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：2305016I	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

Fundamental research on relationship between mechanical properties and mesoscale lamellar structures of polyolefin

パントン パチヤ、八尾滋
Patchiya Phanthong and Shigeru Yao

福岡大学機能・構造マテリアル研究所
Research Institute for the Creation of Functional and Structural Materials, 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（SAXS）により調べ、力学物性との関係を検討する目的で行った。これまでの研究で、SAXS による散乱プロファイルをさらに電子密度相関法により解析することで、界面状態も含めた詳細なサイズ評価を行うことで、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）

Main obstruction of plastic mechanical recycling process is poor mechanical properties of the recycled plastic products. Conventionally, chemical degradation was considered as the main cause of this problem. Based on our previous studies, plastics were not degraded by chemical process; however, physical degradation is the main cause of the reduction of mechanical properties in recycled plastics.

The main goal of this study is to investigate the relationship between the changes of mesoscale lamellar structures, mechanical properties of virgin and/or recycled plastics after treating with various treatments and molding conditions. Small-angle X-ray scattering (SAXS) is the main characterization instrument in order to characterize the thickness of mesoscale lamellar structure of plastic products such as long period, thickness of crystalline layer, amorphous layer, intermediate layer, and degree of crystallinity. It is expected that the regeneration of thickness of lamellar structures is related to the development of mechanical properties of mechanical recycled plastics as similar as its original plastic.

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（SAXS）による内部構造解析を行い、成形履歴と力学的特性ならびに長期耐久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と長期耐久性の関連性を明らかにし、最適な再生プロセスならびに成形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）

In this study, low-density polyethylene (LDPE) grade F522N (MFR = 5 g/10 min) which was obtained from UBE-Maruzen Polyethylene Co., Ltd. was used as a target material. The original thin film (Org) was fabricated by hot compression at 180 ºC, 2 min, 26 MPa, slow cooling (SC). Thin film with 0.1 mm of thickness was obtained. Shear treatment was performed by cone and plate rheometer at 180 ºC for 10 min. Steady shear (S) was operated at 100 s^{-1}. Dynamic shear (D) was operated at 10 rad/s, 50% of strain. Steady shear following by Dynamic shear (S+D) was also performed in order to investigate the effect of dynamic shear on steady-shear treated LDPE. The effect of molding pressure was studied by the re-pressing of shear-treated LDPE with pressure at 26 MPa for 20 min with slow cooling (P-SC) and quench cooling (P-Q). The sample list was tabulated in **Table 1**.

Table 1. *LDPE sample list with shear treatment condition.*

Samples	Steady shear (180 ºC, 10 min)	Dynamic shear (180 ºC, 10 min)	Effect of molding pressure
Org	-	-	-
S	100 s^{-1}	-	-
D	-	10 rad/s, 50% of strain	-
S+D	100 s^{-1}	10 rad/s, 50% of strain	-
S+D_P-SC	100 s^{-1}	10 rad/s, 50% of strain	26 MPa, 20 min, SC
S+D_P-Q	100 s^{-1}	10 rad/s, 50% of strain	26 MPa, 20 min, Q

Shear-treated LDPE samples were also fabricated as thin film (0.1 mm of thickness) by hot compression. Then, all samples were evaluated the mechanical properties by tensile test. Mesoscale lamellar structures were evaluated by SAXS. SAXS at BL-11 of SAGA-LS was used for characterization of thickness of lamellar structures of virgin and shear-treated LDPEs. The characterization condition of SAXS was 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。
- 全散乱パターンを測定できる、PILATUS 300Kを使用する。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。

The analysis of thickness of lamellar structures was calculated based on the electron density correlation function [1-2].

４．実験結果と考察

Based on the characterization of mechanical properties by tensile test, **Figure 1** showed the comparison of elongation at break and yield stress of LDPE original film (Org), shear-treated LDPE (S, D, S+D), and addition of repressing with pressure (S+D_P-SC, S+D_P-Q). Generally, steady shear (S) affected the reduction of elongation at break of LDPE. Interestingly, the elongation at break of dynamic shear (D) was higher than S. In order to investigate the effect of additional pressure, P-SC with slow-cooling condition was further degraded the elongation at break of LDPE. As a result, the elongation at break was obviously reduced from only treated by steady shear (S). On the other hand, repressing with pressure following by cooling with quench (S+D_P-Q) affected the regeneration of elongation at break. It was slightly higher than S+D without any additional molding pressure. For the comparison of yield stress, shear-treated LDPE (S, D, S+D) was slightly higher than Org which was implied to the increasing of brittleness of LDPE from shear treatment. Interestingly, yield stress of treating with addition pressure had no significant effects on yield stress and it was similar to LDPE Org.

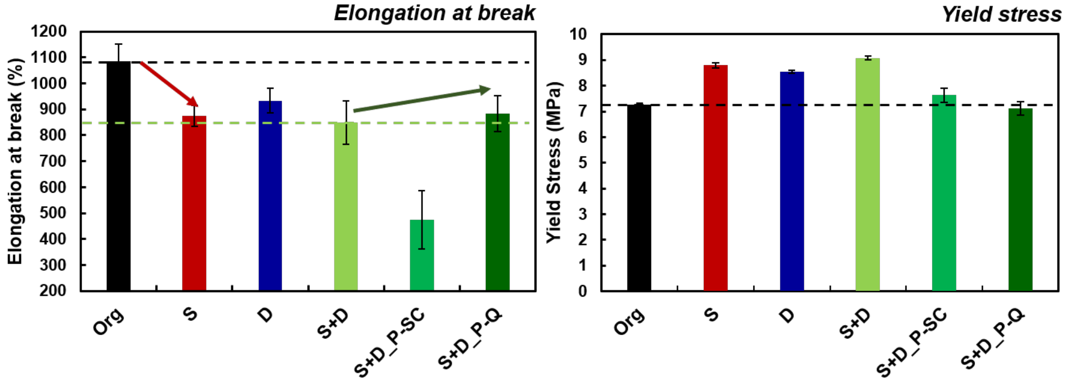

Figure 1. *Elongation at break and Yield stress of Org, shear-treated and re-pressed LDPE samples.*

Figure 2 exhibited the correlation between thickness of lamellar structures and tensile properties of LDPE Org, shear-treated, and re-pressing with pressure. Medium positive correlation was detected between toughness and thickness of amorphous layer. Interestingly, strong negative correlation was observed between yield stress and thickness of core crystalline layer. This can be implied to the changes of thickness of mesoscale lamellar structure of LDPE shear treated samples by dynamic shear following with repressing with

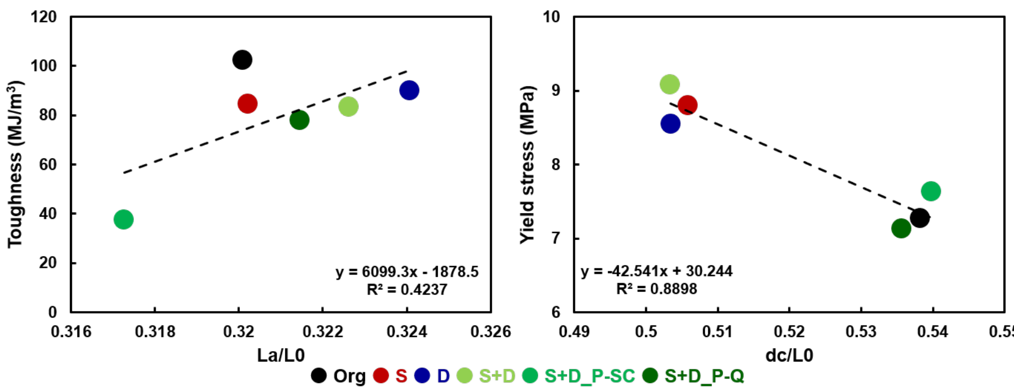

Figure 2. *Correlation between thickness of lamellar structures and tensile properties of Org, shear-treated and re-pressed LDPE samples.*

pressure at 20 min and cooling by quench. Especially in S+D_P-Q, the thickness of crystalline and amorphous layer was similar to LDPE original film (Org).

In conclusion, dynamic shear and repressing with pressure at 20 min with quench cooling affected the regeneration of mesoscale lamellar structure of LDPE. S+D_P-Q also showed the regeneration of yield stress, thickness of amorphous and crystalline layer as similar as LDPE original film (Org). Even the elongation at break has still been not reached to the level of original LDPE, it can be confirmed that dynamic shear and addition of molding pressure affected the regeneration of lamellar structure of shear-treated LDPE. Detailed investigation for the regeneration of elongation at break until reaching the level of original LDPE will be continued to study in order to development LDPE mechanical recycling technique. This is for prolonging of lifetime used of plastics and decreasing the amount of the single-used waste LDPE in environment.

５．今後の課題

• To investigate the optimized molding condition in order to regenerate the elongation at break of mechanical recycled LDPE.

６．参考文献

[1] “Direct evaluation of the electron density correlation function of partially crystalline polymers” G.R. Strobl, M. Schneider, Journal of polymer science, 18, 1343-1359 (1980).
[2] “Model of partial crystallization and melting derived from small-angle X-ray scattering and electron microscopic studies on low-density polyethylene” G.R. Strobl, M.J. Schneider, I.G. Voigt-martin, Journal of polymer science, 18, 1361-1381 (1980).

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).

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）

• Plastic mechanical recycling
• Low-density polyethylene
• 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：　**2026**　年　**3**　月）
② 研究成果公報の原稿提出　（提出時期：　　年　　月）