Investigation of Alkaline Hydrolysis of Polyethylene Terephthalate by Differential Scanning Calorimetry and Thermogravimetric Analysis

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ABSTRACT: The hydrolytic depolymerization of polyethylene terephthalate (PET) with alkaline hydroxides was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The reactions of the mixtures were conducted in their solid states under nitrogen atmosphere. The experimental results showed that potassium hydroxide possessed the hydrolytic activity of depolymerizing PET into small molecules such as ethylene glycol; in contrast, sodium hydroxide did not. The production rate of ethylene glycol was enhanced by increasing charge ratio of potassium hydroxide to PET. The presence of water facilitated the alkaline hydrolysis of PET; however, the presence of metal acetates decreased the hydrolysis rate. The activation energy for alkaline hydrolysis of PET determined by the thermograms was in good agreement with the value obtained from the experiments in a batch reactor. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1939–1945, 1998

Key words: alkaline hydrolysis; polyethylene terephthalate (PET); differential scanning calorimetry (DSC); thermogravimetric analysis (TGA); depolymerization

INTRODUCTION

It has become important to reclaim polyethylene terephthalate (PET) waste, which is extensively recycled from bottles, films, and fibers.^{1,2} There are several ways to process the PET waste,³ depending on the end use of the reclaimed products. The process of hydrolytic depolymerization with water has been proposed to recover terephthalic acid and ethylene glycol from the PET waste.⁴⁻⁷ The recovered products can be used as feedstocks for the synthesis of virgin PET. However, the hydrolysis of PET with water was operated under high temperature and pressure. Sulfuric acid was used as a catalyst to moderate the reaction conditions,^{8,9} but this process also induced other problems, such as corrosion of equipments and difficult separation of liquid products from the acid waste. In contrast to the disadvantages of using strong acids, alkaline hydroxides can be used as catalysts and reaction mediums for the hydrolytic depolymerization of PET.¹⁰⁻¹² In the process of alkaline hydrolysis, PET was depolymerized to produce ethylene glycol and terephthalic salts, instead of terephthalic acid at mild temperatures and pressures. Terephthalic salts can then be hydrolyzed easily to form terephthalic acid. The alkaline hydrolysis of PET was usually carried out using an aqueous solution of sodium or potassium hydroxide. However, the activity of

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alkaline hydrolysis of PET in the solid state was seldom studied. Benzaria et al. described an interesting process, in which the depolymerization was carried out in a mixer-extruder with the use of solid sodium hydroxide at temperatures of 100–200°C.¹³ After the distillation of ethylene glycol from the postreaction mixture under reduced pressure, a corresponding salt of terephthalic acid in the form of a powder was obtained.

In this study, the hydrolytic depolymerization of PET with alkaline hydroxides in solid state was conducted in thermal analysis systems. Although thermal analysis had been found to be a convenient tool to characterize the thermal degradation of polymeric materials, the technique has been rarely applied to investigate the polymerization or depolymerization of PET. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the polycondensation of bis-hydroxyethyl terephthalate to produce PET.^{14,15} In our previous work, the DSC module equipped with a pressurized cell was employed for investigating the glycolysis of PET in the presence of various metal acetate catalysts.¹⁶ In this article, DSC and TGA were used to investigate the alkaline hydrolysis of PET with metal hydroxides in the solid state. The depolymerization reactivity, characteristics, and the kinetic characterization are presented.

EXPERIMENTAL

The PET sample with a particle size of 45/70 mesh used in the thermal analysis was prepared by grinding chips of fiber grade, which were supplied by Nan Ya Plastic Co., Taiwan. The intrinsic viscosity (IV) of PET was measured in a 6:4 (w/w) phenol/1,1,2,2- tetrachloroethane solution at 30°C. The IV value of 0.60 dL/g corresponding to the average molecular weight (M) of 17,000 was calculated from the equation of $M = 3.61 \times 10^4$ IV ^{1.46.17} The melting of this PET material yielded an endotherm about 40 J/g over the temperature range of 245 to 260°C, as determined by DSC at a scanning rate of 10°C/min.

The mixture of PET and alkaline hydroxide was prepared by impregnation to increase the contacting surface area. Alkaline hydroxide was dissolved in water, and the solution was mixed with the PET powder. The mixed sample was obtained after drying at 60°C. Alkaline hydroxides can adsorb water when they are exposed to humid environment. To avoid the hydration, samples were normally stored in an oven. These samples will also be refered to as dried samples in this article. Samples that were not stored in the oven and were subject to hydration will be called hydrated samples. The molar ratio of alkaline hydroxide to PET repeating unit in the mixed sample was 1, 2, 3, or 4. The preparation of mixed sample containing metal acetates followed the same procedures except that a metal acetate was preliminarily mixed with PET powder by impregnation. The metal loading of each sample was controlled at the level of 0.10 mmol per gram of PET.

In a normal DSC measurement, the sample was usually held in a hermetically sealed pan. In the alkaline hydrolysis of PET, liquid will be produced and evaporated. The endothermic peak temperature of liquid evaporation would not be easily predicted and controlled because of using a hermetrically sealed sample pan, which would cause the delay of evaporation under the sealed pressure. Therefore, a sample pan with a small opening was used for DSC analysis in this study. DSC thermogram was measured using a differential scanning calorimeter (Du Pont 910) that was connected to a thermal analyzer (TA 2200) under a flow of nitrogen. A sample of 2.5 mg was placed in an aluminum pan that was pierced with a hole of 1 mm in diameter in the center of upper lid. Another empty pan was used as the reference during measurements. TGA analysis was carried out using a thermogravimetric analyzer (TA 2950) under a flow of nitrogen. A sample of 15 mg was placed in a platinum plate hanging from the balance arm.

RESULTS AND DISCUSSION

DSC Thermograms of PET with Alkaline Hydroxides

Figure 1 shows the DSC thermograms for the hydrated sample of PET with sodium hydroxide or potassium hydroxide. There was an endothermic band around 250°C during each first scanning. In addition, there appeared endothermic peaks around 100°C for the PET/sodium hydroxide sample, and endothermic peaks at 125 and 165°C for the PET/potassium hydroxide sample. After the first scanning, the samples were quickly quenched by liquid nitrogen to room temperature



Figure 1. DSC thermograms for the mixture of PET with sodium or potassium hydroxide (n/n = 1:2). (a) NaOH, first scanning; (b) KOH, first scanning; (c) NaOH, second scanning; (d) KOH, second scanning.

and then heated again. In each case, only one weak endothermic band around 250°C was found during the second heating and scanning. The range of the band was the same as the melting temperatures of PET. Therefore, the band could correspond to the melting endotherm of the unreacted PET. The endothermic bands below 200°C disappeared at the second scanning.

The DSC thermograms for alkaline hydroxides or the mixture of water and ethylene glycol were examined as shown in Figure 2. It was found that the scanning for sodium hydroxide and potassium hydroxide showed endothermic bands around 100 and 120°C, respectively, which may represent the evaporation of water from the hydrated alkaline hydroxides. The DSC thermogram for the mixture



Figure 2. DSC scanning for (a) mixture of water and ethylene glycol (w/w = 1:1); (b) sodium hydroxide; (c) potassium hydroxide.



Figure 3. TGA thermograms for the mixture of PET with (a) sodium hydroxide, or (b) potassium hydroxide (n/n = 1:2).

of water and ethylene glycol showed the evaporating peaks at around 85 and 165-170°C. The evaporating temperatures of water and ethylene glycol were lower than their normal boiling points of 100 and 198°C because of the carrying effect of high rate of nitrogen flow. By comparing with the positions of identified peaks in Figure 2, the ther mograms in Figure1 showed that the low temperature bands at about 100 and 125°C corresponded to the evaporation of water from the hydrated sodium hydroxide and potassium hydroxides, and the band at 165°C corresponded to the evaporation of ethytene glycol. It can be seen that potassium hydroxide reacted with PET to produce ethvlene glycol, but sodium hydroxide did not. In a separate study on the reaction of PET and potassium hydroxide in a batch reactor, ethylene glycol was also indentified as the liquid product by GC analysis.¹⁸ Figure 1 also showed that little further production of ethylene glycol occurred during the second scanning. However, the melting endotherms of unreacted PET became weak and shifted to low temperature range during the second scanning. It may be because the original crystallinity of PET was lowered by mixing with alkaline hydroxides or hydrolyzed products such as TPA salts after the first scanning, or PET was partially depolymerized so that its molecular weight was decreased.

TGA Curves of PET with Alkaline Hydroxides

The thermogravimetric curves of hydrated samples are illustrated in Figure 3. The weight loss of PET with sodium hydroxide occurred below



Figure 4. Water effect on the DSC scanning for the mixture of PET and potassium hydroxide (n/n = 1:2). (a) hydrated sample; (b) dried sample.

100°C and was corresponded to the evaporation of water. In addition to the evaporation of water, the weight loss caused by the evaporation of ethylene glycol was also observed in the range of 140 to 170°C for the sample of PET with potassium hydroxide. The weight loss in the thermogravimetric curves was consistent with the endotherms in the DSC thermograms.

Sodium hydroxide in aqueous solutions was found to have high hydrolytic activity of depolymerizing PET at the temperatures below 150°C.¹⁰ In this study of thermal analysis, sodium hydroxide in its solid state, however, showed no activity during heating to 300°C. It indicates that solid sodium hydroxide cannot be dissociated into hydroxyl ions to catalyze the hydrolysis of PET. On the contrary, potassium hydroxide showed much stronger activity in a solid state than sodium hydroxide. This may be because of their different alkalinity.

Hydration Effect on Alkaline Hydrolysis of PET with Potassium Hydroxide

The DSC thermogram for the well-dried sample of PET with potassium hydroxide is illustrated in Figure 4. The endothermic peaks corresponding to the evaporation of ethylene glycol and the melting of unreacted PET were also observed. However, the production temperature of ethylene glycol was about 10°C higher than that from the corresponding hydrated sample. Separate experiments also showed that the weight loss in the thermogravimetric curves for the well-dried sample also shifted to high temperatures. The results suggest that water contained in the hydrated sample promotes the alkaline hydrolysis of PET with potassium hydroxide. In a study in our lab on the hydrolysis of PET with water in the absence of alkaline hydroxides under pressure to keep water in the liquid state, the hydrolysis did not significantly occur until about 235°C.¹⁹ Therefore, water should not directly participate in the alkaline hydrolysis at lower temperatures. It is noted that the peak shape of ethylene glycol for the hydrated and dry samples (Fig. 4) was different from that for the mixtures of ethylene glycol and water (Fig. 2). The ethylene glycol peak in the alkaline hydrolysis of PET may not be due to the pure evaporation of ethylene glycol. Furthermore, the temperature for the former was typically higher than that for the latter. These results suggest that the production temperature of ethylene glycol was above the true evaporating temperature of ethylene glycol in the absence of reactions. Furthermore, the evaporation of water in the hydrate occurred around 120°C, well below the production temperature of ethylene glycol. Therefore, the hydrolysis reaction of the hydrated sample actually occurred in the dry condition. The results consistently pointed out that water in hydrates did not actually participate in the alkaline hydrolysis reaction. It is likely that the promoting effect by water is because that dispersion of potassium hydroxide on the PET surface is increased in the presence of water, which enhances



Figure 5. Effect of molar ratio on the DSC thermograms for the mixture of PET and potassium hydroxide. PET/KOH = (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4.

the contacting area for the alkaline hydrolysis reaction.

Ratio of Potassium Hydroxide to PET

The DSC thermograms for the dry samples with different ratios of potassium hydroxide to PET are plotted in Figure 5. The peak area of ethylene glycol increased with the concentration of potassium hydroxide; in addition, the production of ethylene glycol generally shifted to lower temperatures when the ratio of potassium hydroxide to PET was increased.

In the progress of PET hydrolysis, the production of ethylene glycol needs to break both ester linkages. The reaction can be expressed as follows.

$$\begin{array}{l} \sim R_{1} \hline C_{6}H_{4} \hline CO \hline O \hline C_{2}H_{4} \hline O \hline CO \hline C_{6}H_{4} \hline \\ R_{2} \sim + 2 \ KOH \rightarrow \sim R_{1} \hline C_{6}H_{4} \hline COOK \\ + \sim R_{2} \hline C_{6}H_{4} \hline COOK + HO \hline C_{2}H_{4} \hline OH \quad (1) \end{array}$$

The extent of PET hydrolysis is usually defined as the percentage of ester linkages being broken to produce the hydroxyl groups and the carboxyl groups. The breakage of polymer chain linkages may follow end-chain scission or random-chain scission. In the latter case, monomers will not be produced significantly until high extent of depolymerization. For example, a pattern of random scission for ester linkages was found in the hydrolytic depolymerization of PET melts,⁷ where the yield of ethylene glycol was low as the extent of PET hydrolysis was smaller than 50% and the yield largely increased as the hydrolysis extent reached 70%.

Figure 5 showed that the production temperature of ethylene glycol generally decreased with the ratio of potassium hydroxide to PET. The higher peak temperature of ethylene glycol in alkaline hydrolysis of PET, especially at the low ratios of potassium hydroxide to PET than the evaporation temperature of ethylene glycol shown in Figure 2 indicated that ethylene glycol was produced at temperatures higher than its evaporation temperature. Ethylene glycol would be evaporated once it was produced. It should be noted that the initialization temperature for the breakage of PET linkages should be independent of the concentration of potassium hydroxide. If the reaction mechanism followed the end-chain



Figure 6. TGA thermograms for the mixture of PET and potassium hydroxide (n/n = 1:1) in the presence of metal acetates. (a) none; (b) zinc acetate; (c) manganese acetate; (d) cobalt acetate.

scission instead of random-chain scission, ethylene glycol would have been produced at the same temperatures, independent of the KOH concentration. If the reaction mechanism followed random-chain scission as in the case of the hydrolytic depolymerization of PET melts, ethylene glycol would not be simultaneously produced with the occurrence of the breakage of PET linkages. Increasing concentration of KOH increased the extent of alkaline ¹⁸ hydrolysis and, therefore, decreased the temperature at which ethylene glycol was produced and evaporated (Fig. 5). At high ratios of KOH to PET such as 3 or higher, the peak temperature of ethylene glycol was close to the evaporation temperature of ethylene glycol shown in Figure 2 and would be limited by the evaporation temperature.

Effect of Metal Acetates

The thermogravimetric curves for samples with the addition of metal acetates are shown in Figure 6. The production of ethylene glycol shifted to high temperatures and the yield decreased with the presence of metal acetates. It indicates that these acetates inhibit the alkaline hydrolysis of PET. It may be because the hydroxide was partially neutralized by the relatively acidic acetates. Therefore, the actual amount of hydroxide capable of participating in the reaction decreased.

Kinetic Analysis

The basic kinetic equation used to describe a decomposition reaction can be expressed as

$$d\alpha/dt = q \ d\alpha/dT = k(T) \ f(\alpha) \tag{2}$$

where α is the degree of conversion, q is the heating rate, k(T) is the rate constant, and $f(\alpha)$ is a functional relationship of conversion. The degree of conversion may be defined as the ratio of actual weight loss to total weight loss in the thermogravimetric measurement of a decomposition process:

$$\alpha = (M_o - M_t) / (M_0 - M_f)$$

where M_t is the sample weight at time t, and M_o and M_f are the initial and final sample weights, respectively.

The temperature dependence of the rate constant, k(T), may be described by the Arrhenius expression and $f(\alpha)$ may be assumed to be a *n*thorder kinetic model. The rate expression can be expressed as follows.

$$d\alpha/dt = q \ d\alpha/dT = A \ \exp(-E/RT)(1-\alpha)^n \quad (4)$$

By the Kissinger's method, the temperature where the rate of weight loss is at maximum is used to obtain the kinetic parameters. Because the maximum rate occurs when d(d/dt)/dt is zero, differentiating eq. (4) with respect to time and setting the resulting equation equal to zero gives:

$$q/RT_m^2 = A/E n(1 - \alpha_m)^{n-1} \exp(-E/RT_m)$$
 (5)

where T_m and α_m are the temperature and conversion at maximum reaction rate, respectively. The Kissinger's method assumes that the value of $n(1-\alpha_m)^{n-1}$ is independent of q. Therefore, a plot of $\ln(q/T_m^2)$ vs. $1/T_m$ gives the activation energy.

It was shown that the production temperature of ethylene glycol was close to the evaporating temperature of ethylene glycol when the concentration of potassium hydroxide in the sample was high (Fig. 5). The result indicates that the true production temperature of ethylene glycol may be uncertain at high concentrations of KOH because ethylene glycol may not be instantaneously detected until reaching its evaporating temperature. In other words, the TGA thermogram for the sample with high loading of potassium hydroxide would not be appropriate for determining the kinetic parameter. Therefore, the kinetic study of alkaline hydrolysis of PET was performed using the lowest concentration of potassium hydroxide.



Figure 7. Effect of scanning rate on the TGA thermograms for the mixture of PET and potassium hydroxide (n/n = 1:1). (a) 2.5°C/min; (b) 5°C/min; (c) 10°C/min.

The effect of scanning rate on the thermogravimetric curves for the alkaline hydrolysis of PET is shown in Figure 7. Differentiating the curves of weight loss gave the peak temperature of maximum hydrolysis rate. The value of R-square for the regression of $\ln(q/T_m^2)$ vs. $1/T_m$ was 0.998, indicating the good linearity of the fitting. The activation energy calculated by eq. (5) was 110 kJ/mol. The activation energy for alkaline hydrolysis of PET in the solid state was close to the value determined by the conventional isothermal kinetic data obtained in an autoclave. The detailed discussion will be presented in the accompanying article.¹⁸

CONCLUSIONS

The techniques of thermal analysis (DSC and TGA) were applied to study the alkaline hydrolysis of PET with metal hydroxides. The hydrolytic reaction was examined by the thermograms, where the evaporating endotherm or weight loss caused by the production of ethylene glycol were illustrated. Potassium hydroxide was found to be active in hydrolyzing PET in the solid state; in contrast, sodium hydroxide had no activity. The concentration of potassium hydroxide affected the production temperature of ethylene glycol. The phenomenon can be explained by a random-scission mechanism for the hydrolysis of ester linkage. Water in hydrated samples promoted the alkaline hydrolysis of PET; however, the presence of acidic metal acetates retarded the production of ethylene glycol. The activation energy for alkaline hydrolysis of PET determined by the Kissinger's method was consistent with the value traditionally obtained from the experimental data in a batch reactor. This study indicates that thermal analysis is a simple and convenient alternative for the depolymerization study.

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