited detector size only one quadrant of the WAXS pattern could be detected in case of the real-time study (the corresponding detectable area is indicated in two conventional WAXS patterns in Fig. 2a by a dashed box). Close inspection of the different WAXS results reveals a fairly high degree of similarity, implying the absence of large artefacts which could have been introduced in performing method A. Via method B weak signals (e.g. the amorphous halo of PE) are not easily detectable because of problems with Vidicon overload due to the presence of intense 110 and 200 reflections. Unfortunately, due to the presence of an elastic deformable initial region, it was impossible to obtain reproducible samples with draw ratios between 1 and 1,7 for the conventional study. Thus a big advantage of method B is shown, i.e. the possibility to study the elastic deformation region.

As was discussed in a former publication about a real-time drawing study on melt-crystallized UHMW-PE, the orthorhombic 110 and 200 reflections are split into two arcs on both sides of the equator, at draw ratios up to 1,8⁶⁾. Additionally an equatorial 200 reflection maximum could be discerned for all draw ratios studied, indicating that a fraction of all crystallites is preferentially oriented with the *a*-axis perpendicular to the drawing direction throughout the whole drawing process.

Because in the conventional WAXS patterns of a tape with a draw ratio of 1,7 the split of the 110 reflection into two arcs cannot be discerned easily, a densitometric azimuthal ϕ -scan along the 200 and 110 reflection was performed. The results, presented in Fig. 3, clearly show the presence of two reflection arcs for the 110 reflection, consistent with the real-time findings presented in Fig. 2b.

Fig. 2. Comparison of wide angle X-ray scattering patterns of a drawing series at 100°C obtained for melt-crystallized ultra-high molecular weight polyethylene (UHMW-PE) via method A (a) and method B (b), see text. The corresponding draw ratios are indicated. The drawing direction is vertical. "○, ●" indicate the position of the primary beam. For the reader's convenience the position of the 110 and 200 reflection is indicated in two scattering patterns. (For dashed boxes in (a) see text)

Fig. 3. Azimuthal diffraction profile of the 110 (a) and 200 (b) reflection arcs, recorded via method A (see text) for a sample with a draw ratio of 1,7. The dashed vertical line indicates the meridian

To investigate whether some (re)crystallization occurs, by cooling samples to room temperature and by relieving the stretching force, equatorial 2θ -scans were compared. In order to have a comparable resolution in the 2θ -scans for both methods, the spotsize of the densitometer was adapted. Furthermore, to facilitate the comparison between different equatorial 2θ -scans, the reflection maxima were rescaled in such a way that the 110 and 200 reflection peaks coincide. Some results are shown in Fig. 4.

As can be seen in Fig. 4a, for a draw ratio of 3 the intensity minimum between the 110 and 200 reflection maxima (in Fig. 4 denoted by an asterisk “*”) is higher in case of method B, pointing to the presence of a larger fraction of amorphous PE. This result suggests that some (re)crystallization indeed occurs, leading to a smaller fraction of amorphous PE in the conventional study (method A). However, as the draw ratio increases up to 5, the intensity minima between the 110 and 200 reflection maxima coincide for both methods (see Fig. 4b). Apparently the difference in amorphous contribution, detected by both methods, decreases as the draw ratio increases.

Fig. 4. Equatorial 2θ -scan of wide angle X-ray scattering patterns, obtained via method A (—) and method B (---), see text, for samples with corresponding draw ratios of $3,0 \pm 0,1$ (a) and $5,0 \pm 0,1$ (b). The asterisks denote the intensity minimum between the 110 and 200 reflection maxima

Additionally it should be noted here, that the real-time WAXS results exhibit increased intensity at 2θ values of $19^\circ - 20^\circ$, which possibly indicates the presence of a small fraction of monoclinic PE. It has been shown in the past that under conditions of stress the orthorhombic modification of crystalline PE is partially transformed into a structure similar to the triclinic form of *n*-paraffins⁷⁾ but more conveniently described in terms of a monoclinic modification^{8,9)}. Characteristic for this structure is a high 010 reflection intensity with a corresponding *d*-spacing of 4,56 Å (i.e., $2\theta \approx 19,5^\circ$ for Cu- K_α radiation). This modification is rather instable upon heating and usually disappears when such a sample is heated unconstrained for a short time to temperatures above 70°C ^{8,9)} (the α -relaxation temperature of PE). In case of method B, however, the sample is kept constrained at 100°C via the applied stretching force during the drawing experiment. Therefore, some monoclinic PE may be still detectable. Furthermore, the existence of some monoclinic PE in method B is supported by former real-time measurements showing the introduction of not less than 20% monoclinic modification of PE during the drawing of melt-crystallized PE at room temperature^{10,11)}. Further research will be necessary for a better understanding.

Finally, it is worth to mention that both real-time and conventional X-ray results are very similar to findings for drawn melt-crystallized lower-molecular-weight PE samples¹²⁻¹⁵⁾. As the draw ratio increases, the split reflection arcs contract and gradually intensify on the equator (at a draw ratio of about 2,1), indicating an increase in preferential orientation of molecular chains parallel to the drawing direction.

Small angle X-ray scattering

In Fig. 5 the SAXS patterns are compared for both methods. They clearly show the formation of so-called four-point patterns, characteristic for polymers like polyethylene and polypropylene, at low draw ratios. It should be noted here that the SAXS patterns of the undrawn sample, recorded via method B, imply some anisotropy, which, however, is caused by a difference in geometry of the primary beam (1 mm $\times$ 4 mm) and the circular beamstop.

As for the WAXS results, the SAXS results in Fig. 5 show good qualitative agreement. Obviously, relieving the stretching force, as well as cooling the sample to room temperature prior to study, does not lead to large artefacts due to re-orientation and/or re-crystallization. Furthermore, the SAXS results presented in Fig. 5 are also consistent with conventional SAXS patterns obtained for linear low-molecular-weight PE at low draw ratios.

Interpretation

Both the WAXS and the SAXS patterns observed can be understood in terms of the deformation model, as proposed by Peterlin et al.¹⁶⁻¹⁸⁾. According to this model, chain tilting and slipping occurs within the lamellae during the initial stages of drawing. Subsequently the lamellae fracture into small blocks of crystallites which, together with non-crystallized material, are incorporated into so-called microfibrils.

Fig. 5. Comparison of small angle X-ray scattering patterns of a drawing series at 100°C obtained for melt-crystallized ultra-high molecular weight polyethylene (UHMW-PE) via method A (a) and method B (b), see text. The corresponding draw ratios are indicated. The drawing direction is horizontal

Although this deformation model is valuable to describe many phenomena observed for solid-state drawn flexible polymers, some questions are still open for discussion. E.g., some scientists propose a temporary melting during the first stages

of drawing¹⁹⁻²²). The strongest and often cited evidence for melting and recrystallization on drawing is found in the correlation between the long period (measured via SAXS) and the drawing temperature, which is independent of the initial lamellar thickness²³). However, it should be noted that the real-time X-ray results presented in this paper deny the presence of a more or less randomized melt (which has been suggested by Juska and Harrison^{20, 21}) during *all* stages of drawing. If there existed a more or less molten polymer fraction *during* the initial stages of drawing, a part of such a molten fraction would be transformed via strain-induced crystallization into a more or less fibre-alike structure during further drawing. During the initial stages of drawing this latter structure should be observable in the real-time WAXS patterns as additional equatorial 110 and 200 reflections besides non-equatorial 110 and/or 200 reflection arcs on both sides of the equator. However, this has not been observed.

Concluding remarks

Summarizing, comparison of WAXS and SAXS patterns obtained via conventional and real-time drawing studies suggest a high degree of similarity in case of melt-crystallized UHMW-PE, implying only marginal morphological changes caused by relieving the stretching force and cooling the sample to room temperature.

Up to now no results have been found in case of melt-crystallized UHMW-PE which prove the necessity to make observations in real-time, in order to elucidate polymer solid-state deformations qualitatively. Fortunately therefore, the conclusions drawn from conventional measurements, as presented in the literature, are in almost all cases still valid. Only if a quantitative X-ray study is needed, a real-time study is to be recommended. Furthermore, a big advantage of real-time drawing studies is found in the possibility to study the orientational changes which occur in the elastic deformation region.

Finally, it should be noted that artefacts due to relaxation phenomena may be more pronounced in lower-molecular-weight polymers and/or at drawing temperatures closer to the melting point of the polymer. This has not been studied in real-time yet.

The authors wish to thank Professor *H. G. Zachmann* for generously allowing them to use the synchrotron facilities of DESY-Hamburg. Furthermore, they are grateful to *S. Buchner* and *P. Bösecke* from the *Institut für Technische und Makromolekulare Chemie*, Hamburg, for their enthusiastic support during the real-time X-ray studies at DESY-Hamburg.

¹) D. M. Bigg, *Polym. Eng. Sci.* **16**, 725–34 (1976)

²) G. Capaccio, A. G. Gibson, I. M. Ward, “*Ultra-High Modulus Polymers*”, edited by A. Ciferri and I. M. Ward, Appl. Sci. Publ., London 1979, pp. 1–76

³) T. Ohta, *Polym. Eng. Sci.* **23**, 697–703 (1983)

⁴) N. A. J. M. van Aerle, A. W. M. Braam, *J. Appl. Crystallogr.* **21**, 106–8 (1988)

⁵) C. G. Vonk, A. P. Pijpers, *J. Appl. Crystallogr.* **14**, 8–16 (1981)

⁶) N. A. J. M. van Aerle, A. W. M. Braam, “*Integration of Fundamental Polymer Science and Technology-2*”, edited by P. J. Lemstra and L. A. Kleintjens, Appl. Sci. Publ., London 1988, pp. 423–30

- 7) A. Turner-Jones, *J. Polym. Sci.* **62**, S53-6 (1962)
- 8) T. Seto, T. Hara, K. Tanaka, *Jpn. J. Appl. Phys.* **7**, 31-42 (1968)
- 9) Y. Kikuchi, S. Krimm, *J. Macromol. Sci., Phys.* **B4**, 461-72 (1970)
- 10) K. Holland-Moritz, K. van Werden, *Makromol. Chem.* **182**, 651-5 (1981)
- 11) W. Stach, private communications (1986)
- 12) A. Brown, *J. Appl. Phys.* **20**, 552-8 (1949)
- 13) R. A. Horsley, H. A. Nancarrow, *Br. J. Appl. Phys.* **2**, 345-51 (1951)
- 14) S. L. Aggarwal, G. P. Tilley, O. J. Sweeting, *J. Polym. Sci.* **51**, 551-67 (1961)
- 15) N. Kasai, M. Kakudo, *J. Polym. Sci., Part A*, **2** 1955-76 (1964)
- 16) A. Peterlin, *J. Polym. Sci., Part C*, **9**, 61-89 (1965)
- 17) P. Ingram, H. Kiho, A. Peterlin, *J. Polym. Sci., Part C*, **16**, 1857-68 (1967)
- 18) A. Peterlin, *J. Mater. Sci.* **6**, 490-508 (1971)
- 19) P. J. Flory, D. Y. Yoon, *Nature* **272**, 226-9 (1978)
- 20) T. Juska, I. R. Harrison, *Polym. Eng. Revs.* **2**, 13-28 (1982)
- 21) T. Juska, I. R. Harrison, *Polym. Eng. Sci.* **22**, 766-76 (1982)
- 22) G. D. Wignall, W. Wu, *Polym. Commun.* **24**, 354-9 (1983)
- 23) R. Corneliussen, A. Peterlin, *Makromol. Chem.* **105**, 193-203 (1967)