Advanced recycling process for waste plastics based on physical degradation theory and its stability

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Abstract
In this study, we evaluated the mechanical properties of pre-consumer recycled polypropylene thin films molded at more various temperatures, times and cooling conditions. We also evaluated the durability toward UV irradiation, and the effects of re-molding and annealing on the stability of these improved mechanical properties. The results of this study show that the mechanical properties of recycled polypropylene can be greatly improved to be almost the same as those of virgin polypropylene by choosing suitable molding condition. The mechanically improved samples also show enhanced durability towards UV. Annealing is also carried out to stabilize the mechanical properties that had been improved by quenching.

Keywords Pre-consumer recycled polypropylene (pre-RPP) · The heat treatment condition · The cooling conditions · Annealing process · The stabilization of mechanical properties

Introduction
In Japan, most waste plastics from households are currently collected and recycled by one of three methods: energy recovery (thermal recycling, chemical recycling, and material recycling) [1]. Energy recovery recovers thermal energy by combustion, and is relatively simple and effective. However, from an environmental perspective, energy recovery should be the last option. Chemical recycling requires considerable amounts of energy and very complex processes and, therefore, is not widely used. An ideal approach would be to repeat material recycling several times, and to use energy recovery only for materials that are difficult to reuse or when material recycling is impractical. However, as shown in Fig. 1, the proportion of material-recycled plastic has remained at about 30% for the past 13 years [2]. This is because the physical properties of products made from material-recycled plastics are inferior to those of products made from virgin plastics. Therefore, material-recycled plastics are only used in low-value-added products and have limited applications.

The poor physical properties of material-recycled plastics are believed to be due to the chemical degradation that results from the heat, ultraviolet light or oxidation in the recycling process. Such chemical degradation is thought to be irreversible because it is associated with the breaking of molecular chains [3–5].

However, our recent research indicated that the molecular properties of material-recycled plastics can be restored to the same levels as those seen in virgin plastics [6, 7]. This means that the main factor in the poor physical properties of material-recycled plastics is physical degradation. Physical degradation arises from changes in the crystal structures and internal structures of polymers, which are caused by deformation during fabrication of the material [7–21].

In the recycled plastic case, from our previous study, the physical degradation was caused by the number decrease of tie molecules. Moreover, our previous report showed that physical properties can be recovered through proper selection of the molding conditions [22–24].

In this study, we investigated the dependence of the mechanical properties of material-recycled plastics on higher temperature processing conditions. We found that...
materials that were melt-processed at a temperature higher than that used in the conventional molding condition, and subsequently quenched, had improved physical properties compared to virgin materials that were formed under standard molding conditions. We also investigated the stability of the enhanced mechanical properties and a method of stabilization.

**Experiment**

**Samples and molding conditions of test thin films**

Transparent, injection-molding-grade virgin isotactic polypropylene (VPP) and pre-consumer recycled polypropylene (Pre-RPP) were used in the experiments. Pre-RPP was made by pelletization of byproducts (such as runner and gate part) of injection-molded VPP, such as the runners generated during injection molding. Detailed molecular properties, including the molecular weight, molecular weight distribution, density, and the melt flow ratio (MFR), of these two materials were confirmed to be almost the same [22, 23, 25].

Thin films were made from pellets of VPP and Pre-RPP by a press molding machine (MH-10; IMOTO Machinery Co. Ltd.). For the formation of the thin films, the hot press temperatures are 210 °C, 230 °C, and 250 °C, hot press times are 2 min, 6 min, and 10 min. Figure 2 shows the process of film molding. Molded films were cooled at room temperature (Slow Cooled : SC) or in an ice-water bath (quench : Q).

To investigate the effect of annealing and re-molding of the mechanically improved films, we also used a press molding machine. Figure 3a shows how annealing was carried out. A thin film was placed between releasing films and then put it between stainless steel plates and annealed. In this study, annealing was performed at 65 °C for 2 h. Figure 3b shows the re-molding process. The thin film was divided into 4 square pieces and they were overlaid and press molded at 210 °C, 2 min, SC.
Measurement of tensile properties

The tensile test specimen was punched from thin films fabricated under various press mold conditions. The length of the specimen is $8 \pm 0.5$ mm and the width is $2 \pm 0.2$ mm according to JIS K 7113 2(1/3). The thickness of the thin films used in the tensile tests was about 60–100 µm. Five specimens were used for each tensile test. Tensile tests were carried out at 26.0 °C and 41.5% RH. The elongation rate was 5 mm/min. A screw-type uniaxial tester (LSC-02/30-2; Tokyo Testing Machine Company) was used for the evaluation. Toughness was evaluated from the area surrounded by the load–displacement curve by the initial cross-section of the specimen.

Crystallinity evaluation by DSC

To investigate the crystallinity of thin films, we used DSC measurement. The sample mass was approximately 4–6 mg. A DSC3100 from Mac Science was employed for the melting point measurements, and a heating rate of 5°C/min was used. The heat of fusion of the polypropylene crystal used in this study was 210.0 J/g.

Durability evaluation by UV irradiation

To investigate the UV stability of virgin film and the mechanical properties of improved films, we examined the UV durability. The UV durability machine was an EYE SUPER UV TESTER SUV-W161 (IWASAKI ELECTRIC CO., LTD) [6, 26]. The temperature near films in the machine was about 63–64 °C. The irradiation time was 2 h, 6 h, and 12 h. After the UV irradiation treatment, we measured the toughness of the irradiated films.

Results and discussion

Tensile properties

As described in our previous report, we evaluated the mechanical properties and internal structures of thin films of VPP and Pre-RPP that were molded at various temperatures, times, and cooling conditions [22–24]. In this investigation, the thin film specimens used for the evaluation of mechanical properties were molded at temperatures of 230 or 250 °C, mold times of 2 min, 6 min, or 10 min, and the quench condition. Table 1 summarizes the yield stress, Young’s modulus, fracture elongation, tensile fracture energy, and breaking stress. As shown in Table 1, there was not much difference in the yield stress or Young’s modulus between Pre-RPP thin films and VPP film molded at the standard condition (210 °C, 2 min, SC). The fracture elongation and tensile fracture energy were significantly different and greatly inferior to those of VPP. However, the tensile properties of quenched samples were significantly improved. Conversely, quenched Pre-RPP specimens molded at 210 °C showed ductility even with a mold time of 2 min. Moreover, Pre-RPP thin films under the quench condition showed high fracture elongation and tensile fracture energy under all mold temperatures and times. Young’s modulus is slightly low under the (210 °C, 2 min, quench) and (210 °C, 6 min, quench) conditions, however, in the other quenched conditions, the Young’s modulus is higher than the VPP (210 °C, 2 min, SC) condition. This indicates that molding at high temperature and quenching improves the tensile property to a level comparable to that of VPP.

Figure 4 shows the results of the tensile property tests for VPP and Pre-RPP thin films. The inside figure is the details of early stage of the tensile test. Difference in
Figure 4 shows the results for VPP molded at 210 °C, 2 min, SC. All samples are very ductile. Figure 4b shows the results for Pre-RPP molded at 210 °C, 2 min, SC. Most of the samples were brittle. Figure 4c shows the results for Pre-RPP molded at 230 °C, 10 min, quench. The samples showed high breaking stress and large elongation. Figure 4d shows the results for Pre-RPP molded at 250 °C, 10 min, quench. Very large elongation and good ductility were observed, as well as very high breaking stress.

Figure 5 shows photo image of the test pieces after the tensile strength test of Pre-RPP. The mechanical properties of Pre-RPP improved by changing hot pressing and cooling conditions.

Figure 6 shows a comparison of the tensile fracture energies of two cooling conditions (SC and quench), various compression temperatures (210 °C, 230 °C, 250 °C) and compression times (2 min, 6 min, 10 min). The bar graphs show the average value and the black error bars show standard deviation of tensile fracture energy. In the SC and 210 °C case, the tensile fracture energy increased with increasing the compression time. However, the average tensile fracture energies of all the Pre-RPP specimens in the SC condition were very low compared to the VPP value. On the other hand, the stress–strain curves of quenched Pre-RPP samples showed that the fracture energies were significantly higher than those of the VPP samples.

Table 1: Mechanical properties of the tensile test standard-condition VPP, standard-condition Pre-RPP, and quench-condition Pre-RPP

| Sample | Tensile fracture elongation (mm) | Tensile fracture energy (MJ/m²) | Tensile fracture stress (Pa) | Yield point (Pa) | Young’s modulus (Pa) |
|--------|---------------------------------|---------------------------------|-----------------------------|-----------------|---------------------|
| VPP 210 °C 2 min, SC | 114.9 ± 0.71 | 2.51 ± 0.034 | 3.0 ± 0.038 × 10⁷ | 2.4 ± 0.036 × 10⁷ | 3.0 ± 0.073 × 10⁸ |
| Pre-RPP 210 °C 2 min, SC | 11.1 ± 3.24 | 0.20 ± 0.059 | 7.9 ± 1.21 × 10⁶ | 2.5 ± 0.015 × 10⁷ | 4.4 ± 0.045 × 10⁷ |
| Pre-RPP 210 °C 2 min, Q | 65.6 ± 8.24 | 1.10 ± 0.15 | 2.0 ± 0.098 × 10⁷ | 1.8 ± 0.012 × 10⁷ | 1.9 ± 0.16 × 10⁸ |
| Pre-RPP 210 °C 6 min, Q | 78.6 ± 4.57 | 1.41 ± 0.10 | 2.2 ± 0.091 × 10⁷ | 2.1 ± 0.009 × 10⁷ | 2.4 ± 0.13 × 10⁸ |
| Pre-RPP 210 °C 10 min, Q | 47.7 ± 7.91 | 0.79 ± 0.14 | 1.4 ± 0.050 × 10⁷ | 1.9 ± 0.035 × 10⁷ | 3.0 ± 0.035 × 10⁸ |
| Pre-RPP 230 °C 2 min, Q | 43.2 ± 4.79 | 0.86 ± 0.15 | 2.0 ± 0.21 × 10⁷ | 3.2 ± 0.072 × 10⁷ | 3.7 ± 0.39 × 10⁸ |
| Pre-RPP 230 °C 6 min, Q | 68.3 ± 7.88 | 1.91 ± 0.23 | 3.0 ± 0.26 × 10⁷ | 3.2 ± 0.029 × 10⁷ | 3.7 ± 0.38 × 10⁸ |
| Pre-RPP 230 °C 10 min, Q | 50.9 ± 9.56 | 1.47 ± 0.29 | 2.4 ± 0.15 × 10⁷ | 3.3 ± 0.024 × 10⁷ | 3.8 ± 0.33 × 10⁸ |
| Pre-RPP 250 °C 2 min, Q | 55.1 ± 6.64 | 1.48 ± 0.19 | 2.6 ± 0.11 × 10⁷ | 3.1 ± 0.054 × 10⁷ | 3.5 ± 0.29 × 10⁸ |
| Pre-RPP 250 °C 6 min, Q | 36.8 ± 7.60 | 1.09 ± 0.23 | 2.2 ± 0.26 × 10⁷ | 3.6 ± 0.013 × 10⁷ | 3.6 ± 0.47 × 10⁸ |
| Pre-RPP 250 °C 10 min, Q | 70.3 ± 7.82 | 2.07 ± 0.24 | 3.2 ± 0.11 × 10⁷ | 3.4 ± 0.029 × 10⁷ | 3.4 ± 0.36 × 10⁸ |
In the Quench condition, the values of tensile fracture energy are significantly increased. Also, there are some slight tendencies that with increasing the compression time, the tensile fracture energy increases especially at 230 °C case and 250 °C case. In particular, specimens under 250 °C, 10 min, quench, showed almost the same fracture energy as VPP. This result indicates that, through the selection of suitable molding conditions (in this case, high temperature, long compression time, and Quench), Pre-RPP samples can show mechanical properties comparable to those of VPP.

Table 2 shows the crystallinity derived from the DSC measurement. The crystallinity of VPP and Pre-RPP (SC condition) samples was around 31%, on the other hand Pre-RPP quenched samples (210 °C, 2 min, Q), (210 °C, 6 min, Q), and (250 °C, 6 min, Q) were around 27%. However, the tensile properties of these samples did not coincide with these values. As an example, the crystallinity of Pre-RPP (210 °C, 2 min, SC) is same as the VPP, but the former Young’s modulus is much higher than the latter; on the other hand, the crystallinity of Pre-RPP (250 °C, 10 min, Q) is lower than the VPP, but the former Young’s modulus is higher than the latter. Especially, the tensile fracture energy does not depend on the crystallinity. These results also indicate that the difference of the tensile properties comes not only from the crystallinity but the difference of these inner structures.
Durability under UV irradiation

Figure 7 shows the UV irradiation time dependence of tensile fracture energy. The horizontal axis shows the duration of irradiation in hours and the vertical axis shows the elongation fracture energy. Figure 7a shows the results for VPP thin film molded at the standard molding condition (210 °C, 2 min, SC). The tensile fracture energy decreases gradually with an increase in the irradiation time. Figure 7b shows the results for Pre-RPP thin film molded at the same conditions. The tensile fracture energy at time 0 is very low compared to that of VPP thin film. On the other hand, the UV irradiation time dependence of tensile fracture energy in the improved films in Fig. 7c (210 °C, 2 min, Quench) and Fig. 7d (210 °C 6 min, Quench) is almost the same as that of VPP film. This result shows that by choosing a suitable molding condition the stability also increases.

Fig. 7 UV irradiation time dependence of elongation fracture energy. a VPP 210 °C 2 min SC, b Pre-RPP 210 °C 2 min SC, c Pre-RPP 210 °C 2 min Q, d Pre-RPP 210 °C 6 min Q

Fig. 8 Tensile fracture energies of various original films (molded by each temperature, time, and Q conditions) and after re-molding by (210 °C, 2 min SC) condition
The UV is believed to break the molecules between crystal lamella, [20] and the above results indicate that the number of tie molecules in a thin film of Pre-RPP molded at standard molding conditions is very low compared to that in VPP. However, the number of tie molecules in improved films of Pre-RPP is close to that in VPP. This result also indicates that the physical degradation and physical regeneration are much related with the number of tie molecules.

Effects of re-molding and annealing on stability

Figure 8 shows the transition of fracture elongation length between original and remolded results. The original values were obtained from thin films molded at various quench conditions. Re-molding was performed under the standard conditions (210 °C, 2 min, SC). As shown in this figure, the mechanical properties that had been improved under the quench conditions deteriorated after re-molding.

These results indicate that the excellent mechanical properties of materials prepared under the quench condition were lost after further heat treatment. Therefore, stabilizing the high performance is very important.

Annealing is a well-known method for stabilizing the inner structure of polymers [27–32]. Therefore, we evaluated the effects of annealing.

For the annealing investigation, we used a thin film molded at 210 °C, 6 min, quench. Thin films made under this condition show very high fracture elongation and tensile fracture energy.

In Table 3, we summarize the film-preparation conditions. Table 4 shows the tensile test results for all of the specimens. From the results, the original film was very ductile and fracture elongation was also large. The annealed film (C) was ductile and showed almost same value compared to the original film (A). However, the annealed film (D) became brittle. The annealed-remolded film (E) had the same mechanical properties as the original film (A) and the annealed film (C). This result indicates that annealing is effective for stabilizing improved mechanical properties. However, the annealed-remolded film (F) showed poor mechanical properties. From the

![Fig. 9](image-url)
sight of the tensile fracture energy, it was stabilized after performing annealing processing for 2 h (E). However, it was not stabilized after performing annealing processing for 8 h (F).

This result indicates that the annealing conditions must be optimized to stabilize the mechanical properties.

Figure 9 shows a comparison of Young’s modulus of the samples. Young’s modulus was slightly smaller for the original film (A). However, the values were improved by annealing and re-molding under standard conditions. This means that annealing improves Young’s modulus.

Figure 10 shows photo images of the samples after tensile tests. From this figure, the tensile property of original sample has very excellent elongation properties. And simple re-mold without any other processing degrades the mechanical properties; however, the application of suitable annealing treatment could stabilize the enhanced mechanical properties.

Summary

We evaluated the mechanical properties of thin films of pre-consumer recycled polypropylene that were molded at various temperatures, times and cooling conditions. From the results, by molding higher temperature, longer time and quenching improve the mechanical properties of the recycled polypropylene very much. Especially, quenching after high-temperature molding significantly improves the material properties.

These results indicate that the poor mechanical properties of recycled polymer are mainly due to reversible physical degradation, rather than to irreversible chemical degradation. Also, by choosing the suitable molding conditions, the mechanical properties of recycled polypropylene became almost the same as those of virgin polypropylene. The durability toward UV irradiation was also improved in the mechanically improved samples.

On the other hand, re-molding worsened the improved mechanical properties. This indicates that the inner structure obtained by quenching is not very stable toward heat treatment, i.e., the tie molecules between the lamellar layers formed by the selected molding condition are thermally unstable and significantly decrease during re-molding.

However, by annealing the samples for an appropriate time at a suitable temperature, we can stabilize the mechanical properties.

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