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Influence of Coagulation Time on the Structure and Morphology of PBO Fiber during Spinning Process

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Beamline(s): X27C

Introduction: In previous work, we studied the structural changes of PBO fiber during spinning process by in-situ synchrotron WAXD. The results showed that a significant ordering had taken place after the fiber had passed through the coagulation water bath, ranging from 25-60 °C (see the previous report). The results indicated that the coagulation process was very crucial to the final structure of PBO fiber. The question is that how the structure has been changed in the coagulation stage. Is the structure changed directly from lyotropic spinning solution to the final crystal structure or there are some transferred structures in between? In this work, we made a modification on the spinning machine, which can control the coagulation time sequence going down to 0.03 sec. We studied the influence of the coagulation time on the structure of PBO fiber.

Methods and Materials: Spinning experiment was carried out at X27C SUNY beam line at NSLS/BNL. The x-ray beam ($\lambda = 0.137$ nm) passes through 3-pinhole system (190 cm long) with the first and last pinhole size of 0.10 mm and 0.37 mm in diameter, respectively. The spin unit is a modified version of the experimental unit used by The DOW Chemical Company^[1], which was introduced before. Compared with the previous experiment, two major improvements were made:

- 1) A new spinneret was redesigned and made (by Toyobo Inc. Japan), which was smaller and shorter than the previous one.
- 2) A new water bath was designed to meet the requirement of short time coagulation.

The dope, provided by Toyobo Inc., Japan, seated in the barrel for about 50 min and then was plunged. In this study, the extrusion speed is fixed to 21 mm/min. Monofilament fiber from spinneret was exposed to x-ray beam for about 2 min.

Results: From our observation, the new exit diameter (0.3mm) of the spinneret yield a good quality of the PBO fibers in terms of smoothness. It is also probably true that the coagulation process is more uniform (not necessarily complete) within the fiber since the diameter of the fiber is much thinner than before.

Fig.1 shows the one-dimensional equatorial scattered intensity of PBO fibers with different coagulation times. It was found that there were two peaks ($q = 0.65 \text{ \AA}^{-1}$ and 1.41 \AA^{-1} , respectively) before coagulation, which was corresponding to the extruded PBO/PPA dope structure possessing lyotropic liquid-crystalline order. We contributed this structure to the complex of PBO and PPA in the previous work. After the fiber passed through the water bath, even the coagulation time was down to 0.03 sec, an additional peak at $q = 1.82 \text{ \AA}^{-1}$ ($d = 3.5 \text{ \AA}$) appeared, which was corresponding to the 010 reflection of PBO crystal. With increasing the coagulation time, the 010 peak became stronger, indicating that more PBO crystals were formed from the PBO/PPA complex as more PPA molecules were hydrolyzed and washed away during coagulation. However, we did not observe the appearance of 200 reflection ($q = 1.15 \text{ \AA}^{-1}$ and $d = 5.5 \text{ \AA}$) after short time coagulation. This suggests that the first step of the coagulation is likely the formation of face-to-face stacks of PBO on top of each other at the 3.5 Å spacing (corresponding to $q = 1.82 \text{ \AA}^{-1}$). The results of this work indicate that PBO began to crystallize as soon as the extruded dope passed through the water bath, even the coagulation time was as short as 0.03 seconds.

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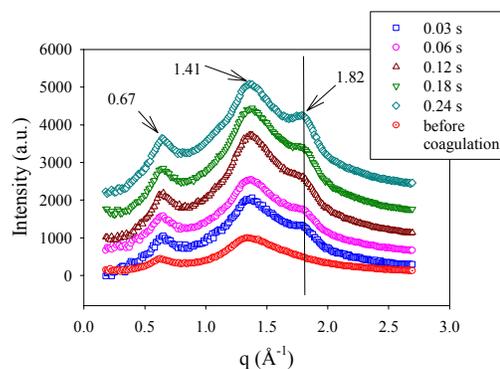


Fig.1 1D equatorial scattered intensity of PBO fibers with different coagulation times.