Effect of Polymerization and Preheating Processes on Poly(ethylene terephthalate) Depolymerization

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ABSTRACT: The depolymerization reaction of poly(ethylene terephthalate) (PET) was analyzed on the basis of experimental and numerical data obtained from molecular orbital calculations. Various types of PETs polymerized by different methods and preheated by microwave irradiation were used to investigate the depolymerization mechanism. The activation energies obtained from the optimized structures of the ground state and the transition state were compared with the experimental data. On the basis of these comparisons, it was found that not only the crystallinity but also configuration changes caused by preheating were essential for realizing a high rate of transesterification reactions, such as depolymerization. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1161–1165, 2012

Key words: activation energy; degradation; simulations

INTRODUCTION

Plastic waste is a global problem that must be addressed, both for the sake of reducing environmental pollution and for conserving increasingly scarce natural resources because plastic is made from limited resources, such as petroleum. Poly(ethylene terephthalate) (PET) is a versatile plastic material that is used extensively in the manufacture of high-strength fibers, photographic film, and bottles for soft drinks. PET recycling has gained public attention as a means of conserving natural resources and protecting the global environment. Recently, feedstock recycling (chemical recycling) has become an attractive process because PET can be chemically decomposed into its original feedstock monomers.[1–3] The most commonly studied chemical recycling method is the reaction between PET and monoalcohols, diols, or other solvents under basic conditions.[4–6] The depolymerization reaction is shown in Figure 1 with ethylene glycol (EG) as one of the products of the glycolysis reaction. However, a rapid reaction rate is necessary for the industrialization of this recycling process. In our previous study, the rate of PET depolymerization rate was improved by microwave irradiation (MW) in the presence of water[7] because water has a high dielectric constant and is, thus, microwave active. Although the importance of the solvent is clear in the mechanism of microwave-mediated reactions, the effects of MW on the PET properties and the depolymerization process need to be clarified. The change in the PET properties by MW was predicted to be one factor leading to rapid reaction rates. First, PET was heated by MW to alter its properties before the depolymerization reaction, and the reaction rate of the preheated PET was measured. Second, various types of PETs synthesized by different polymerization methods were decomposed by EG with sodium hydroxide under atmospheric pressure. Moreover, the mechanism of PET depolymerization with different physical properties was considered from kinetic data obtained from experiments and simulation.

EXPERIMENTAL

Material

Three types of virgin PET flakes ($5 \times 5 \times 1$ mm^3, Teijin, Ltd., Japan), as listed in Table I, were used to check the reactivity for different crystallinities. Samples PET(A) and PET(B) were polymerized by solid-state polymerization. On the other hand, sample PET(C) was synthesized by melt polymerization. Accordingly, each PET showed different (IV) Intrinsic Viscosity values and crystallinities. Figure 2 shows the X-ray diffraction (XRD) pattern of each PET. The crystallinity of PET(C) was lower and showed an amorphous phase because of its preparation by a different polymerization method. As a pretreatment for the second experiment, PET(B) was heated in EG solution at 180°C for 2 h before the depolymerization reaction. Conventional heating (CH; on a hot plate) and MW were used. In this case, no

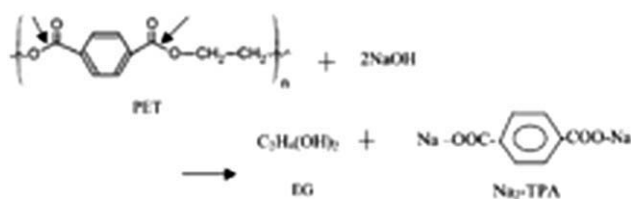*Correspondence to:* Y. Asakuma (asakuma@eng.u-hyogo.ac.jp).

Figure 1 Depolymerization reaction of PET.

notable differences between the pretreated and untreated PETs were observed in the SEM images.

Procedure

Untreated or preheated PET flakes (3 g), NaOH (1 g), and EG (50 mL) were inserted into a flask under atmospheric pressure. The mixture was heated to 140–180°C while being stirred. After the specified reaction time (10–120 min), 50 mL of distilled water at room temperature was poured into the mixture to stop the reaction, and the unreacted PET was filtered.[4] Furthermore, a small amount of HCl (5 mL) was added to the filtrate, and the terephthalic acid (TPA) was precipitated. At the same time, the pH of the solution was confirmed to be neutral. The reaction rate at each operating condition (reaction time and temperature) was calculated from the amount of unreacted PET after the first filtration and the precipitated amount of TPA after the second filtration. The reaction rates determined with both methods were confirmed to be the same. The activation energy of the depolymerization reaction for each PET was calculated by the preparation of Arrhenius plots of the kinetic constant (k) obtained from the decomposition amounts. In this experiment, the surface area of a flat pellet before and after the reaction was assumed to be same for a certain period, and the following equation was obtained:[4]

$$\ln\{C_0/(C_0 - [COONa])\} = kt \qquad (1)$$

where C_0, [COONa], and t are the initial concentration of NaOH, the half-concentration of disodium terephthalate in Figure 1, and the time, respectively. The kinetic expression of eq. (1) showed a linear relation for every experimental condition, and the

kinetic model used in this research was applicable in PET depolymerization.

CALCULATION

The depolymerization reaction of PET is a type of transesterification reaction triggered by the addition of alcohol under basic conditions. Transesterification is the process of substituting the alkoxyl group of an ester compound with that of an alcohol. The single bond between the carbon atom and the oxygen atom of a carboxyl group, as shown by the arrows of Figure 1, is decomposed by the attachment of an alkoxide. Therefore, the ester linkage in PET is cleaved by the alkoxide, and PET is gradually decomposed into smaller components. Finally, disodium terephthalate and EG are produced. When the carbonyl carbon atom is attacked by the alkoxide, this reaction should proceed through a tetrahedral intermediate as the transition state.[8] We studied the characteristics of transesterification considering the activation energy.

It was first necessary to calculate the optimized structure of the ground and transition states with respect to the transesterification of PET because each state has a different energy. In this study, the quantum data for each state was derived with the Gaussian software package (Gaussian R 03W, version 6, Gaussian, Inc., Pennsylvania). The molecular structures of the ground state (PET, alkoxide, and TPA ester) and the transition state of the depolymerization reaction were simulated. In addition, the activation energy of the depolymerization reaction was calculated from structures optimized in a minimum-energy configuration from appropriate initial coordination of the atoms.[8,9] HF/6-31G(d) was used as basis set and method of this calculation.

In this study, microwaves were introduced to alter the properties of PET. One characteristic of MW is molecular polarization because the frequency of microwaves is very high (2.45 GHz). For example, PET consists of an ester bonded with highly electronegative oxygen atoms, and each C—O and C=O bond of the ester bond is easily rotated around the carboxyl carbon at high frequency. Accordingly, electric charge is intermolecularly distributed as much as possible. In this study, two types of PET

TABLE I
Properties of the PET Samples

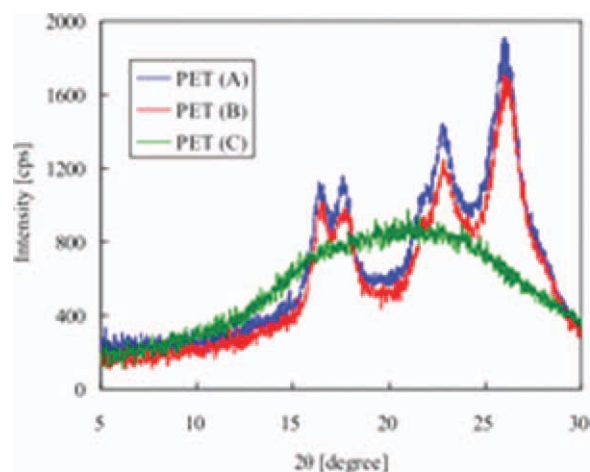| Sample	IV	Crystallinity	Molecular weight (polymerization degree)	Polymerization method
PET(A)	0.86	High	30,000 (155)	Solid-state polymerization
PET(B)	0.76	High	26,000 (135)	Solid-state polymerization
PET(C)	0.52	Low	16,000 (80)	Melt polymerization

Figure 2 XRD pattern of various crystallinities of PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structural model, as shown in Figure 3, were proposed to determine the effect of preheating by MW on the reaction. One structural model was PET formed by straight chains, as shown in Figure 3(a), which is a reasonably periodic structure. It was predicted that this structure was formed through ester bond rotation caused by MW. The other structural model was a curved chain, as shown in Figure 3(b), in which the ester bond around carboxyl carbon was twisted.

RESULTS AND DISCUSSION

Figure 4 shows an example of the decomposition ratio of PET(B), and k was calculated by eq. (1). The Arrhenius plot was obtained from k for each temperature, as shown in Figure 5. k of PET(C) was much higher than those of PET(A) and PET(B). Accordingly, a higher activation energy and higher frequency factor were shown for the reactivity of PET(C), as listed in Table II. This was caused by the
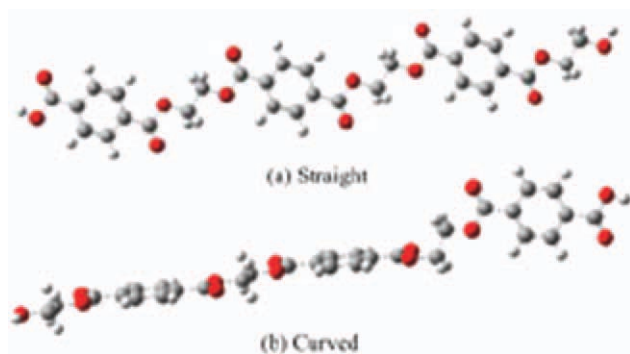

Figure 3 Molecular model of PET for different crystallinities: (a) straight and (b) curved. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
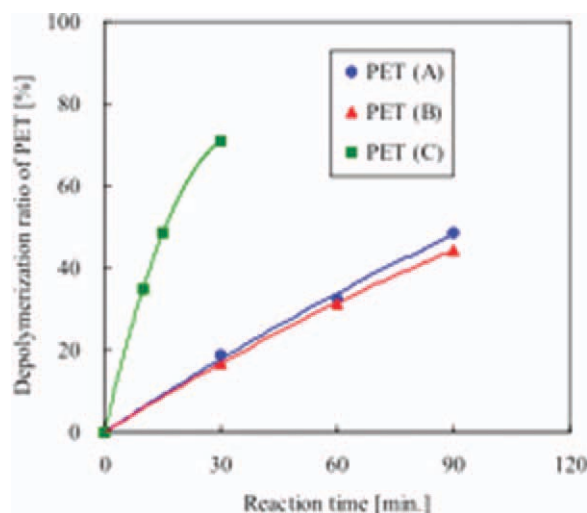

Figure 4 Depolymerization ratio for various crystallinities of PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lower crystallinity and amorphous structure of PET(C), as shown in Figure 2. In the case of PET(C), a higher frequency factor was obtained because the curved structure of the PET, as in Figure 3(b), had a wider space around the ester bond.

The higher activation energy of lower crystallinity, as in PET(C), might have been related to the torsion angle of the PET periodic structure, as modeled in Figure 3(b); the reason is discussed in the next section. On the other hand, the reactivities of PET(A) and PET(B) were similar, and the molecular weight and polymerization degree values did not markedly affect the depolymerization rate. The independence of the reactivity from the degree of PET
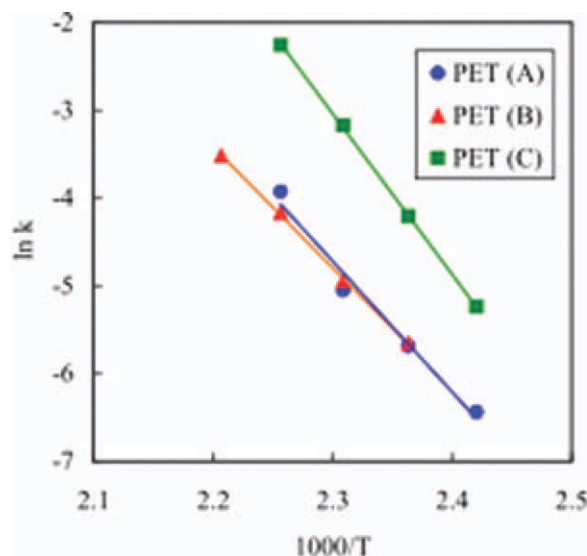

Figure 5 Arrhenius plot of the depolymerization reaction for various crystallinities of PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Activation Energy (E) and Frequency Factor (A) for the PET Samples

Sample	A	E (kJ/mol)
PET(A)	1.8×10^{10}	103.2
PET(B)	4.8×10^{11}	114.6
PET(C)	9.1×10^{16}	152.2

TABLE III
Activation Energy (E) and Frequency Factor (A) for the Preheated PET

Sample	A	E (kJ/mol)
PET(B) heated by hot plate	1.43×10^{7}	70.2
PET(B) heated by MW	4.30×10^{8}	79.6

polymerization was proven by the molecular orbital method in our previous study.[9]

Figure 6 shows the Arrhenius plot of preheated PET(B), and the effect of preheating, by MW and CH by hot plate, on the depolymerization is clearly visible. Preheating by MW or a hot plate enhanced the reactivity. In particular, k for preheating by MW exhibited the highest value, as shown in Figure 6; a lower activation energy and lower frequency factor were obtained in comparison with untreated PET(B), as listed in Tables II and III. To check the reason for the difference between the preheated and untreated PET(B), the XRD pattern was measured for each preheated PET(B), as shown in Figure 7. However, a notable difference between the preheated and untreated PET(B) was not observed, and thus, the increase in reactivity could not be attributed to changes in the crystallinity. The calculation in the next study will help to explain the effect of preheating on depolymerization.

Figure 8 shows the theoretical activation energy of PET with straight and curved ester chains. The activation energy of straight PET was lower than that of curved PET. The polarization of the oxygen atoms in the ester bond at the molecular level was caused by MW because oxygen atoms with high electronegativity rotated frequently around the ester bond.
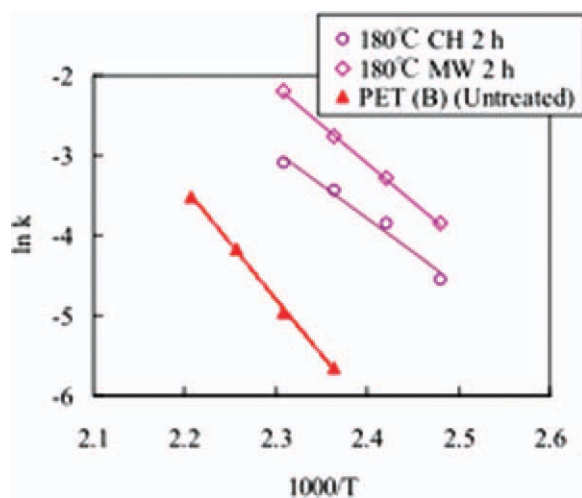
Although a notable change in crystallinity was not observed in the case of MW, polarization caused the minimization of the torsion angle around the ester bond and the distribution of electric charge across the entire molecule. Accordingly, no difference due to the effects of preheating was observed in the XRD patterns shown in Figure 7. Minor changes, such as the rotational isomerism of the PET periodic structure caused by MW, might have been the reason for the higher reactivity. k of PET(B) preheated by microwave for 2 h exhibited the highest values, as shown in Figure 6. Moreover, a lower frequency factor was obtained, as listed in Table III, because space for the attachment of an alkoxide on the carboxyl carbon became narrower than for untreated PET because of the change in configuration from mesh (curved) to layered (straight). On the other hand, the rotation of the ester bond introduced by CH was not stronger than that for MW. In the case of CH, heat transfer occurred via conduction of molecular vibration, and MW caused the direct vibration of molecules with higher electronegativity.

CONCLUSIONS

Various types of PET were used under basic conditions in an attempt to investigate the effect of preheating on depolymerization and to compare the
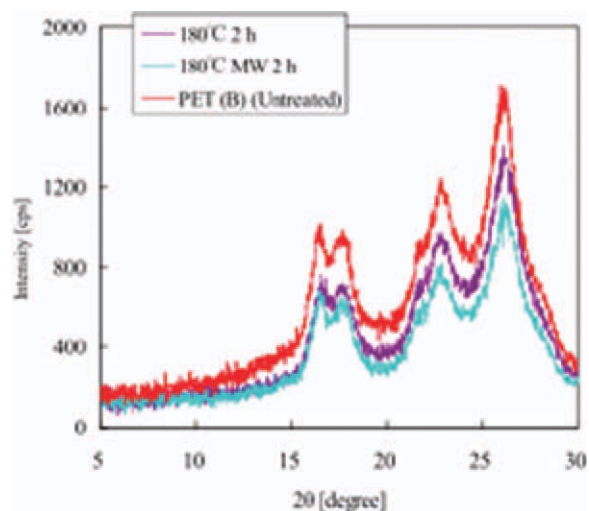

Figure 6 Arrhenius plot of the depolymerization reaction for different preheating processes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 XRD pattern of PET obtained different preheating processes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
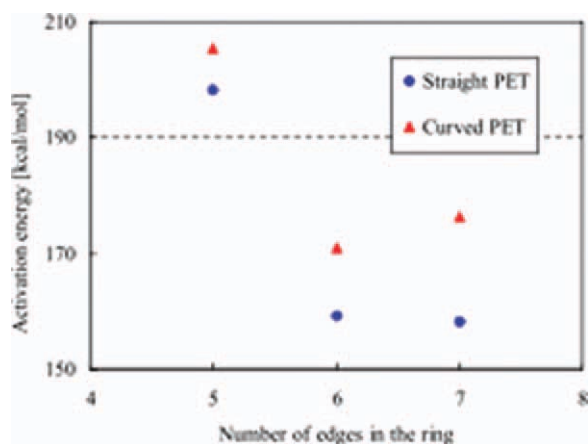
Figure 8 Activation energy for PET obtained from the molecular orbital method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activation energy obtained from both experiment and simulation. First, the crystallinity of PET was essential for the decomposition reaction, and the rate was strongly dependent on the polymerization method. Second, two types of PETs preheated by MW and CH were depolymerized. Although it was confirmed that the crystallinity of the preheated and untreated PET was maintained from the XRD pattern, the effect on the depolymerization rate of the pretreatment was much stronger. Moreover, heating by MW had a greater effect than CH on the depolymerization process because of configuration changes. Finally, the mechanistic basis of the reaction rate improvement due to crystallinity and the preheating method was clarified with straight- and curved-chain models of the PET structure on the basis of the relationship between polarization and the torsion of the ester bond.

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