Application Brief

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Evaluation of Recycled Polymers by Thermal Analysis

1. Introduction

Efforts to recycle plastic products are becoming more and more active in many countries for the purpose of effective use of resources and prevention of environmental pollution. Recycling includes material recycling, in which crushed materials are melted and molded after removal of foreign substances, and chemical recycling, in which materials are chemically decomposed and repolymerized. There are concerns that these processes may cause impurities, changes in molecular weight, differences in crystal structure, etc., which may alter the properties of the virgin product[1]. Thermal properties such as glass transition temperature, melting temperature, crystallization temperature, and decomposition temperature may vary, and thermal analysis can be used to select materials suitable for final products and to study processing temperature conditions.

This report introduces an example of evaluating the differences in thermophysical properties of three types of PET molded products with different mixing ratios of recycled PET and virgin PET by the DSC and the Sample Observation TG measurements[2,3].

2. Measurements

Three types of commercially available PET molded products with recycled PET content of 0, 60, and 90 % were used as samples for the measurements.

DSC measurements were performed using the DSC7000X High-Sensitivity Differential Scanning Calorimeter for constant rate heating and cooling measurements and isothermal crystallization measurements. In the constant rate heating and cooling measurement, the first heating, cooling, and second heating were scanned repeatedly at 10 °C/min in the temperature range of 25 to 280 °C. In the isothermal crystallization measurement, the crystallization was measured by quenching the specimen from 280 °C to 220 °C and then holding it for 60 min.

TG measurement was performed using the STA200RV Simultaneous Thermogravimetric Analyzer equipped with the RVST0010 Sample Observation System Option. Measurements were performed over a temperature range of 25 to 600 °C at 20 °C/min under dry air atmosphere. In addition to measuring the mass change, an attempt is made to quantitatively analyze the color change by performing $L^*a^*b^*$ color space analysis[4,5] of the sample observation images from after melting to the initial decomposition process.

3. Measurement Results

3-1. Constant rate heating and cooling measurements

Figure 1 shows the results of constant rate heating measurement by DSC. In order to compare the effect of recycled PET content on thermal properties, the thermal history of each sample was reset by the first heating, and the results of the second heating after cooling are shown here. For each sample, an endothermic shift due to glass transition is observed around 80 °C, and an endothermic peak due to melting is observed around 250 °C. The start and end temperatures of the glass transition are shown in Figure 1. The glass transition temperature (T_{ig}) is the highest for the recycled PET content of 0 %. And T_{ig} lowered with an increase in the content of the recycled PET.

Also, the temperature range of the transition region from the start temperature to the end temperature of the glass transition was 11.4 °C for 0 %, 12.8 °C for 60 %, and 13.7 °C for 90 %. T_{ig} tends to become higher with increasing molecular weight and to become wider with increasing molecular weight distribution. In this measurement, it is assumed that the molecular weight and T_{ig} shifted lower with increasing the content of the recycled PET and the broadening of the molecular weight distribution is described to an expanded temperature range of transition region.

Similarly, there are differences in the melting peaks, which may be due to the effect of molecular weight and molecular weight distribution. The melting temperature decreases with increasing recycled PET content, and the width of the peaks becomes wider, and there is a tendency for double peaks. Figure 2 shows the integral curves of these melting peaks. For the samples with 60 % and 90 % recycled PET content, melting starts around 200 °C. It is suggested that this is due to the melting of components that were changed to low molecular weight in the process of recycling.

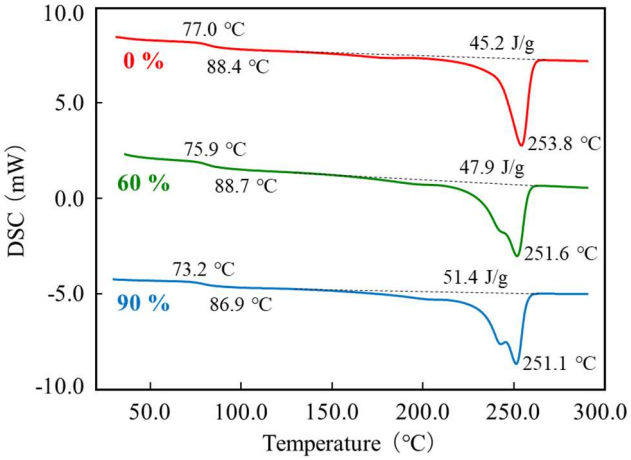

Figure 1 DSC curves of PET after 10 °C/min cooling

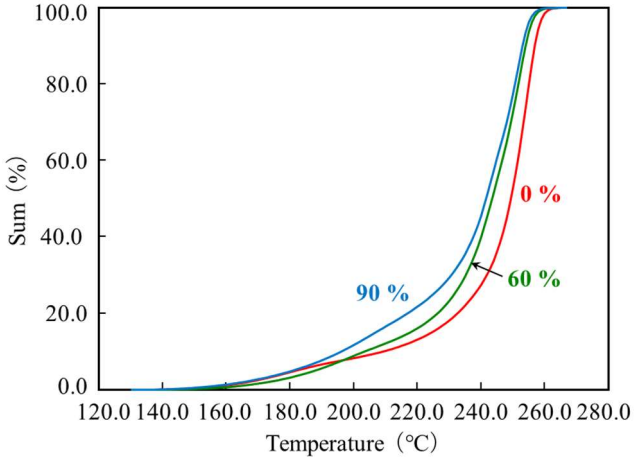

Figure 2 Integral curves of melting peak for PET

By analyzing the heat of melting, ΔH_m, the degree of crystallinity of the samples can be compared. From result of Figure 1, it is found that the heat of melting decreases with decreasing content of recycled PET. This phenomenon means that more amount of crystallized components formed during the 10 °C/min cooling after the 1st heating. Crystallization tends to progress easily the components that form the nucleus of the crystal are included. Impurities mixed in the recycling process may remain in the recycled materials. It is thought that the higher the recycled material contains, the higher the heat of melting of the crystals as the impurities act a nucleus to promote crystallization.

3-2. Isothermal crystallization measurements

The temperature and time required for crystallization is an important factor when considering the processing conditions for molding into products. Figure 3 shows a comparison of the crystallization peaks when the molten sample was cooled at 10 °C/min. It can be seen that the higher the recycled PET content in the sample, the higher the temperature at which crystallization begins. It is thought that the impurities in the mixture become the nucleus of the crystal, thereby accelerating crystallization. Figure 4 shows the results of isothermal crystallization measurement based on this result. The horizontal axis is time, and the time when the temperature reaches 220 °C after cooling from 280 °C is defined as 0 min. An exothermic peak due to crystallization was observed immediately after the start of the isotherm at 220 °C. The elapsed time to the top of the peak was 3.53 min for 90 % recycled PET, 8.54 min for 60 % and 17.10 min for 0 %. It can be seen that the higher the recycled PET content, the shorter the time required for crystallization. It is generally thought that when comparing crystallization at a constant temperature, the higher the melting temperature is, the shorter the crystallization time is. However, the measurement results in Figure 4 show that the crystallization of the recycled PET content of 0 %, which has the highest melting temperature, takes the longest time. This is thought to be due to the fact that a small amount of impurities mixed in during the recycling process became the nucleus for crystal formation, which accelerated the crystallization of samples containing recycled PET.

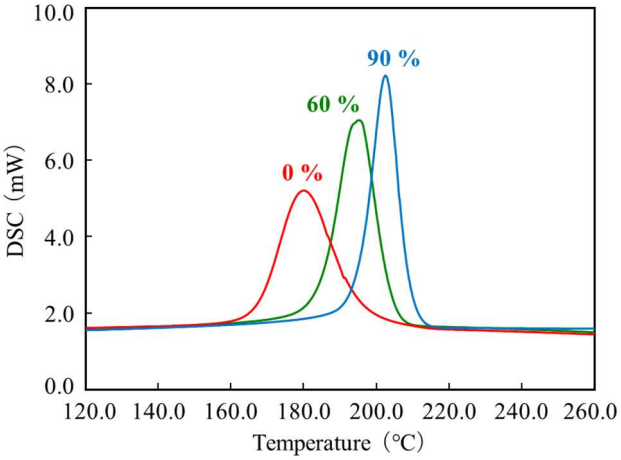

Figure 3 DSC curves of crystallization by constant rate cooling
Cooling rate : 10 °C/min

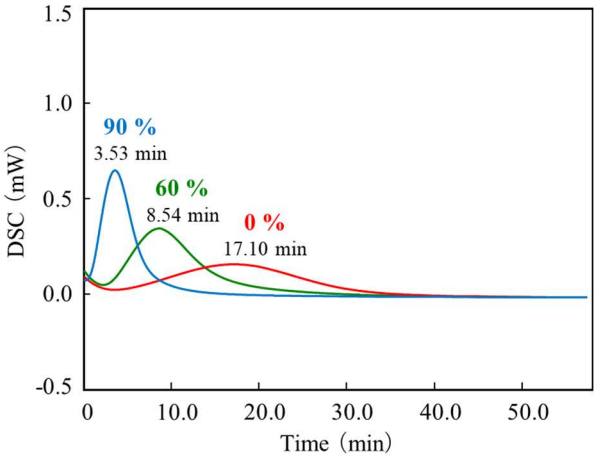

Figure 4 DSC curves of crystallization by isothermal measurement
Isothermal temperature : 220 °C

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3-3. Sample observation TG measurements

The heat resistance of plastic materials can be evaluated from the starting temperature of mass change by thermogravimetry (TG). In addition, changes in the shape and color of the sample can be simultaneously observed by sample observation thermal analysis. Figure 5 shows the results of TG measurement of the samples. In the TG curve, mass loss due to oxidative decomposition of PET is observed from around 300 °C for all samples. For the samples with 60 and 90 % recycled PET content, the mass loss started slowly around 250 °C, showing that the decomposition started at a lower temperature than 0 %. In the sample observation images at 280 °C, when the melting was completely finished, the 60 and 90 % recycled PET content showed a discoloration from transparent to brown, which is considered to be caused by decomposition, compared to the images at 220 and 250 °C. In order to quantitatively evaluate this color change, $L^*a^*b^*$ color space analysis[4,5] was performed on the observed image and the b^* values are shown in Figure 5. As the shape of the sample changed, the b^* value also changed at 250 to 270 °C for 0 % recycled PET content and around 240 °C for 90 %. For subsequent changes, the b* value increases from 271.0 °C for 90 %, 273.5 °C for 60 %, and 308.1 °C for 0 %. This is thought to be due to the fact that the higher the recycled PET content, the lower the molecular weight of the components, and the lower the temperature from which they start decomposing.

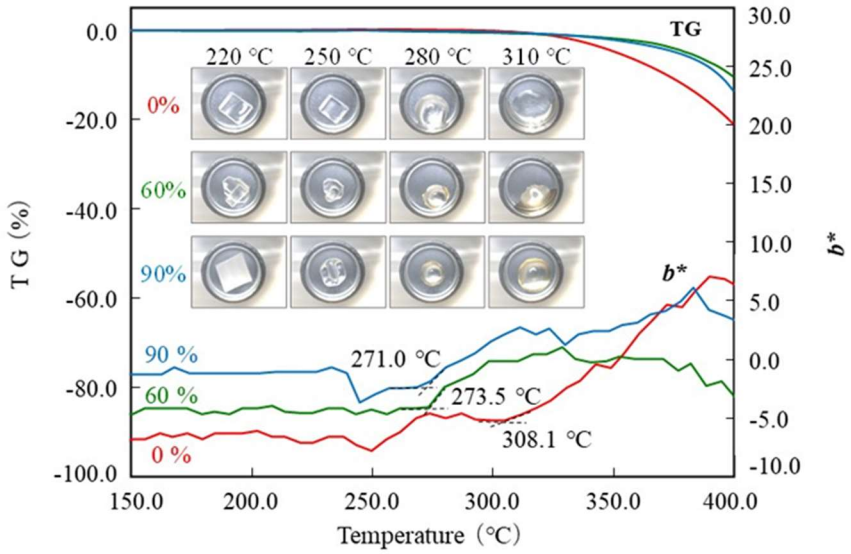

Figure 5 TG and b^* curves of PET by Sample observation measurements
Heating rate : 10 °C/min

4. Conclusion

This report compared the differences in thermal properties of three types of PET molded products with different recycled material content which are analyzed using DSC and sample observation TG measurements. As the recycled material content increased, it was observed that the glass transition temperature and melting temperature decreased, crystallization was accelerated, and oxidative decomposition and discoloration temperatures decreased. These results suggest that differences in thermal properties are affected by decreases in molecular weight, changes in molecular weight distribution, and contamination and residual impurities from recycling.

The recycling of plastics is being actively pursued worldwide, but the properties of polymer materials may change due to recycling. Thermal analysis is an effective analysis method to examine molding process conditions and to evaluate heat resistance and thermal stability required for products.

Reference

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