様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　３ 年　 ６ 月　 ７ 日現在

機関番号：１３３０２
研究種目：若手研究
研究期間：2018～2020
課題番号：１８Ｋ１４２８２

研究課題名（和文）エピタキシャルな結晶成長を利用した分子鎖配向の高度な制御とその応用

研究課題名（英文）Control of molecular orientation using epitaxial crystal growth and its application

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交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：押出プロセスでは、特定のβ核剤を含むポリプロピレン（PP）フィルムは、PP鎖が流れ方向に垂直に配向した、異常な分子配向を示している。押し出しシートの変形挙動は延伸方向に依存することを説明した。ミクロボイドの形成は機械方向への延伸中に発生するため、多孔性の高い構造には、結晶子間を接続する十分な量の結合分子が必要である。さらに、結晶相の変態、および延伸中の鎖軸の回転が、頻繁なボイドの開放の原因である。これらの結果は、結晶相とアモルファス領域の両方の異方性が、変形中の異なる形態の原因であることを示している。この材料は、電池セパレーター用の微孔性フィルムの開発に適用できる。

研究成果の学術的意義や社会的意義
The fact that plastic deformation mechanism is strongly dependent on the deformation direction leads to further understanding of deformation behavior of not only PP but also any crystalline polymers. The finding will widen the material design in both extrusion and injection-molding processes.

研究成果の概要（英文）：In extrusion process, polypropylene (PP) films containing the specific β nucleating agent exhibit the anomalous molecular orientation, in which PP chains are oriented perpendicular to the flow direction, irrespective of the molecular weights of PP. We explained that the deformation behavior of the extruded sheet depends on the stretching direction. As the microvoid formation occurs during stretching in a machine direction, a sufficient amount of tie molecules connecting between crystallites is required for highly porous structure. Moreover, the transformation of crystalline phase as well as the rotation of chain axis during stretching is responsible for the frequent void opening. These results indicate that the anisotropy of both the crystalline phase and the amorphous regions is responsible for the different morphologies during the deformation. The material would be applicable to the development of microporous films for battery separators.

研究分野：Polymer physics

キーワード：polypropylene　nucleation　morphology　molecular orientation

1. 研究開始当初の背景

Polypropylene (PP) product having high content of the β-form crystals usually shows the excellent mechanical toughness. Generally, high content of β-form crystals is obtained only through adopting suitable conditions such as addition of β-nucleating agents and controlled processing conditions. In this research, a small amount of β-nucleating agent, *N,N'*-dicyclohexyl-2,6-naphthalenedicarbox-amide, is employed to prepare PP with a large amount of β-form crystals. We introduced a method to control the molecular orientation of β-form PP, resulting in an extraordinary structure. Because of the hydrodynamic force at extrusion, long axis of needle crystals of the nucleating agent orients to the flow direction. Consequently, PP molecules orient perpendicular to the flow direction. As the unusual molecular orientation was perpendicular to the flow direction, the deformation mechanism was different from that observed for conventional products. We explained that the deformation behavior of the extruded sheet depended on the stretching direction. Cavitation, with numerous microvoids and fibrils, was prominent in the sample drawn in the machine direction (MD), whereas a shear yielding deformation was apparent in the sample drawn in the transverse direction (TD). Based on these results, we suggest that the concept of orientation control in a PP sheet containing a nucleating agent (PP/NA) would be applicable to the development of polymeric microporous films for battery separators by a melt extrusion process followed by stretching. To control the porosity and uniformity of a fabricated film, the structural control of the crystalline lamellae and amorphous phase was studied considering the molecular weight of PP, which is a key factor affecting the pore interconnectivity.

2. 研究の目的

The objective of this research is to clarify the relationship between the molecular weight of PP and its morphology based on the deformation mechanism of PP/NA during uniaxial stretching. The results will provide the important information for engineering microporous films.

３．研究の方法

Three types of commercially available isotactic PP with different molecular weights (low, medium, and high) were used as raw materials. The nucleated PPs were prepared by melt-mixing PP, β-nucleating agent; *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide, thermal stabilizers, and neutralizing agent using a counter-rotating twin-screw extruder. Kneading was performed at 260°C to complete the dissolution of the nucleating agent. The resulting PP mixtures were extruded and cut into pellets.

To prepare the oriented PP films, the PP pellets containing the nucleating agent were fed into a single-screw extruder equipped with a T-die. The temperature of the die was controlled at 200°C and that of the chill roll was 120 °C. The thickness of the obtained films was 200 μm.

To clarify the deformation behavior, the as-extruded sheets of PP containing the nucleating agent (PP/NA) were stretched in the MD and TD using a biaxial stretching machine. The PP/NA sheet was held in the machine for 40 minutes at 100°C and then stretched in the uniaxial direction while maintaining a constant width, with a strain of 300%.

４．研究成果

As revealed by WAXD measurements, a unique molecular orientation, in which both the *c*-axis and crystalline lamellae were oriented perpendicular to the flow direction, was formed in all undrawn film samples, irrespective of the molecular weights. A greater degree of crystallinity was exhibited in the medium-molecular weight sample (M-PP/NA). A decrease in the melting temperature for both α- and β-form crystals and the enhanced long period by SAXS demonstrated an evolution of the amorphous fraction in the high-molecular-weight sample (H-PP/NA).

In the drawn films uniaxially stretched with a constant width, a marked void opening with a rotation of the crystal molecules was dominant in the MD stretching for the medium-molecular-weight sample, as seen in FIGURE 1. The increase in the molecular weight promoted the generation of numerous amorphous chains acting as tie molecules between the neighboring lamellae and reduced the lamellar thickness. As a result, cavitation with void openings was inhibited, leading to a small number of voids for high-molecular-weight sample. In contrast, low-molecular-weight sample (L-PP/NA) showed brittle properties in the MD stretching, which can be explained by the shortage of the tie chains in the stretching direction.

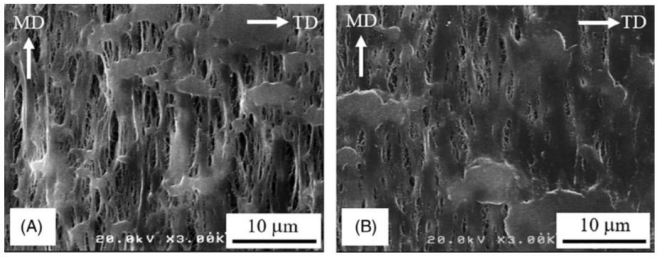

FIGURE 1 SEM micrographs of the drawn MD samples for PP/NA; (A) medium- molecular-weight sample, and (B) high-molecular-weight sample.

The occurrence of defects, including voids, in the MD stretching was further confirmed by the ultrasonic coefficient in FIGURE 2. It is obviously seen that the attenuation coefficient for M-PP/NA was higher than that for H-PP/NA in the MD stretching, suggesting the presence of a large number of voids in the medium-molecular-weight sample. In the case of the TD stretching, shear yielding with the β-to-α phase transformation was apparent for all samples containing the nucleating agent, except for the low-molecular-weight sample. These results indicate that the anisotropy of both the crystalline phase and the tie molecules between the crystallites was responsible for the different morphologies obtained during the deformation. The finding demonstrated the influence of the molecular weight on the void structure, which will be useful in the field of microporous membranes.

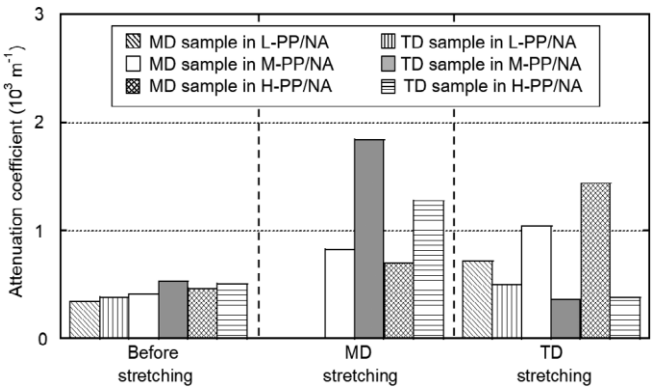

FIGURE 2 Ultrasonic attenuation coefficient of PP/NA sheets. The samples were stretched at a strain of 300% in the MD and TD directions.

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５．主な発表論文等

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３．雑誌名 Polymer Journal	６．最初と最後の頁 529-538
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41428-019-0286-0	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Masayuki Yamaguchi, Yoko Fujii, Panitha Phulkerd	４．巻 48(2)
２．論文標題 Rheological properties of polyolefin blends containing long-chain branched polypropylene as dispersed phase (in Japanese)	５．発行年 2020年
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1122/1.2008297	査読の有無 有
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/pen.25580	査読の有無 無
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s10965-020-02198-y	査読の有無 無
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関