九州シンクロトロン光研究センター
県有ビームライン利用報告書

課題番号：2101010A	ＢＬ番号：11

（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（Ⅱ）
Basic research of the relationship between mechanical properties and mesoscale internal structure of polyolefins（Ⅱ）

パントン　パチヤ
Patchiya Phanthong

福岡大学工学部化学システム工学科
Department of Chemical Engineering, Faculty of Engineering, Fukuoka University

※１　先端創生利用（長期タイプ）課題は、実施課題名の末尾に期を表す（Ⅰ）、（Ⅱ）、（Ⅲ）を追記してください。
※２　利用情報の公開が必要な課題は、本利用報告書とは別に利用年度終了後２年以内に研究成果公開｛論文（査読付）の発表又は研究センターの研究成果公報で公表｝が必要です（トライアル利用を除く)。
※３　実験に参加された機関を全てご記載ください。
※４　共著者には実験参加者をご記載ください（各実験参加機関より１人以上）。

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 high-density polyethylene pellet (HDPE, FX201A) was obtained from Keiyo Polyethylene Co., Ltd. and use as received. HDPE thin film with thickness of 100 μm was fabricated by pressed molding at 180 ºC, 25 MPa, 2 min and slowly cooled down to room temperature (25 ºC). The obtained thin film was named as VPE.

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

1) Steady (定常); Steady shear treatment at 180 ºC, 100/s, 10 min
2) Dynamic (動的); Dynamic shear treatment at 180 ºC, 10 rad/s, 10 min with various strain deformation at 10, 50, 100, and 200%
3) Steady+Dynamic (定常＋動的); 1)+2)

Then, the shear-treated samples were remolded as thin film (thickness of 100 μm) with the same molding condition as VPE.

VPE and shear-treated thin films were characterized the 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
〇カメラ長: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}
〇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。
〇透過による小角 X 線散乱
〇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}
〇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 studies, dynamic shear deformation affected the regeneration of elongation at break of HDPE with the changes of thickness of intermediate layer and core-amorphous layer. This study, the detailed study for finding the optimized dynamic shear treatment condition was performed. **Fig.1** showed the toughness of VPE, steady shear, dynamic shear (10-200% of strain) and the steady+dynamic shear (10-200% of strain) of HDPE. The steady shear affected the decreasing of toughness from VPE. Dynamic shear at 10% and 50% of strain showed the higher of toughness than the steady shear; however, toughness was less than VPE. It is worth noting that the dynamic shear with high strain at 100% and 200% showed the increasing of toughness over than VPE. For the addition of dynamic shear after steady shear (Steady+Dynamic) with various condition of strain (10, 50, 100, 200%), toughness was regenerated and increased than only steady shear treatment. Especially at high strain (100% and 200%), toughness was not only improved as compared to the steady shear, but it was also regenerated and higher than its original VPE.

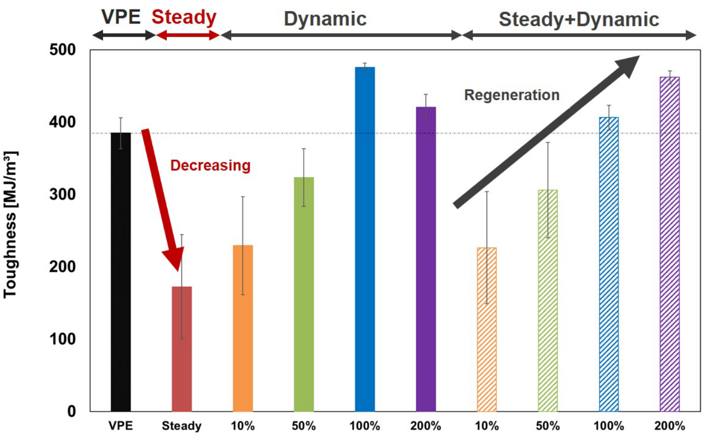

Fig. 1 *Toughness of VPE, steady shear-treated sample, dynamic shear-treated sample, and steady+dynamic shear treated sample with different strain condition (10, 50, 100, 200%).*

Due to the highest regeneration of toughness, dynamic shear condition at 200% of strain was selected to be a representative for the detailed evaluation of thickness of mesoscale lamellar structure which were characterized by SAXS and evaluated by electron density correlation function method. **Table 1** showed the thickness of long period (L_0), intermediate layer (d_{tr}), mean amorphous layer (L_a), mean crystalline layer (L_c), and the ratio with long period. The mesoscale structure of the only steady shear which showed the most degradation of toughness was different from VPE; long period was longer while the thickness of intermediate was shorter than VPE. In case of dynamic shear at 200%, long period and lamellar structure was similar to VPE. Especially in thickness of intermediate layer, dynamic shear and steady+dynamic showed the similarity of thickness as compared to VPE. This can be implied to the similarity of toughness between VPE, dynamic (200%), and steady+dynamic (200%).

Table 1 *Thickness of mesoscale lamellar structure of VPE, steady shear, dynamic shear at 200%, and steady+dynamic shear at 200%.*

	Thickness of mesoscale structure [nm]						
	Long period (L_0)	Intermediate (d_{tr})	d_{tr}/L_0	Mean-Amorphous (L_a)	L_a/L_0	Mean-Crystalline (L_c)	L_c/L_0
VPE	20.90	1.52	0.145	3.80	0.182	17.10	0.818
Steady	21.10	1.48	0.140	3.82	0.181	17.28	0.819
Dynamic (200%)	20.50	1.52	0.148	3.87	0.189	16.63	0.811
Steady+Dynamic (200%)	20.60	1.52	0.148	3.84	0.186	16.76	0.814

The relationship between ratio of thickness of intermediate layer to long period (d_{tr}/L_0) and toughness was shown in **Fig.2**. Positive correlation was detected between VPE and shear-treated samples. Steady shear which related to the most degradation of toughness showed the decreasing of thickness of intermediate layer as compared to VPE and other dynamic shear conditions. At low strain (10% and 50%), ratio of d_{tr}/L_0 and toughness was similar in only dynamic shear and steady+dynamic. This can be implied that dynamic shear had strongly affected which can be recovered toughness and mesoscale lamellar structure as compared to only steady shear. At high strain (100% and 200%), dynamic and steady+dynamic samples were slightly different in d_{tr}/L_0; however, their toughness was higher than VPE. The best condition at 200% of strain in steady+dynamic sample showed the increasing of the ratio of thickness of intermediate layer which related to the most toughness value over than VPE.

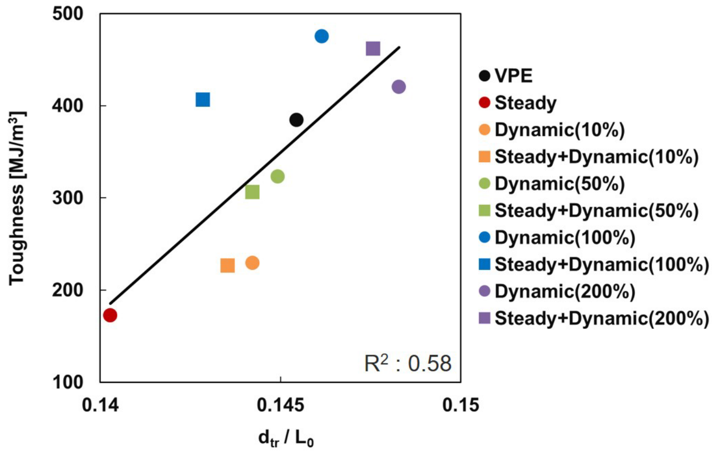

Fig. 2 *Correlation of ratio between thickness of intermediate layer to long period (d_{tr}/L_0) and toughness of VPE and shear-treated samples.*

In conclusion, steady shear affected the decreasing of thickness of intermediate layer which related to the degradation of toughness. In other way, dynamic shear treatment affected the increasing of thickness of intermediate layer which also related to the regeneration of toughness. This is because the increasing of thickness of intermediate layer in HDPE affected the generation of chain entanglement which also related to the regeneration of toughness in mechanical-recycling HDPE.

Based on this study, dynamic shear treatment with high strain (100% and 200%) was successfully regenerated the toughness of mechanical recycling HDPE and thickness of intermediate layer. These findings can be further applied to the practical extrusion process for improvement of physical properties of mechanical recycling HDPE.

５．今後の課題

- To apply the optimized dynamic shear treatment to the practical mechanical recycling process for the development of physical properties of mechanical recycling HDPE products.

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）

• "Investigation of Degradation Mechanism from Shear Deformation and the Relationship with Mechanical Properties, Lamellar Size, and Morphology of High-Density Polyethylene", Haruka Kaneyasu, Patchiya Phanthong, Hikaru Okubo, Shigeru Yao, Appl. Sci., 11, 8436 (2021).

•"Relationship between the long period and the mechanical properties of recycled polypropylene", Aya Tominaga, Hiroshi Sekiguchi, Ryoko Nakano, Shigeru Yao, and Eiichi Takatori, Nihon Reoroji Gakkaishi, 45(5), 287-290 (2017)

•"Creation of Advanced Recycle Process to Waste Container and Packaging Plastic -Polypropylene Sorted Recycle Plastic Case-", Nozomi Takenaka, Aya Tominaga, Hiroshi Sekiguchi, Ryoko Nakano, Eiichi Takatori, Shigeru Yao, Nihon Reoroji Gakkaishi, 45(3), 139-143 (2017)

・「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 涼子，八尾 滋，高取 永一，高分子論文集，74(3), 225-232 (2017)

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）

High-density polyethylene, Plastic mechanical recycling, Shear deformation

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）