Restoring mechanism of mechanical properties of recycled polyethylene pellet moldings by a repelletizing treatment using a twin-screw extruder

H. Okubo¹ · S. Yao¹

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Abstract

To develop material-recycling processes for used plastic products, it is necessary to design new material-recycling techniques to optimize the mechanical properties of the recycled plastics since the mechanical properties of recycled plastic products are normally deteriorated. In this study, we suggest one of the approaches that is a repelletizing treatment for improving the mechanical properties of recycled-polyethylene moldings using a twin-screw extruder. The results of the tensile test revealed the significant effect of the repelletizing treatment on the tensile performance of the recycled-polyethylene moldings. The tensile performance of the repelletized recycled-polyethylene moldings was significantly higher than that of the original recycled-polyethylene moldings under specific repelletizing conditions. The analysis of the polymeric structures revealed the significant effect of the repelletizing treatment on the secondary and higher-order structures such as the lamellar shape, aggregation of the crystal domains, amorphousness, and polyethylene chain conformation in the recycled-polyethylene moldings. The repelletizing treatment increased the tensile performances by optimizing the internal structure of the recycled-polyethylene moldings. The results confirmed the efficacy of the repelletizing treatment to optimize the mechanical performance of the recycled-polymer materials, thereby facilitating the reuse of waste plastics as value-added materials for various industrial applications.

Keywords Plastics · Repelletizing · Recycled-polyethylene moldings · Tensile performance · Amorphousness

Introduction

Plastics are widely used in various industrial applications due to their multiple advantages over iron-based materials such as lightweight, low cost, and ease of molding. It is crucial to develop material-recycling processes for used plastic products to alleviate the global environmental concerns [1]. However, the marked changes in the structural and chemical states (e.g., molecular chain length, crystallinity, and functional groups) of the plastic polymers during recycling operations pose a major challenge [2–4]. These changes generally induce a deterioration in the mechanical properties of the recycled-plastic products. It is necessary to design new

material-recycling techniques to optimize the mechanical properties of the recycled plastics.

In the conventional concept, the deterioration in the mechanical properties of the recycled-plastic compounds is attributed to the chemical degradation of the polymer structure during recycling that breaks the molecular chains [3, 4]. On the other hand, despite the similarities in the molecular weights and chemical states of the material-recycled and virgin plastics, the tensile performance of the material-recycled plastics is inferior to that of the virgin plastics [5–9]. This indicates that the deterioration in the mechanical properties of the recycled products cannot be solely attributed to the chemical degradation. It is well known that the crystal structures of polymers are easily changed by shear-induced deformations and the structures strongly depend on the shear-treatment conditions [9–17]. Cavallo et al. reported that the survival time of shear-induced nucleation precursors is extremely large compared to typical rheological relaxation times and it is longer for the precursors originated at higher shear rate [9]. Hayashi et al. also reported that

✉ H. Okubo
h.okubo.ni@adm.fukuoka-u.ac.jp

¹ Collaborative Research Institute for Creation of Functional and Structural Materials, Fukuoka University, Fukuoka, Japan

the flow-induced shear treatment for isotactic polystyrene played important roles in the specific crystal structure formation such as a string-like object [15–17] and the structure strongly depended on the share rate conditions [15]. It is also well known that the inner crystalline structure of polymeric moldings strongly affected the mechanical properties of the moldings [18–20]. Zuidema et al. reported that the polymer blends of PP and PE fail at low elongation because of their two-phase structure, consisting of interpenetrating networks or of islands of PE in a PP matrices [18]. Zhou H et al. reported that the tensile properties were significantly dependent on the orientation of molecular structure originating from different morphologies developed during the polymer deformation processes [19]. Based on the several previous studies, for the recycled polymeric moldings, physical deformations during molding and recycled processes can induce a physical deterioration, which can change the internal crystal structures and deteriorate the mechanical properties of the moldings. In our previous study [21], the tensile properties of the non-chemically degraded material-recycled plastic compounds can be restored to the same level as that of the virgin plastics by molding the plastic pellets under optimal molding conditions; furthermore, the results of our analysis revealed the changes in the polymeric structure depending on the molding conditions [21]. Therefore, the physical treatment of the physically degraded recycled-plastic compounds under optimal conditions changes the polymeric structures, thereby restoring the mechanical properties to the same level as that of the virgin plastics. The recycling of plastic materials involves the pelletization of the sorted waste plastics to produce the recycled-plastic pellets that are subsequently utilized to mold the final products [22]. The pelletization involves the application of physical energy to the melted waste plastics by rotating the screw elements of the pelletizer. This results in the physical energy-activated structural transformation of waste plastics during pelletization. Therefore, the pelletization of the waste plastics under optimal conditions modifies the internal structure of the recycled-plastic pellets, thereby optimizing the mechanical properties.

In this study, we demonstrated the repelletizing treatment to optimize the mechanical properties and polymeric

structures of the recycled-plastic moldings. The recycled pellets were subjected to physical treatment in a screw pelletizer. The effects of the repelletizing treatment using a twin-screw extruder on the tensile performance and internal structure of the recycled-polyethylene (RPE) moldings were investigated. We focused on the material composition of the recycled pellets [low-density polyethylene (LDPE) and high-density polyethylene (HDPE)] and the repelletizing parameters such as the temperature and screw-rotation speed. The tensile properties of the original and repelletized RPE pellets were evaluated using a universal tensile tester. The polymeric structures of the original and repelletized RPE pellets were analyzed by energy-dispersive X-ray spectroscopy (EDS) in conjunction with scanning electron microscopy (SEM), imaging Fourier transform infrared (FT-IR) spectroscopy, and atomic force microscopy (AFM). Thus, the effect of the repelletizing method on the mechanical structure and polymeric structures of the RPE moldings was determined.

Materials and methods

Characteristics of RPE pellets

The three types of RPE pellets that were used in this study were the RPE-HARD, RPE-SOFT, and RPE-MIX (Toyama Kankyo Seibi, Toyama, Japan). The pellets were characterized based on their composition into the LDPE and HDPE pellets. The composition and melt flow rate (MFR) of the pellets were estimated by differential scanning calorimetry (DSC, DSC 8500, PerkinElmer, Inc., Waltham, USA) and melt flow indexing (Melt Indexer-G-02, Toyo Seiki Seisaku-Sho Ltd., Tokyo, Japan). The original recycled pellets images and their characterization are shown in Fig. 1 and Table 1, respectively.

Repelletizing conditions in the twin-screw extruder

The RPE-HARD, RPE-SOFT, and RPE-MIX pellets were repelletized in a twin-screw extruder (SBTN26-S2-60L, Research Laboratory of Plastics Technology Co., Osaka,

Fig. 1 Original recycled pellet images (provided by TKS CO.)

Table 1 Characterization of each original recycle pellets

		RPE-HARD	RPE-SOFT	RPE-MIX
MFR	g/10 min	0.59	0.56	0.59
HDPE: LDPE	–	100:0	30:70	50:50

Japan). A schematic of the extruder is shown in Fig. 2. The effects of the repelletizing parameters on the tensile performance of the RPE moldings were analyzed under different repelletizing conditions (temperature = 170 °C, 200 °C, and 230 °C; screw-rotation speed = 100 rpm, 200 rpm, and 300 rpm). The repelletizing conditions are summarized in Table 2. The charge-coupled device (CCD) images of the cross sections of the repelletized pellets were obtained using a digital camera.

Press molding and tensile test conditions

The original and repelletized pellets (10 ± 0.05 g) were pressed using a press-molding machine (pressure-switch-type, PEC-700, Riken, Saitama, Japan) at a setting temperature of 180 °C under 25 MPa (pressure-holding time = 120 s). Subsequently, they were cooled to the 25 °C (room temperature) to obtain a 1-mm-thick film.

The specimen for the tensile test was punched from the press-molded films. The dimensions of the specimen (length = 56 ± 0.5 mm; width = 7 ± 0.2 mm; thickness = 1 mm) were in compliance with JIS K 7113 2(1/2). Five specimens were used for each tensile test to confirm the repeatability of the test results. The tensile tests were performed using a universal tensile tester (AGS-X; Shimadzu Corporation, Kyoto, Japan) at 26.0 °C (relative humidity (RH) = 41.5%) with an elongation rate of 5 mm/min. The breaking elongation, toughness, and Young's modulus were calculated from the load–displacement curves using a material-testing software (Trapezium Lite X, Shimadzu Corporation, Kyoto, Japan).

Table 2 Characterization of each original recycle pellets

	Screw speed [rpm]	Temperature [°C]	Feed [kg/h]	Cutting speed [m/min]
Effects of screw speeds	100	200	10	10
	200	200	10	10
	300	200	10	10
Effects of temperature	200	170	10	10
	200	200	10	10
	200	230	10	10

Analysis

The concentration of the contaminants in the RPE moldings was determined by EDS (scanning control unit (SCU), Bruker Corporation, Billerica, USA) in conjunction with SEM (the accelerating voltage: 15 eV, backscattered electron scanning mode, TM 4000 Plus- Hitachi, Ltd., Tokyo, Japan).

The RPE moldings were subjected to imaging FT-IR spectroscopy (Nicolet iN10, Thermo Fisher Scientific, Waltham, USA) before and after the tensile tests using the reflection method with a gold reflection plate (wave number range: 600 cm^{-1} – 4000 cm^{-1} , number of scan: 32 times, scanning time = 60 s; imaging area = $200\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$) to determine their secondary structure.

The higher-order structure of the RPE moldings was determined by AFM (Nanowizard, Bruker Corporation, Billerica, USA). The specimens were etched for 2 h in an etching liquid that was prepared by dissolving a 1% w/v solution of potassium permanganate in a 2:1 mixture of sulfuric and dry ortho-phosphoric acid [23, 24]. The etched specimens were directly observed in the tapping mode using a silicon pyramidal cantilever (PPP-NCHAuD, Nanosensors, Neuchatel, Switzerland). The phase images were obtained to distinguish between the crystal lamellar and amorphous regions in the etched specimens [23, 24].

Fig. 2 Schematic diagram of the screw extruder

Results

Cross-sectional density of the repelletized RPE pellets

Figure 3 and Fig. 4 show the cross-sectional CCD and binary images of the repelletized RPE pellets, respectively. The appearance of the cross section of the RPE-HARD pellets was approximately identical for all the repelletizing conditions (Fig. 3), whereas the appearances of the cross sections of the RPE-SOFT and RPE-MIX pellets were different under the various repelletizing conditions. The area ratio of the white pixels in the binary images (Fig. 4) was calculated and defined as the cross-sectional density of the RPE pellets. Figure 5 shows the cross-sectional density of the repelletized RPE pellets. The cross-sectional density of the RPE-SOFT and RPE-MIX pellets at a temperature and screw-rotation speed of 230 °C and 100 rpm, respectively, was less than 50%. However, the cross-sectional density was approximately 70% under the other repelletizing conditions. Therefore, the repelletizing conditions had a significant influence on the density of the repelletized RPE pellets.

Tensile performance

Figure 6 shows the representative tensile stress–strain curves of the RPE-HARD, RPE-SOFT, and RPE-MIX moldings. Figure 7 shows the representative CCD images of the elongated tensile specimens of the RPE-HARD, RPE-SOFT, and RPE-MIX moldings. The breaking elongation of all the repelletized RPE-HARD moldings (2.3–3.2%) was significantly higher than that of the original RPE-HARD moldings (0.3%) (Fig. 6a). The breaking elongation of the repelletized RPE-SOFT moldings (0.2–0.7%) was higher than that of the original RPE-SOFT moldings (0.15%) (Fig. 6b), except at a temperature and screw-rotation speed of 230 °C and 100 rpm, respectively. The breaking elongation of the RPE-MIX moldings (0.1–0.3%) was consistently lower than that of the original RPE-MIX moldings (0.6%) (Fig. 6c). The results confirmed the significant influence of the repelletizing treatment on the tensile performance of the RPE moldings. Furthermore, the effects of the repelletizing treatment on the tensile performance depended on the repelletizing parameters and the type of the RPE pellets.

Figure 8 shows the breaking elongation, Young's modulus, and breaking energy, as a function of the repelletizing temperature and screw-rotation speed, that were calculated

Fig. 3 Cross-sectional CCD images of repelletized RPE pellets

Fig. 4 Cross-sectional binary images of repelletized RPE pellets

Fig. 5 Cross-sectional density of the repelletized RPE pellets

Fig. 6 Representative tensile stress–strain curves for **a** RPE-HARD, **b** RPE-SOFT, and **c** RPE-MIX

(a) RPE-HARD

(b) RPE-SOFT

(c) RPE-MIX

Fig. 7 Representative CCD images of elongated tensile specimens of RPE-HARD, RPE-SOFT, and RPE-MIX

from the tensile stress–strain curves (Fig. 6) of the RPE moldings. There was no change in the Young's modulus of the RPE moldings with the repelletizing conditions (Fig. 8a–c). The RPE-HARD (Fig. 8a) moldings exhibited the highest breaking elongation and breaking energy at a repelletizing temperature of 200 °C. Furthermore, the breaking elongation and breaking energy of the RPE-HARD moldings increased and decreased, respectively, with the increase in the screw-rotation speed. The RPE-SOFT moldings (Fig. 8b) exhibited the highest breaking elongation and breaking energy at a repelletizing temperature and screw-rotation speed of 200 °C and 200 rpm, respectively. The breaking elongation and breaking energy of the RPE-MIX moldings (Fig. 8c) decreased with the increase in the repelletizing temperature and increased with the increase in the screw-rotation speed.

Therefore, the breaking elongation and breaking energy of the various RPE moldings were highly dependent on the repelletizing parameters and the type of the RPE pellets.

SEM-EDS

Figure 9 shows the SEM images of the RPE moldings. As can be seen in Fig. 9, the morphologies of the RPE-SOFT moldings, which were molded from low-density pellets (Fig. 4), at a repelletizing temperature of 230 °C and a screw-rotation speed of 100 rpm were significantly different from that of the others. The specific square domains that are surrounded by the red-dotted lines in Figs. 9b, c were observed in the SEM images of the moldings that were derived from low-density pellets. Although the CCD images and roughness values are not shown here, the moldings

Fig. 8 Breaking elongation, Young's modulus, and breaking energy of the RPE-moldings calculated from the tensile stress–strain curves as a function of the repelletizing temperature and screw rotating speeds

(a) RPE-HARD

(b) RPE-SOFT

(c) RPE-MIX

Fig. 9 SEM images of the **a** RPE-HARD, **b** RPE-SOFT, and **c** RPE-MIX moldings

(a) RPE-HARD

(b) RPE-SOFT

(c) RPE-MIX

Fig. 10 **a** Representative EDS spectrum and **b** the concentration of oxygen:O, titanium:Ti, and chlorine:Cl for each RPE molding

that were derived from low-density pellets appeared to be rougher than the others. Hence, the morphology of the RPE moldings was significantly affected by the density of the RPE pellets.

Figure 10 shows the representative EDS spectrum and the concentration of O, Ti, and Cl in each RPE molding. The three contamination peaks in the EDS spectrum (Fig. 10a) represented O, Ti, and Cl that might be derived

from the pigments. Furthermore, the change in the concentrations of O, Ti, and Cl with the repelletizing conditions was negligible (Fig. 10b).

Imaging FT-IR spectroscopy

Secondary structure of the RPE moldings

The typical PE peaks corresponding to the CH_2 asymmetric strong stretching (2920 cm^{-1}), CH_2 symmetric strong stretching (2850 cm^{-1}), bending strong deformation (1473 and 1463 cm^{-1}), CH_3 symmetric weak deformation (1375 cm^{-1}), and rocking medium deformation (728 cm^{-1} and 718 cm^{-1}) were observed in the representative FT-IR spectrum (Fig. 11) of the RPE moldings before the tensile test [25]. The peak intensity ratios, I_{1375}/I_{2920} and I_{718}/I_{728} , that represented the degree of branching of the PE chains and the amorphousness of the trans-conformational PE chain, respectively, were calculated from the FT-IR spectrum to analyze the secondary structure of the RPE moldings.

Figures 12 and 13 show the imaging FT-IR results of I_{1375}/I_{2920} and the average values of I_{1375}/I_{2920} that were calculated from the imaging FT-IR results, respectively, for each RPE molding. The difference in I_{1375}/I_{2920} of the original and repelletized RPE-HARD moldings was negligible (Fig. 12a). Therefore, the degree of the branching of the PE

chains in the RPE-HARD moldings remained unchanged after the repelletizing treatment. The repelletized RPE-SOFT (Fig. 12b) and RPE-MIX (Fig. 12c) moldings two-dimensionally showed a higher value of I_{1375}/I_{2920} (degree of the branching of the PE chains) in comparison with that of the original moldings; however, the value of I_{1375}/I_{2920} for the RPE-SOFT molding at 100 rpm and $170\text{ }^\circ\text{C}$ was an exception. The results indicated that the repelletizing treatment affected the degree of the branching of the PE chains in the RPE-SOFT and RPE-MIX moldings.

Figures 14 and 15 show the imaging FT-IR results of I_{718}/I_{728} and the average values of I_{718}/I_{728} that were calculated from the imaging FT-IR results, respectively, for each RPE molding. The value of I_{718}/I_{728} for the repelletized RPE-HARD (Fig. 14a) and RPE-SOFT (Fig. 14b) moldings was generally higher than that for the original moldings; however, I_{718}/I_{728} for the RPE-SOFT molding at $230\text{ }^\circ\text{C}$ and 100 rpm was an exception. Therefore, the amorphousness of the trans-conformational PE chain in the RPE-HARD and RPE-SOFT moldings increased after the repelletizing treatment. However, the RPE-MIX (Fig. 14c) moldings exhibited two or three domains depending on I_{718}/I_{728} (Fig. 14). Therefore, the repelletizing treatment contributed to the formation of several domains that were characterized by the differences in the amorphousness (crystallinity) in the RPE-MIX moldings.

Fig. 11 Representative FT-IR spectrum for RPE moldings before the tensile test

Fig. 12 Imaging FT-IR results of the I_{1375}/I_{2920} ratio for the **a** RPE-HARD, **b** RPE-SOFT, and **c** RPE-MIX moldings

Fig. 13 Average value of the I_{718}/I_{728} ratio calculated from the imaging measurement results for each RPE molding

Secondary structure of the elongated regions of the RPE moldings after the tensile test

The typical PE peaks in the representative FT-IR spectra for the elongated regions of the RPE moldings after the tensile test (Fig. 16) were similar to those of the RPE moldings before the tensile test. The gauche-conformational PE chain peaks such as those corresponding to the twisting weak deformation (1302 cm^{-1}) were observed in the FT-IR spectra of the RPE moldings after the tensile test; however, they were absent in the FT-IR spectra of the RPE moldings before the tensile test [26, 27]. The effects of the conformational transformation of the PE chains on the tensile performance of the RPE moldings were determined by calculating the peak intensity ratios, I_{718}/I_{2920} and I_{1302}/I_{2920} , from the FT-IR spectra of the elongated RPE moldings. I_{718}/I_{2920} and I_{1302}/I_{2920} were defined as the abundance ratio of the trans-conformation and gauche-conformation PE chains, respectively, in the amorphous regions of the elongated RPE moldings.

Figure 17 shows the imaging FT-IR results of I_{718}/I_{2920} and I_{1302}/I_{2920} for each RPE molding. Figure 18 shows the average values of I_{718}/I_{2920} and I_{1302}/I_{2920} that were calculated from the imaging FT-IR results for each RPE molding. The 2D-distribution and average values of I_{718}/I_{2920} and I_{1302}/I_{2920} depended on the repelletizing conditions and the type of the RPE pellets (Figs. 17 and 18). The relationship between the ratios and the tensile performances will be discussed in the “Discussion” section.

AFM analysis of the etched RPE moldings.

The AFM phase images were obtained to analyze the higher-order structure of the RPE moldings. The original and repelletized RPE moldings were etched for 2 h in an etching liquid that selectively etched the amorphous regions [24], thereby facilitating the clear demarcation between the crystal and amorphous regions of the RPE moldings in the AFM phase images. The bright and dark regions in the AFM phase images of the etched RPE moldings (both the original and repelletized (200°C)) (Fig. 19) corresponded to the high and low phase-shift regions, respectively. Therefore, the bright and dark regions in the AFM images represented the crystal and amorphous domains, respectively [24].

The low-magnification AFM images (Fig. 19) showed that the size and degree of the distribution of the crystal domains of the repelletized RPE moldings were significantly different from those of the original RPE moldings. The large crystal domains (surrounded by red dotted lines) that were observed in the original RPE moldings disappeared in the repelletized RPE-HARD and RPE-SOFT moldings. However, the large crystal domains (surrounded by red dotted lines) were observed in both the original and repelletized RPE-MIX moldings. The results indicated that the effect of the repelletizing treatment on the degree of the distribution of the crystal domains depended on the type of the RPE pellets.

Fig. 14 Imaging FT-IR results of the I_{718}/I_{728} ratio for the **a** RPE-HARD, **b** RPE-SOFT, and **c** RPE-MIX moldings

Fig. 15 Average value of the I_{718}/I_{728} ratio calculated from the imaging measurement results for each RPE molding

Fig. 16 Representative FT-IR spectrum for elongated regions of RPE moldings after the tensile test

The high-magnification AFM images showed the presence of stripe-shaped lamellae in all the original RPE moldings. There were discernible differences in the lamellar

shapes of the RPE moldings before and after the repletizing treatment. The knobbly stripe-shaped lamellae were uniformly observed in the original RPE-HARD and

Fig. 17 Imaging FT-IR results of the I_{718}/I_{2920} of **a** RPE-HARD, **b** RPE-SOFT, and **c** RPE-MIX moldings and I_{1302}/I_{2920} ratios of **d** RPE-HARD, **e** RPE-SOFT, and **f** RPE-MIX moldings

Fig. 17 (continued)

Fig. 18 Average value of **a** the I_{718}/I_{2900} and **b** I_{1302}/I_{2900} ratios calculated from the imaging measurement results for each RPE molding

RPE-SOFT moldings, while the small stripe-shaped lamellae were uniformly observed in the original RPE-MIX moldings. However, all the repelletized RPE moldings exhibited knobbly round or elliptical lamellae. Therefore, the repelletizing treatment changed the shape of the lamellae in the RPE moldings.

Discussion

The repelletizing treatment affected the cross-sectional density of the RPE pellets. Figure 5 shows the specific conditions that resulted in the relatively low density of the RPE-SOFT and RPE-MIX pellets. Figure 20 shows the CCD images of the relatively high- and low-density

Fig. 19 AFM phase images of the etched RPE moldings (original-RPE and repelletized RPE for the repelletized condition of 200 °C)

RPE-SOFT pellet moldings. Figure 20 shows the presence and absence of surface defects in the relatively low-and high-density pellet moldings, respectively. The concentration of the tensile stress at the surface defects lowered the tensile performance of the relatively low-density pellet

moldings in comparison with that of the other repelletized moldings.

Here, the effects of the contamination, lamellar shape, polymeric higher-order structure, and secondary structure

Fig. 20 CCD images of **a** the relatively high- and **b** low-density pellet moldings for RPE-SOFT

on the tensile performance of the RPE moldings were discussed.

The SEM–EDS results indicated the presence of several contaminants in the RPE moldings (Figs. 9 and 10). The abundance ratio of the contaminants was determined from the area ratio of the white region in the binarized SEM images that represented the contaminants in the RPE moldings. Figure 21(a) shows the binarized SEM images of the RPE moldings, and Fig. 21b shows the relationship between the abundance ratio of the contaminants and the breaking elongation of the RPE moldings. There was no relationship between the abundance ratio of the contaminants and the breaking elongation of the RPE moldings (Fig. 21b). The EDS results indicated that the concentration of each contaminant in the RPE moldings was extremely low (Fig. 10). Therefore, the presence of the contaminants did not have a significant effect on the tensile performance of the RPE moldings in this study.

The imaging FT-IR results indicated the change in the amorphousness of the RPE moldings due to the repelletizing treatment (Fig. 15). The amorphousness of the RPE-HARD and RPE-SOFT moldings increased, regardless of the repelletizing conditions. The AFM images indicated the change in the lamellar shapes from stripe-like to elliptical in the RPE-HARD and RPE-SOFT moldings (Fig. 19); furthermore, the elliptical lamellae in the repelletized RPE moldings were separated by the amorphous regions. The original RPE moldings exhibited continuously bonded stripe-like lamellae. The repelletizing treatment also affected the aggregation state of the lamellae in the RPE moldings. The aggregated crystal domains that are surrounded by the red dotted lines in Fig. 19 disappeared after the repelletizing

treatment. Therefore, the repelletizing treatment increased the dispersion of the aggregated crystal domains, thereby increasing the tensile performances of the RPE-HARD and RPE-SOFT moldings.

The change in the lamellar shape of the RPE-MIX moldings due to the repelletizing treatment was similar to that of the RPE-HARD and RPE-SOFT moldings (Fig. 19). However, the tensile performance of the repelletized RPE-MIX molding was inferior to that of the original RPE moldings. The high-magnification AFM phase images of the original RPE-MIX molding showed the presence of two types of crystal domains, corresponding to LDPE and HDPE, that were mixed together. The crystal domains in the repelletized RPE-MIX molding were aggregated and significantly larger than those in the original RPE-MIX molding. The imaging-FT-IR results also showed the presence of two or three domains depending on the amorphousness of the repelletized RPE-MIX moldings (Fig. 15c). Normally, crystallization kinetics in polymer blends are very complex in relation to the different crystallization behavior of the two components since the crystallization kinetics were affected by several factors such as the production of primary nuclei, formation and spreading of surface nuclei, and inter-diffusion of crystallizable and non-crystallizable chains at the advancing front of the growing crystal [28–30]. The factors can be divided into two groups: (i) the properties of the minor phase polymer in the blend, including miscibility, glass transition temperature, ability to crystallize, the temperature range in which crystallization is possible and surface tension of the polymer melt [30]. (ii) The mixing processes [31]. The crystallization process of such polymer blends can be affected by the size of several inclusions, which can be controlled

Fig. 21 **a** Binarized SEM images and **b** the relationship between the abundance ratio of contaminants and the breaking elongation of the RPE moldings

by the parameters of the mixing process [31]. Therefore, in the case for RPE-MIX moldings, the crystallization kinetics changed by the repelletizing treatment, and the changes occurred negative effects on the mechanical properties of the

RPE-MIX moldings due to the formation of the aggregation of the crystal domains.

The presence of both the trans-conformational and gauche-conformational PE chains was observed in the amorphous regions of the elongated RPE moldings; however, the

Fig. 22 Relationship between the abundance ratio of the trans-PE-chains and gauche-PE-chains in the amorphous regions that were corresponded to the I_{718}/I_{2920} and I_{1302}/I_{2920} ratios

FT-IR peaks corresponding to the trans-conformational PE chains were only observed in the FT-IR spectra of the RPE moldings before the tensile test (Figs. 17 and 18). Therefore, the tensile stress contributed to the conformational

transformation of the PE chains in the amorphous regions. Figure 22 shows the relationship between the abundance ratios of the PE chains (both the trans- and gauche-conformational) in the amorphous regions and the tensile

performance of the RPE moldings. The abundance ratios of the trans-conformational and gauche-conformational PE chains corresponded to I_{718}/I_{2920} and I_{1302}/I_{2920} , respectively, that were calculated from the FT-IR spectra of the elongated regions of the RPE moldings. There was no relationship between the abundance ratio of the trans-conformational PE chains in the amorphous regions and the tensile performance of the RPE moldings (Fig. 22a). On the other hand, there was a strong correlation between the abundance ratio of the gauche-conformational PE chains in the amorphous regions and the tensile performance of the RPE moldings (Fig. 22b). This indicates that the gauche-conformational PE chain-richer molding after the tensile test exhibited better tensile performance. Therefore, the repelletizing treatment affected the number of PE chains in the amorphous regions that could undergo a conformational change due to the applied tensile stress. Such PE chains had a significant effect on the tensile performance of the RPE moldings. Moreover, AFM phase images of the elongated region of the original and repelletized RPE-HARD moldings are shown in Fig. 23. As can be seen in Fig. 23, the lamellar was partially broken down by the tensile stress for the original RPE-HARD molding, which showed lower tensile performance compared to the

repelletized one (Fig. 23a). On the other hand, the lamellar was completely unraveled by the tensile stress for the repelletized RPE-HARD, which exhibited much higher tensile performance compared to the other conditions (Fig. 23b). Therefore, repelletizing treatment changed the inner structure of the RPE moldings to the structure that can be easily unraveled. Based on the FT-IR and AFM analysis results, there are some large differences between the inner structure of the original and repelletized RPE moldings, and the difference plays important roles in the improvement of the tensile performance of the RPE moldings.

It was concluded that the repelletizing treatment had a significant effect on the dispersion of the agglomerated crystals, the change in the lamellar shape, and the secondary structures of the RPE moldings. These changes facilitated the transmission of the tensile stress in the RPE moldings, thereby increasing the tensile performance. The results confirmed the efficacy of the repelletizing treatment to increase the mechanical performances of the recycled-polymer products, thereby enabling the reuse of waste plastics as value-added materials for various industrial applications.

Fig. 23 AFM phase images of the elongated regions of **a** original RPE-HARD molding and **b** the repelletized RPE-HARD molding (the repelletizing screw-speed of 200 rpm)

Conclusion

In this study, we investigated the effects of the repelletizing treatment in a twin-screw extruder on the tensile performance and internal structure of the RPE moldings. The main conclusions are as follows:

1. The repelletized RPE-HARD and RPE-SOFT moldings, except those that were derived from low-density pellets, exhibited superior tensile performances in comparison with that of the original moldings. However, all the repelletized RPE-MIX moldings exhibited inferior tensile performances in comparison with that of the original moldings. Therefore, the effects of the repelletizing treatment on the tensile performances depended on the repelletizing parameters and the type of the RPE pellets.
2. From the FT-IR and AFM results, the repelletized RPE-HARD and RPE-SOFT moldings exhibited excellent tensile performances since the amorphousness and degree of dispersion of the aggregated crystal domains in the repelletized RPE-HARD and RPE-SOFT moldings were higher than those in the original moldings.
3. The repelletizing treatment affected the number of PE chains in the amorphous regions that could undergo a conformational change due to the applied tensile stress from the FT-IR results. Furthermore, these PE chains had a significant effect on the tensile performance of the RPE moldings. Hence, the repelletizing treatment plays important roles in the improving the mechanical properties of the moldings through optimizing the polymer structure of the pellets.

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