ESRF	**Experiment title:** **Formation of self-reinforced thermoplastics from ultraoriented fibers at elevated pressure**	**Experiment number**: ME-358
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Report:

The effect of pressure on phase transformations of ultra-drawn ultra-high molecular weight polyethylene (UHMWPE) fibers was studied in this project. The mesomorphic hexagonal phase was observed to be stable even at relatively low pressure about 100 bar. The effect of pressure on the melting transitions was larger then in chain-folded structures. The existence and stability of the hexagonal phase is suggested as the basis of compaction technology of UHMWPE fibers in composite materials.

We have chosen the range, which is relevant to the technological processes of fiber compaction: pressure 100 - 600 bar, temperature 30 - 300 °C. Figure 1 displays several characteristic X-ray patterns, obtained in a temperature scan under pressure of 104 bar. At a temperature of 175 °C the $(1\ 0\ 0)_m$ monoclinic reflection disappears (Figure 1b). On raising temperature to 183 °C appearance of the hexagonal $(1\ 0\ 0)_h$ reflection is seen (Figure 1c). Upon further heating the amorphous halo, due to the melt state, is observed, yet the $(1\ 0\ 0)_h$ reflection is still prominent at 224 °C (Figure 1d). Only above about 250 °C is the amorphous halo observed without noticeable trace of polyethylene crystallinity. When the material is subsequently cooled, from a maximal temperature of 270 °C, the hexagonal phase reappears at about 230 °C (Figure 1e).

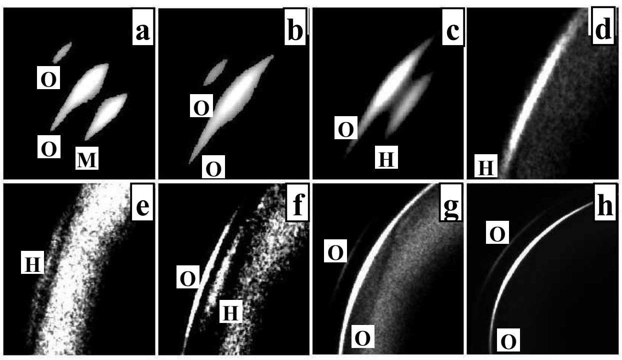

Figure 1. X-ray diffraction patterns of unidirectional UHMWPE fibers under fixed pressure of 104 bar during heating: (a) 100; (b) 175; (c) 183; (d) 224; and cooling: (e) 230; (f) 190; (g) 170; (h) 140 [°C] at 5 °C/min.
The displayed reflections are part of the equatorial region of the fiber diffraction pattern, whereby (0 0 0) is about the lower right corner and the equatorial direction is along the diagonal. M, O, H – monoclinic, orthorhombic and hexagonal reflections, respectively.

The orthorhombic phase reappears at about 190 °C (Figure 1f), and seems to coexist with the hexagonal phase as well as the melt. Figure 1g shows the orthorhombic reflections together with amorphous scattering at 170°C, whereas the reflection from the hexagonal phase completely disappears. When the fibers are cooled further below 155 °C, intensity from the amorphous region diminishes whereas the intensity of the orthorhombic reflections increases continuously. Scattering from the amorphous regions becomes barely discernible below 140 °C (Figure 1h).

Similar behavior is observed at a somewhat higher pressure of 224 bar (Figure 2). In the diffraction patterns observed during temperature scans under pressure of 600 bar, the spacing of the $(110)_o$ reflection does not change appreciably in the measured temperature range, whereas the $(200)_o$ and $(100)_h$ exhibit a significant temperature dependence.

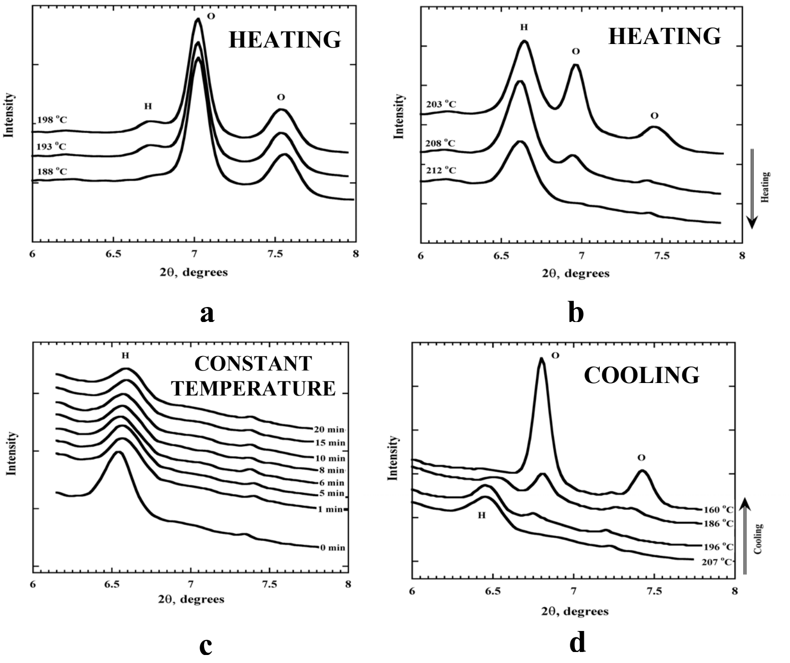

Figure 2. X-ray diffractograms of unidirectional UHMWPE fibers under fixed pressure of 224 bar The heating/cooling rate is 10 °C/min; O, H –orthorhombic and hexagonal reflections respectively.

(a) entry of the hexagonal phase reflection with increasing temperature.
(b) melting of the orthorhombic crystals via the hexagonal phase with increasing temperature;
(c) quasi-stability of the hexagonal phase reflection during isothermal annealing at 212 °C under the constant pressure;
(d) recrystallization of UHMWPE fibers during cooling

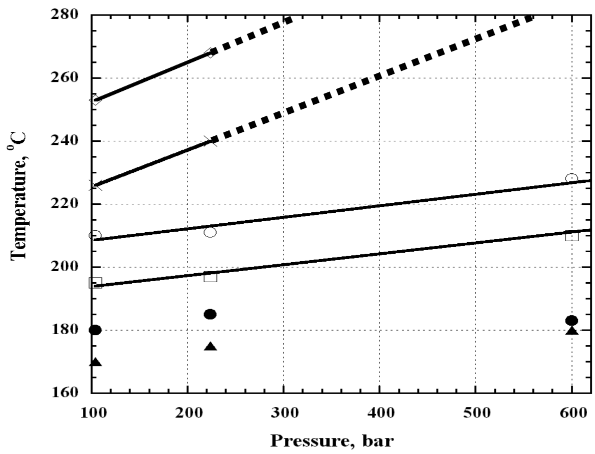

Figure 3. The influence of pressure on the temperature of:

(●) appearance of the H reflection
(○) disappearance of O reflections;
(◇) sample melting;

(×) reappearance the H reflection during coolingl cooling;
(□) reappearance of O reflections and
(▲) disappearance of the H reflection during cooling

The stability of the hexagonal phase was demonstrated in a specific experiment at constant temperature (277 °C) and pressure (600 bar), whereby the relevant reflection appeared to be unchanged for over 15 mins following an initial change of the peak intensity in less then 30 seconds.

The present study confirms that in UHMWPE fibers under pressure the hexagonal phase is significantly stable in a well-defined temperature range that is pressure dependent. The effect of pressure on the relevant transition temperatures can be estimated from the diffraction experiments, as summarized in Figure 3. The hexagonal phase appears upon heating at temperatures about 180 °C with negligible pressure dependence. Subsequently, the orthorhombic crystals disappear at 210-230 °C with slight pressure dependence. Full melting of the hexagonal phase (observed in our experiments only at relatively low pressure, at 250-270 °C) exhibited strong pressure dependence. Similar effects of pressure were observed in the onset temperatures of the hexagonal and orthorhombic phases upon cooling, as shown in Figure 3.

Even when the crystalline phase is completely transformed to the melt state, preferred chain-orientation is maintained for times relevant to composite fabrication. For example, Figure 4 shows the azimuthal breadth of reflections from the initial fiber yarn, after heat treatment at 271 °C under 104 bar pressure for 15 mins and after cooling to ambient temperature. It can be seen that although orientation is completely lost in the melt state, the recrystalized material still exhibits a reasonable degree of orientation.

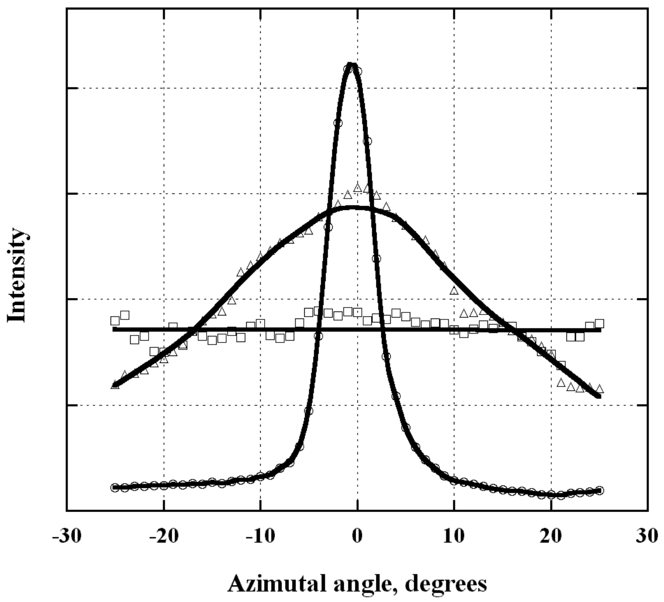

Figure 4. Azimuthal breadth of reflections: - initial fiber; - after heat treatment at 271 °C under 104 bar for 15 mins; - after sequential cooling to ambient temperature (cooling/heating rates – 5 °C/min).

The effect of pressure on the phase transformations observed upon heating oriented fibers of fully extended UHMWPE was evaluated by in-situ x-ray diffraction measurements under pressure using synchrotron radiation. In these unique fiber structures the effect of pressure on phase transitions is significantly stronger then was predicted and observed before in chain-folded and extended-chain crystalline structures. Moreover, even at relatively low pressure (about 100 bar) the hexagonal phase is observed both during melting and recrystallization. The existence and stability of the mesomorphic hexagonal phase, in which the chain conformation is less regular and more mobile on the segmental level, can explain the basis of compaction technology of UHMWPE fibers in composite materials. The intermediate hexagonal phase promotes good bonding of the fibers to form the composite, while preserving the essential fiber structure and mechanical properties.

<u>Publication:</u>
D.M. Rein, L. Shavit, R.L. Khalfin, Y. Cohen, A. Terry, S. Rastogi, "Phase Transitions in Ultra-Oriented Polyethylene Fibers under Moderate Pressures - A Synchrotron X-ray Study" to be submitted to J. Polym. Sci. Part B: Polym. Phys.