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（様式第５号）

ポリオレフィンのメソスケールの内部構造が及ぼす力学的特性に関する基礎研究
Basic research of the relationship between mechanical properties and mesoscale internal structure of polyolefins

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１．概要（注：結論を含めて下さい）

プラスチックのマテリアルリサイクルが進展しない大きな要因として、力学物性の低下が上げられる。従来この原因は化学劣化であると考えられてきた。しかしながら最近の我々の研究により、化学劣化していないリサイクルプラスチックにおいても力学物性が低下していることが明らかとなった。またプレス成形条件により、この力学物性が大きく改善できることも明らかとなった。これらの結果は、リサイクルプラスチックの力学物性の低下は化学劣化ではなく構造的な物理劣化であることを示している。
本研究は様々なプレス成形を行ったバージンプラスチックおよびリサイクルプラスチックの内部構造をＸ線小角散乱により調べ、力学物性との関係を検討する目的で行った。その結果、力学物性により内部構造に違いがあることが明らかとなった。

（English）
The main obstruction in material recycling process is the poor mechanical properties in recycled products. Conventionally, chemical degradation was considered as the main cause. However, based on our previous studies, it can be found that plastics are not degraded by chemical. In other way, physical degradation is the main cause for the poor mechanical properties in recycled plastics.
The purpose of this study is to investigate the relationship between the changes of inner structures and mechanical properties of virgin and recycled plastics after annealed by various treatments and molding conditions. SAXS is the main instruments which can be used for characterization of inner structure such as long period, thickness of crystalline layer, and amorphous layer of plastics products. The results can be shown that the different of inner structures related to the degradation of mechanical properties in plastics.

２．背景と目的

従来廃棄プラスチックは分子鎖切断などの化学劣化により再生不可能な物性低下が生じているとされてきた。しかし福岡大学の八尾らの研究により、物性低下の主原因が高分子の内部構造変異による物理劣化であることが明らかにされた（例えば、Journal of Material Cycles and Waste Management, 21(1), 116-124 (2019)）。またこの成果はNEDOの国家プロジェクト（2020～2024年度）として採択されている

（https://www.nedo.go.jp/news/press/AA5_101345.html）。

本研究はこの国プロに関連したものであり、実際に物性が低下あるいは向上したプラスチックを試料として用い、X 線小角散乱法による内部構造解析を行い、力学的特性との関係性を明らかにすることを目的としている。これにより、廃棄プラスチックのマテリアルリサイクルプロセスの運転条件と内部構造ならびに力学特性の関連性を明らかにし、最適な再生プロセスの確立を目指す。

３．実験内容（試料、実験方法、解析方法の説明）

Virgin polypropylene (VPP, J700GP) was obtained from Prime Polymer Co., Ltd. and used as received. VPP thin film with thickness of 100 µm was fabricated by pressed molding at 210 ºC, 25 MPa, 2 min and slowly cooled down to room temperature (25 ºC).

The mechanical recycling of VPP was performed by shear treatment using a cone and plate rheometer. Two different types of shear treatment conditions were conducted;

1) Steady shear (SS): Steady shear treatment at 180 ºC, 100/s, 10 min

2) Steady shear following by Dynamic shear (D): Steady shear treatment at 180 ºC, 100/s, 10 min, then dynamic shear was performed at 210 ºC, 5 min, 10% of strain with various angular velocity at 1.3, 6.3, and 18.8 rad/s. The products were defined as D1.3, D6.3, and D18.8 with different of angular velocity.

Then, the shear-treated PP samples were remolded as thin film with thickness of 100 µm at the same molding condition as VPP thin film. The schematic diagram of shear treatment and thin film fabrication was showed in **Fig. 1**.

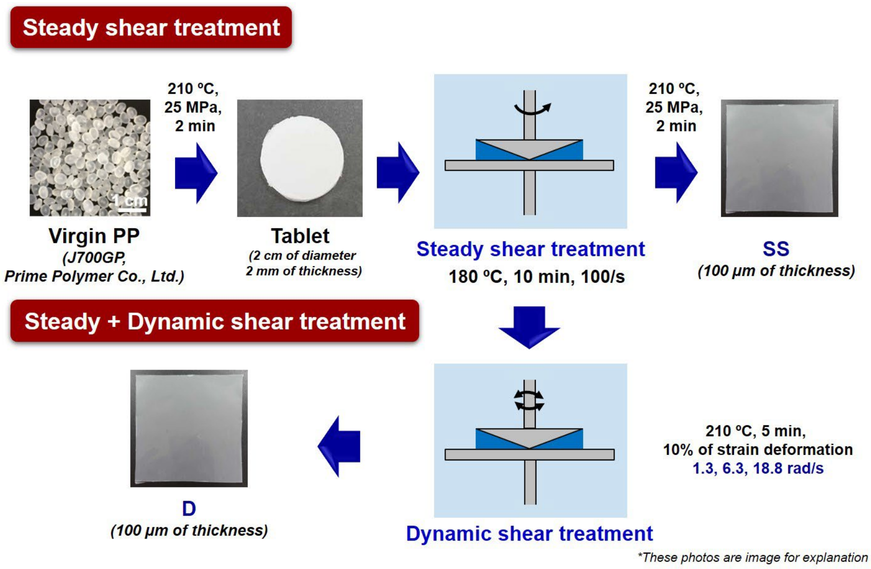

Fig. 1 *Schematic diagram of shear treatment process and thin film fabrication.*

VPP and shear-treated PP thin films were characterized mechanical properties by tensile test. In addition, the thickness of mesoscale lamellar structure was characterized by a small-angle X-ray scattering (SAXS) at BL11 of SAGA-LS. The characterization conditions were performed as follows;

測定方法：透過による小角 X 線散乱

○カメラ長:1000 mm、X 線エネルギー8 keV を選択した場合

測定角度範囲：q = 約 0.14-3.0 nm^{-1}

○測定試料の密度に適切した X 線のエネルギー(8-11 keV)を選択する。

○透過による小角 X 線散乱

○全散乱パターンを測定できる、PILATUS 300K を使用

ビームストッパーサイズは 0.16 nm^{-1}

○試料の透過率測定を SAXS 測定と同時に行う。

試料前後にイオンチェンバーを配置
測定は常温、常圧下で行う。フィルム系はそのままで、あるいはスライドガラスに挟み込んで測定に供する。
試料からの適切な散乱強度を得るために必要とする照射時間は、時間とともに X 線強度が減衰することを考慮して(試料の入れ替えを含み)算出すると、8 時間あたり 40 点の測定を行う。

４．実験結果と考察

Based on our previous works, dynamic shear affected the regeneration of elongation at break and toughness of high-density polyethylene (HDPE). This regeneration of mechanical properties related to the increasing of intermediate layer thickness which can be implied to the increasing of entanglement from the effect of dynamic shear.

In this study, dynamic shear treatment was applied on virgin polypropylene (PP). The mechanical properties and the relationship with thickness of mesoscale lamellar was studied.

Fig. 2 showed the elongation at break **(a)** and Young's modulus **(b)** of virgin PP thin film (VPP), PP treated by only steady shear (SS), and PP treated by steady shear following by dynamic shear at various angular velocity (D1.3, D6.3, D18.8). It can be found that steady shear affected the degradation of elongation at break and Young's modulus as compared to its virgin sample (VPP). This is because the mechanical treatment by heat and steady shear affected the physical degradation of PP.

Interestingly, the addition of dynamic shear affected the regeneration of elongation at break. As a result, the elongation at break of dynamic shear was regenerated and higher than the only steady shear (SS). Especially at 18.8 rad/s of angular velocity (D18.8), the elongation at break and Young's modulus was recovered and similar to its VPP. This can be confirmed that the addition of dynamic shear with the suitable of angular velocity and strain affected on the regeneration of elongation at break and Young's modulus in PP.

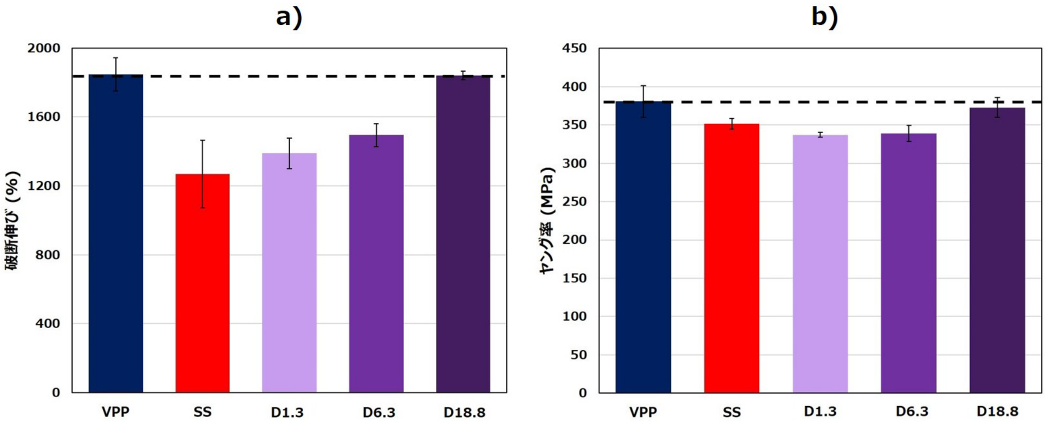

***Fig. 2 (a)** Elongation at break, and **(b)** Young's modulus of VPP, steady shear treated sample (SS), and steady+dynamic shear treated samples (D) with different angular velocity (1.3, 6.3, 18.8 rad/s).*

Due to the regeneration of elongation at break and Young's modulus, the detailed characterization of mesoscale lamellar structure and the relationship with mechanical properties were discussed. The thickness of mesoscale lamellar structure was characterized by SAXS at BL11 of SAGA-LS and the results were analyzed by using the electron density correlation method. Then, the relationship with tensile properties was evaluated. **Fig. 3(a)** showed the correlation between elongation at break and long period which was the combination between the thickness of crystalline, amorphous, and intermediate layer. One can see that the moderate negative correlation with 0.77 of correlation factor (R^2) was detected. SS which consisted of the degradation of elongation at break showed the increasing of long period as compared to VPP. However, the addition of dynamic shear affected the increasing of elongation at break with the decreasing of long period. Especially at 18.8 rad/s (D18.8), the elongation at break was regenerated to be similar to VPP. In addition, the long period of D18.8 was also decreased from SS and similar to VPP.

Fig. 3(b) showed the correlation between elongation at break and thickness of amorphous layer. The weak negative correlation was detected with 0.45 of correlation factor (R^2). The correlation trend was similar to long period. SS showed the longest of amorphous layer; however, D18.8 showed the regeneration of elongation at break and thickness of amorphous layer as similar to VPP.

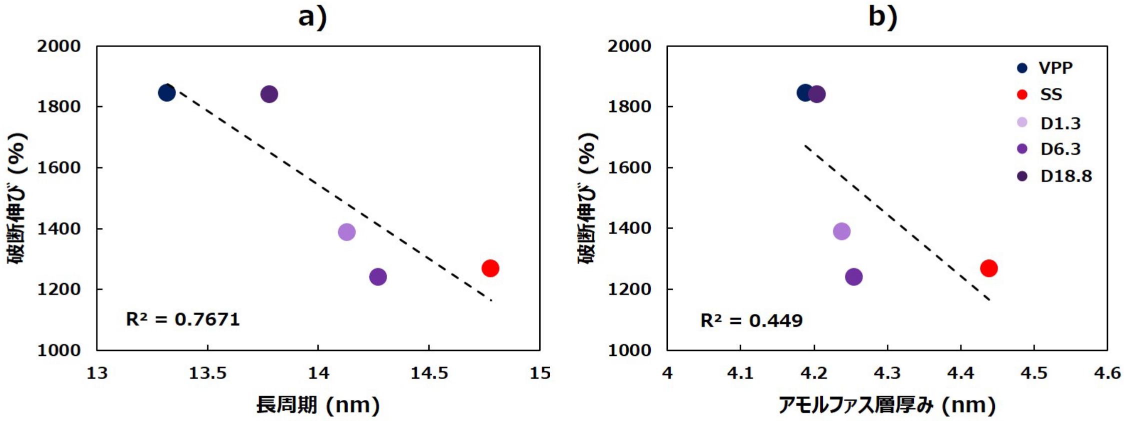

Fig. 3 *Correlation between elongation at break with long period* ***(a)*** *and thickness of amorphous layer* ***(b)*** *of VPP, SS, and D with various angular velocity.*

In conclusion, steady shear treatment affected the degradation of elongation at break and Young's modulus of PP. This reduction of mechanical properties was strongly related to the increasing of long period and thickness of amorphous layer. In other way, the addition of dynamic shear treatment related to the regeneration of elongation at break and Young's modulus of PP. The optimized dynamic shear condition at 210 ºC, 5 min, 10% of strain, 18.8 rad/s of angular velocity affected the recovery of elongation at break and Young's modulus of PP as similar as its VPP. In addition, this recovery of mechanical properties was related to the regeneration of long period and thickness of amorphous layer as similar to its VPP. From this study, it can be concluded that the addition of dynamic shear at suitable angular velocity affected the regeneration of mechanical properties and thickness of mesoscale lamellar structure in mechanical-recycled PP.

５．今後の課題

- To optimize the %strain of dynamic shear condition in order to recover the mechanical properties higher than its VPP.
- To apply the optimized dynamic shear condition to the practical mechanical recycling process for the development of mechanical properties of recycled PP.

６．参考文献

７．論文発表・特許（注：本課題に関連するこれまでの代表的な成果）

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・「バージン樹脂およびプレコンシューマリサイクル樹脂ブレンド系における射出成形品の入口部位・終端部位の結晶構造および力学特性」，冨永　亜矢，関口　博史，中野　涼

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８．キーワード（注：試料及び実験方法を特定する用語を２～３）
Polypropylene, Plastic mechanical recycling, Dynamic shear

９．研究成果公開について（注：※２に記載した研究成果の公開について①と②のうち該当しない方を消してください。また、論文（査読付）発表と研究センターへの報告、または研究成果公報への原稿提出時期を記入してください。提出期限は利用年度終了後 2 年以内です。例えば 2018 年度実施課題であれば、2020 年度末（2021 年 3 月 31 日）となります。
長期タイプ課題は、ご利用の最終期の利用報告書にご記入ください。

① 論文（査読付）発表の報告　　　（報告時期： **2024** 年 **3** 月）
② 研究成果公報の原稿提出　　　　（提出時期：　　年　　月）