

Title	結晶核剤を添加したポリプロピレンの流動場での結晶化挙動
Author(s)	岩崎, 祥平
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氏名	岩崎 祥平		
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論文審査委員	山口 政之	北陸先端科学技術大学院大学	教授
	谷池 俊明	北陸先端科学技術大学院大学	教授
	松見 紀佳	北陸先端科学技術大学院大学	教授
	桶葺 興資	北陸先端科学技術大学院大学	准教授
	杉本 昌隆	山形大学大学院	教授

論文の内容の要旨

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 °C, 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 °C, 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 widened 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

論文審査の結果の要旨

この論文では、溶解型の結晶核剤を添加したポリプロピレンの構造と性質について研究した内容を纏めている。「溶解型結晶核剤」とは、加熱下で熔融した高分子中に一旦溶解した後、冷却過程で析出し、高分子に対して結晶核として作用する物質である。このような結晶核剤は古くから知られており、工業的にも使われてきた。しかしながら、流動場で結晶核剤がどのように作用して構造形成に影響を及ぼすのか、ということに関してはほとんど研究が実施されていなかった。実際に用いられる場合、高分子物質は必ず流動を伴う成形加工プロセスを経て製品が得られることから、実用的にも重要な課題である。

本研究では二つの溶解型結晶核剤を扱っている。ひとつはソルビトール誘導体であり、ポリプロピレン中で直径 10nm 程度の繊維形状で析出することが過去の研究で知られている。一般的にはこの化合物を添加した場合、かなり高温で成形加工が行われる。一度、ソルビトール誘導体をポリプロピレン中に溶解せねばならないためである。本材料に対して、混練・成形温度と、得られた成形体の固体構造との関係を詳しく調べた。その結果、一度、高温で混合した材料を低温で成形すると、繊維状の結晶核剤が高度に配向し、その表面からポリプロピレンが結晶化することがわかった。このようにして得られた成形体ではポリプロピレンの分子配向が進み、高い弾性率の成形体を得られる。現在、プラスチック材料の薄肉軽量化に対するニーズは強く、本結果はこれを実現する新技術となりえる。さらに、本物質を対象とし、ポリプロピレンに一般的に添加されているステアリン酸塩の影響を調べた。その結果、ステアリン酸塩のカチオン種により、ソルビトール化合物の析出挙動が大きく変化することを新たに見出した。この現象を利用することで、ソルビトール化合物の添加量が少なくても結晶核剤能を顕著に発現させることが可能になる。

アミド系の結晶核剤についても研究を実施している。本研究で用いたアミド系結晶核剤はポリプロピレン中に針状の結晶として析出し、ポリプロピレンはその表面からエピタキシャルな結晶成長を行う。その際、ポリプロピレンの分子鎖は、針状結晶核剤の長軸と垂直方向に配向して結晶化する。このようにして得られたポリプロピレン成形シートの延伸特性を調べたところ、方向によって塑性変形の様式が大きく異なることを見出した。流れの方向に延伸するとボイド形成が主となり、それと垂直方向ではせん断降伏が主となる。この現象を利用することで、多孔質フィルムを調製することが可能になる。なお、本結晶核剤は上記の機能フィルム調製剤として工業化されている。

以上、本論文は、結晶核剤を添加したポリプロピレンの高性能化、機能性付与について、構造制御の観点から明らかにしたものであり、学術的に貢献するところが大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。