ESRF	**Experiment title:** In-situ structural and thermal measurements on the ultralong monodisperse linear and branched alkanes with high time and spatial resolution	**Experiment number**: SC-4766
Beamline: ID13	**Date of experiment**: from: 15.07.2018 to: 17.07.2018	**Date of report**: 13/04/20
Shifts: 6	**Local contact(s)**: Martin Rosenthal	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Denis Anokhin*, Lomonosov Moscow State University, Russia

Prof. Dr. Dimitri Ivanov*, Institute of Materials Science of Mulhouse, France

Mr. Alexey Piryazev, Lomonosov Moscow State University, Russia

Report:

Recently a cheap and environmentally friendly dry (solvent-free) method of producing high-strength high-modulus fibers of ultra-high-molecular weight polyethylene (UHMWPE) directly from reactor powder (RP) has been developed [1-3]. The fabrication of monolithic pellets includes two stages (compactization and sintering), which eliminate boundaries between particles due to their coalescence. This process prevents braking of the pellets during the orientation hardening process. The powder is compactizised at room temperature and sintered occurs below melting point to preserve the original structure obtained after the polymer synthesis. In our previous work we have shown that the presence of monoclinic phase (MF) in RPs of UHMWPE can be considered as a criterion of the suitability of the powder for processing into a high strength material by a solvent-free method [4]. Since surface of the particles is involved in particle coalescence and the development of cohesive bonds, it was important to find out how the MF is actually distributed over the volume of the particle. The problem of analysis of MF localization is that the surface of the reactor powder is extremely developed and the particles are rather small (tens of micrometers) [5,6]. The objective of the present work was to study the volume distribution of the monocline phase in UHMWPE microparticle by microfocus X-ray diffraction technique.

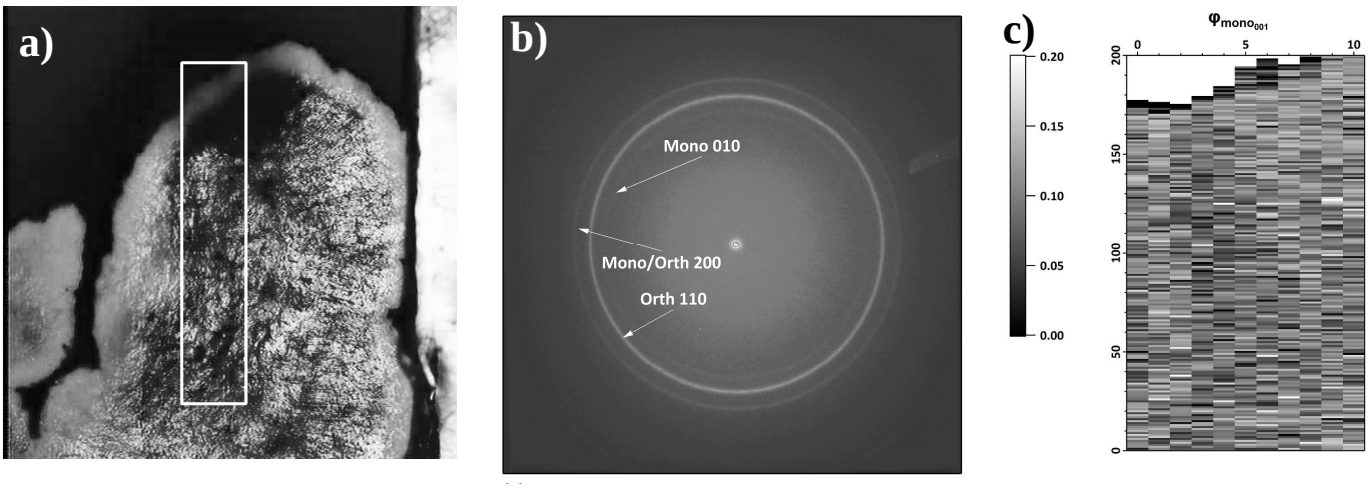

Fig. 1 Micrograph of UHMWPE particle with scanning region (a), single 2D diffractogram with marked reflections of monoclinic and orthorhombic phase (b), map of volume fraction of the monoclinic phase φ_{mon001} in the scanned region (c)

As a material, the native particles of UHMWPE powder with molecular weight of $3.5x10^6$ g/mol were used. Microfocus X-ray diffraction measurements have been performed on beamline ID13 with wavelength λ=0.83Å. A selected section of the particle with the size (100x20) μm^2 was scanned with a microbeam (0.3x0.3) μm^2 in steps of 2 μm horizontally and 0.5 μm vertically. Two-dimensional diffractograms were recorded with the Frelon CCD detector. One-dimensional diffractograms obtained by integrating 2D diffraction patterns were analyzed using the software package designed by the authors in Igor Pro environment (Wavemetrics Inc.).

Fig.1a shows a microphotograph of the UHMWPE particle with the scan area (white rectangle). Micrograph size is 576x768 pxl^2 (144x192 μm^2), magnification x50. Reflexes of both orthorhombic and monoclinic phases of PE were observed on all difactograms (fig.1b). Arrows indicate reflexes of monoclinic and orthorhombic phases and their indexes. To estimate the content of monoclinic and orthorhombic phases, the experimental diffraction curves were fitted with a set of separate Voith peaks corresponding to these phases. From the fitting results, the position and integral intensity of reflexes with indices 001_{mon} and 110_{orth} were determined. To visualized phase distribution, we constructed a map of the volume fraction of monoclinic phase φ_{mon001} (Fig.1c) calculated by the following formula:

$$\varphi_{mon_{001}} = \frac{V_{mon_{001}}}{V_{orth_{110}} + V_{mon_{001}}} = \frac{\frac{V_{mon_{001}}}{V_{orth_{110}}}}{1 + \frac{V_{mon_{001}}}{V_{orth_{110}}}} \qquad \frac{V_{mon_{001}}}{V_{orth_{110}}} = \frac{I_{mon_{001}}(s_{mon}) \cdot {F_{orth_{110}}}^2}{I_{orth_{110}}(s_{orth}) \cdot {F_{mon_{001}}}^2}$$

where s_i is the modulus of scattering vector of phase i, $I_{ij}(s_i)$ is the integral intensity of reflex j of the phase i determined from fitting procedure, F_{mon001}= 16 [7] and $F_{orth110}$ =51 [8] are the structural factors of the corresponding reflexes.

As can be seen from the map in Fig. 1c, the volume fraction of the monoclinic phase does not exceed 20%, and mainly rests in the range from 5 to 15%. Interesting, that monoclinic phase absent on the particle edge.

The formation and localization of the metastable monoclinic phase of PE can be explained from analysis of electron microscopy (SEM) images. The images show, along with lamellar stacks, development of fibrillar “shish-kebab” structures. Thus, heterogeneity of the monoclinic phase distribution over the particle volume is related to localization of fibrillar and lamellar regions. It can be assumed that the monoclinic phase is formed mainly in the stressed fibrillar regions in the central part of the “shish-kebab” and in interlamellar junctions formed by stressed tie chains. Such monoclinic phase is stable and can be considered as a structural-stabilized modification, as opposed to the monoclinic phase that occurs during plastic deformation.

The obtained results provide additional understanding of the relationship between PE morphology and its mechanical properties. An article in the Journal of Solid State Physics has been accepted for publication.

References

1. P. Smith, H.D. Chanzy, B.P. Rotzinger. Polym. Commun., 26, 258 (1985)
2. Y.L. Joo, H. Zhou, S-G. Lee, *et. al*. J.Appl. Polym. Sci., 98, 718 (2005)
3. A Pandey, Y. Champouret, S. Rastogi. Macromolecules, 44, 4952 (2011)
4. M.V. Baidakova, P.V. Dorovatovskii, Ya.V. Zubavichus, E. M. Ivan’kova, S.S. Ivanchev, V.A. Marikhin, L.P. Myasnikova, M.A. Yagovkina. Solid State Physics 60, 897 (2018)
5. Aulov, V.A.; Shcherbina, M.A.; Chvalun, S.N.; Makarov, S.V.; Kuchkina, I.O.; Pantyukhin, A.A.;Bakeev, N.F.; Pavlov, Yu.S. Polymer, Sci. Ser. A**.,** 46, 620 (2004)
6. Y.L. Yoo, O.H. Han, H.-K. Lee, J.K Song. Polymer**,** 41,1355 (2000)
7. T. Seto, T.Hara, K.Tanaka. Jpn. J. Appl. Phys.,7, 31 (1968)
8. C.W. Bunn. Trans. Faraday Soc., 35, 482 (1939)