Crystallization behavior under flow field for polypropylene containing a nucleating agent

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I elucidated the crystallization behavior of polypropylene (PP) from crystal nucleating agents under flow field with the evaluation of mechanical properties and deformation behaviors of products.

Firstly, a new method to improve the stiffness of PP was proposed using a sorbitol derivative, i.e., 1,3:2,4-bis-o-(4-methylbenzylidene)-D-sorbitol (MDBS). This material is commercially available and known to improve the transparency of PP products. MDBS is once dissolved in molten PP and segregated as fine fibers during cooling. Then, it acts as a crystal nucleating agent for PP. In general, PP containing MDBS is processed beyond the dissolution temperature of MDBS to improve the transparency of a product. Therefore, the dissolution temperature, which depends on the MDBS content, has to be comprehended. Such information was obtained by the direct measurement of transparency of an injection-molded product. In this study, a simple method to predict the dissolution temperature was proposed using thermal analysis, which provided us important information on the appropriate resin temperature for actual processing operations. At injection molding performed beyond the MDBS dissolution temperature, MDBS fibers appeared after filling in a mold, at which molecular orientation of PP was fully relaxed at least in the core layer of a product. Then, a network structure of MDBS fibers is formed without specific orientation of fibers. In this case, the nucleation activity was slightly reduced because it took some periods for the fiber formation, i.e., MDBS segregation, from molten PP. In contrast, when the injection molding was performed below the dissolution temperature, the segregation period was not required, and MDBS fibers were oriented in the flow direction. This situation resulted in significant nucleation activity immediately after filling in a mold. Because PP crystallization occurred from the oriented MDBS fibers, a pseudo shish-kebab structure was developed, leading to improved mechanical properties such as flexural modulus. These results indicated that sorbitol-based nucleating agents can improve the stiffness of PP by controlling only the processing temperature.

Secondly, the effect of a metal stearate compound, that is usually added as an acid acceptor and called “neutralizer”, on the transparency of PP containing a sorbitol derivative was investigated, because the fiber formation of a sorbitol derivative can be affected by another polar compound, i.e., metal stearate. In this thesis, the effect of calcium stearate (StCa), a common neutralizer, on the fiber formation and transparency of injection-molded PP products was investigated. Lithium stearate (StLi) was used as a comparison. It was found that the addition of StLi, instead of StCa, improved transparency at low MDBS amounts. This phenomenon suggested that fiber formation was accelerated by the StLi addition. However, as the MDBS amount increased, the advantage of StLi decreased, and the product containing StCa exhibited better transparency. Furthermore, it was found that the transparency well corresponded with the molecular orientation: i.e., High molecular orientation provided good transparency.

Finally, the optimal process temperature and stretching method to prepare a porous film of PP containing N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide (NU-100) as a crystal nucleating agent were proposed. PP sheets prepared by conventional processing conditions were composed of α-monoclinic form crystals. In this case, it was almost impossible to obtain a porous film by stretching procedure at any conditions. However, the addition of only 0.1 wt% of NU-100 made it possible for PP films to provide numerous pores, when the orientation of PP chains in the sheet and the stretching conditions were carefully selected. In this study, PP sheets composed of β-trigonal form crystals with different orientation states were stretched under various conditions. The structure of stretched films was analyzed by scanning electron microscope, wide-angle X-ray diffraction, and ultrasonic propagation characteristics. When a sheet was extruded at 260 °C, at which NU-100 was dissolved, it showed almost no orientation with β-form crystals. In such a sheet, a porous film was unable to be prepared regardless of the stretching method. In a sheet extruded at 200 ºC, at which NU-100 was not dissolved, β-form crystals were highly oriented in the transversal direction (TD), i.e., perpendicular to the flow direction. This was originated from epitaxial crystallization of PP from the needle-shaped nucleating agent, in which PP chains orient perpendicular to the long axis of needle nucleating agents. When stretching in the machine direction (MD) of this sheet around at 100 ºC, numerous voids appeared. In the TD-stretched films, in contrast, shear yielding was dominated with few voids. During deformation, a large number of β-form crystals transformed to α-form ones at TD stretching. Moreover, it was found that large deformation in the same direction should be avoided to prepare a film with numerous pores because it caused integration of voids. Biaxial deformation, i.e., stretching in both MD and TD, was preferable to provide a large number of micro-voids. In addition, sequential biaxial stretching, i.e., MD stretching followed by TD stretching, was effective than equi-biaxial one, because the voids generated by the initial MD stretching were widen by the TD stretching. This operation provided a noticeably higher pore content in a film.

The methods found in this thesis can be employed in industry immediately, and therefore, I wish various PP products with high performance will be prepared soon using these crystal nucleating agents.

Keywords: Polypropylene, Sorbitol derivative, Nucleating agent, Flow field