Origin on the High Orientation and Fibrillar Structure of As-spun Acrylic Fibers from Hydrated Melt

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The outstanding properties of the as-spun acrylic fibers prepared in the supercooled state from the hydrated melt were its high orientation and fibrillar structure in spite of they have not undergone any other aftertreatment including drawing. Moreover, no subsequent cold drawing is necessary or possible. It's very peculiar phenomena that as-spun fibers made by low spin draw ratio not exceeding 3 exhibits high molecular orientation as well as fibrillar structure. High orientation and fibrillar structure of as-spun fiber have been reported only for the spinning of liquid crystalline solution or melts as well as solid state extrusion .

(1) Origin for the High Orientaion of the As-spun PAN Fibers

According to Ziabicki, orientation in the as-spun fiber is mainly due to elongational flow past the spinneret, since relaxation in the die-swell bulge removes most of the orientation due to shear in the spinneret. However, for the present spinning of hydrated melt of PAN it is apparent that orientaion in elongational flow after extrusion hardly contribute to ultimate orientation of fiber due to very long relaxational time of the supercooled melt and fast solidification of extrudate. In addition, shear flow within the spinneret was also not the dominant origin for the high orientation of as-spun fibers.

It is concluded that particularly high orientation of as-spun fibers prepared from supercooled state is mainly originated from the elongational deformation within the conical entrance region of the spinneret with the help of fast solidification after extrusion which enables to fix the deformation.

In solid state extrusion, the maximum extrusion draw ratio of the extruded material is defined as the ratio of the initial entrance and exit cross-sectional areas of the conical die. For the present case, it is supposed that the same drawing effect as solid state extrusion was obtained by elongational deformation in conical region because the supercooled state is semi-solid state, as discussed previously. In other words, it is the same effect as drawing unoriented as-spun fiber after extrusion by several times.

(2) Origin for the Fibrillar Structure of the As-spun PAN Fibers

It is interesting that our as-spun fiber without additional drawing process has fibril structure that is able to be separated easily, as shown in Fig. 1. The surface of the fibers retain luster and fractured cross-sections show a distinct skin-core structure. Fig. 2 shows that micropores within core part form cylidrically parallel to the fiber direction and that each fibril sparates along to the cylinderical micropore. From isothermal crystallization study it has been known that considerable amount of water has already dehydrated from PAN in supercooled state from which extrusion was carried out. Therefore, the extrusion in supercooled state of this work is similar to bicomponent spinning that is used for manufacturing ultrafine fiber. It has enough basis to consider that phase separation of water and PAN in supercooled state helps the formation of fibril structure and makes it easy to separate each fibril.

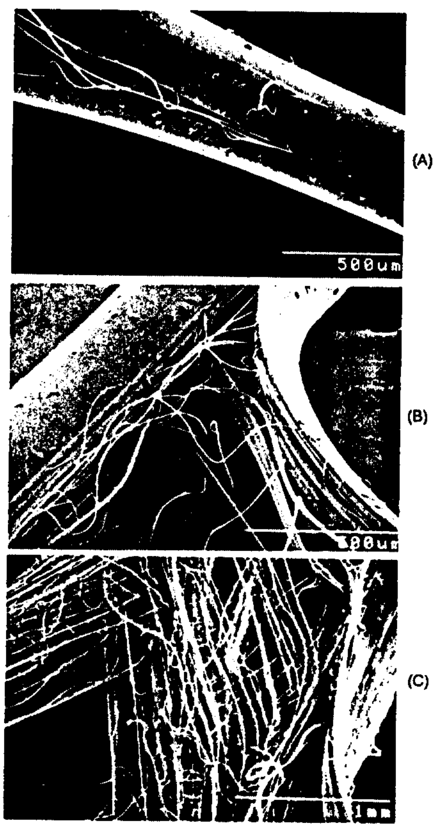

Fig. 1 . Fibrillar structure of the fibers spun with L/D = 0(A), L/D = 3(B) and L/D = 15(C), respectively.

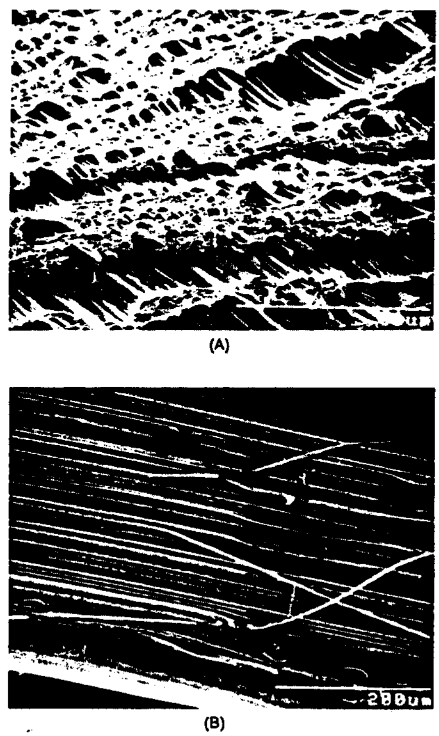

Fig. 2 . SEM micrographs showing cylindrical micropores parallel to the fiber axis for the fibers spun with L/D = 15(A) and L/D = 0(B), respectively.