Kinetics of Hydrolysis of Polyethylene Terephthalate Pellets in Nitric Acid

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ABSTRACT: The hydrolysis of polyethylene terephthalate (PET) pellets in nitric acid was investigated to determine the kinetic parameters. Experiments were conducted with cylindrical shaped pellets in 13*M* nitric acid at 80, 90, and 100°C respectively. Also, an experiment was conducted with a waste PET bottle sheet in 9.5*M* nitric acid at 100°C. The kinetics of the reaction was explained by the shrinking core model with surface chemical reaction as rate controlling step and accounting for surface area reduction due to the deposition of the product terephathalic acid (TPA) on the reaction surface. The activation energy for the reaction was found to be 135 kJ/mol. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1781–1783, 2003

Key words: polyesters; thermoplastics; degradation; kinetics (polym.)

INTRODUCTION

Polyethylene terephthalate (PET) is a semicrystalline thermoplastic used in the manufacture of high strength fibers, photographic films, mineral water, and soft drink bottles. Since the disposal of used PET bottles has been the focus of environmental problems, the chemical recycling of waste polymers have been gaining greater attention in recent years as a means of obtaining valuable products from waste plastics. An economically feasible process for disposal of PET is its degradation to terephthalic acid and ethylene glycol.

Many researchers have studied the kinetics of degradation of PET by methanolysis, glycolysis, and hydrolysis. The literature on hydrolysis of PET was thoroughly reviewed and also investigated by Yoshioka et al.[1] These authors have reported the effects of nitric acid concentration, particle size, and temperature on the hydrolysis rates, and proposed a modified shrinking core model to explain the reaction mechanism and the results.

To further investigate the hydrolytic depolymerization of PET, in the present work experiments were carried out with bigger sized particles in small cylindrical and slab-like geometries. A new modified shrinking core model was proposed to explain the experimental results and to obtain the rate parameters.

EXPERIMENTAL

Materials

The PET used in the experiments were commercially available, small, cylindrical-shaped pellets of about 3.5 mm in diameter and length. A 0.55 mm thick sheet of 1 cm^2 area was cut from PET bottles. Analar nitric acid was diluted to give 9.5 and 13 molal solutions for the reaction.

Apparatus

The apparatus consisted of a standard round-bottomed flask of 500 mL capacity fit with a refluxing condenser and thermometer. The flask was heated by a mantle heater and the temperature was controlled by a temperature controller.

Procedure

The nitric acid solution of about 150–200 mL was taken in the reaction flask and heated to the desired reaction temperature and maintained constant at that temperature. Then, about 500 mg of PET pellets were added to the flask and the contents were kept under stirring condition by a stirrer arrangement. After the desired reaction time, the flask was cooled quickly to room temperature, and the solid material was filtered and washed thoroughly with water and then with liquid ammonia ($\simeq$ 6*M*) to remove the product terephathalic acid (TPA) from unreacted PET. The unreacted PET was filtered from the ammonia solution, washed, and then dried in an oven. The percentage conversion of PET was determined from the difference in weights of the sample before and after the reaction.

THEORETICAL

The reaction of hydrolysis of PET in nitric acid below its melting point is a heterogeneous noncatalytic solid–liquid reaction and can be represented as

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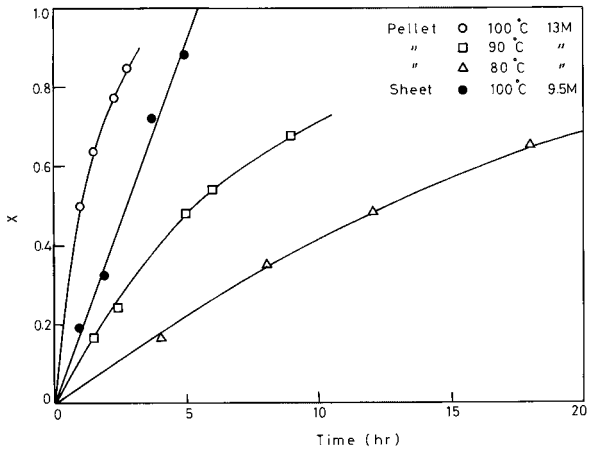

Figure 1 Fractional degradation against time for PET pellets and sheet at different temperatures.

$$A_{(l)} + bB_{(s)} \rightarrow \text{Products}$$

where A is the liquid reactant and B the solid reactant. The PET pellets being nonporous, the reaction can be satisfactorily represented by shrinking core model.[2] Preliminary analysis of the data according to the three rate controlling steps, viz., gas–film, ash layer diffusion, and chemical reaction of the model was not satisfactory. Yoshioka et al. have also observed the same trend and modified the shrinking core model to account for reduction in the active surface area at the unreacted core surface as observed by deposition of teraphathalic acid product particles on the reaction core surface. It is found that Yoshioka's model also was not satisfactory for our experimental data obtained with bigger size particles. In view of this, the shrinking core model was modified assuming that the reduction in surface area at the reaction core was proportional to the radius of the unreacted core, in contrast to the assumption of Yoshioka that it is proportional to the extent of conversion. According to shrinking core model, the rate equations are given by

$$-\frac{\rho}{b}\frac{4\pi r_c^2}{3}\frac{dr_c}{dt} = S_c K_r C_{A0} \tag{1}$$

where ρ is the molar density of PET, b the stoichiometric constant, r_c the radius of the unreacted core, S_c the surface area of the unreacted core, K_r the surface chemical reaction rate constant, and C_{A0} the concentration of nitric acid. Now, the affective surface area for reaction becomes

$$S_c = 4\pi r_c^2 \frac{r_c}{R} \tag{2}$$

where R is the initial radius of the pellet. Substituting S_c in eq. (1), gives

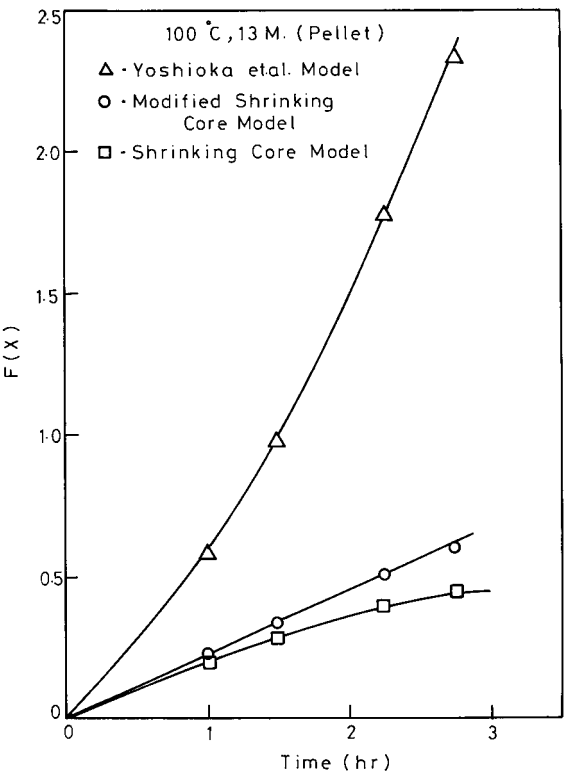

Figure 2 Conversion function $F(X)$ for different models against time for PET pellets at 100°C and 13M nitric acid.

$$-\frac{dr_c}{dt} = \frac{3b}{\rho}\frac{r_c}{R}K_r C_{A0} \tag{3}$$

Integrating,

$$\text{Ln}\,\frac{R}{r_c} = \frac{3bK_r C_{A0} t}{\rho R} \tag{4}$$

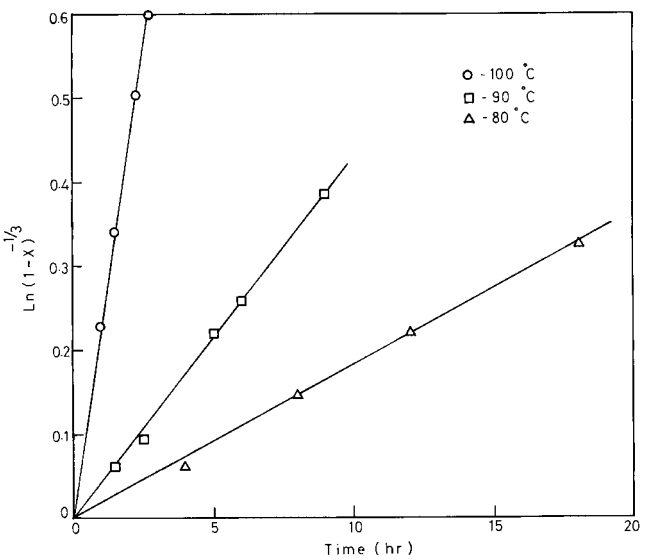

Figure 3 Plot of $F(X)$ vs time for PET pellets and sheet according to the modified shrinking core model.

where t is the reaction time. The above equation in terms of percentage degradation becomes

$$F(X) = \mathrm{Ln}(1 - X)^{-1/3} = Kt \tag{5}$$

where $F(X)$ is the conversion function defined by eqs. (5) and (7)–(9), X the percentage degradation of PET, and K is the apparent rate constant equal to $(3bK_rC_{A0}/\rho R)$.

For slab-like pellets, as the unreacted core surface is constant throughout the reaction unlike for spherical particles, it is assumed that the reduction in surface are a due to the deposition of TPA is also constant. Consequently, the rate expression is given by

$$-\frac{S_l \rho dl}{bdt} = S_l \alpha K_r C_{A0} \tag{6}$$

where S_l is the surface area of the unreacted core of the slabs and α is the fractional surface coverage by deposition of TPA.

Integrating,

$$F(X) = X = \bar{K}t \tag{7}$$

where $\bar{K}$ is the apparent rate constant $\rightarrow 2bK_rC_{A0}\alpha/\rho L$ (L is the thickness of the PET sheet).

The Yoshioka et al. equation is

$$F(X) = (1 - X)^{-2/3} - 1 = K't \tag{8}$$

where K' is the apparent rate constant given by eq. (8). The shrinking core model equation is

$$F(X) = 1 - (1 - X)^{1/3} = K''t \tag{9}$$

where K'' is the apparent rate constant given by eq. (9).

The experimental percentage degration against time for the PET pellets at different conditions is shown in Figure 1. Figure 2 shows a comparison of the three models for the experimental data at 100°C. It is seen that eq. (5) represents the experimental data satisfactorily compared to the conventional shrinking core model and the modified shrinking core model of Yoshioka et al. The experimental data at other temperatures was analyzed according to eq. (5) and eq. (6), and is shown in Figure 3. It can be seen that the modified shrinking core model proposed in the present work quite satisfactorily represents the experimental data. An Arrhenius plot of the apparent rate constant K obtained at different temperatures from the slopes of the straight lines in Figure 3 is shown in Figure 4. The activation energy obtained was 135 kJ/mol. The activation energy obtained in this work was slightly higher than the value 101.3 kJ/mol reported by Yoshioka et al. The apparent rate constant values for the pellets and sheet material obtained in this study was of similar magnitude as those reported by Yoshioka et al.

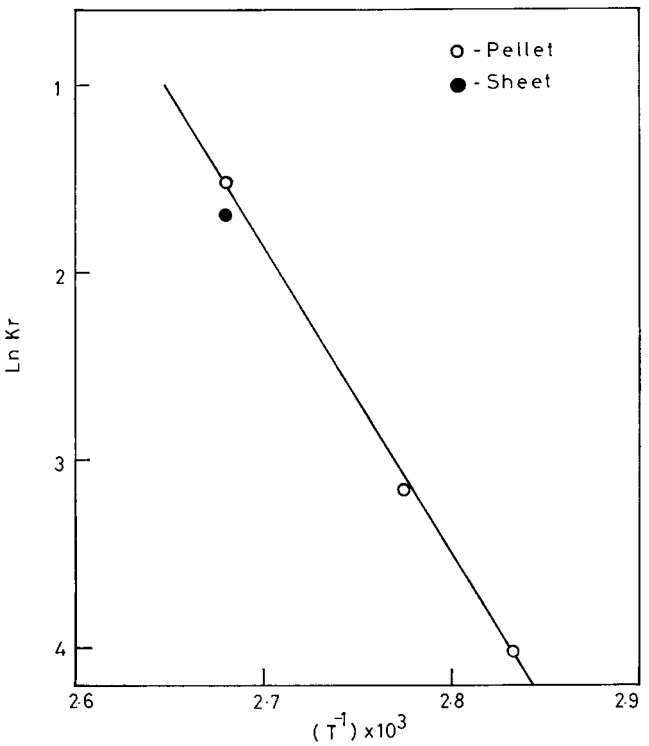

Figure 4 Arrhenius plot of the rate constants of hydrolysis of PET.

CONCLUSION

The hydrolysis of PET pellets and sheet in nitric acid was investigated to determine the kinetics of the reaction. It was found that the conventional shrinking core model with different rate controlling steps was not satisfactory and a modified shrinking core model was proposed to analysis the experimental. In this it is assumed that the reaction is chemical reaction step controlled and the effective surface area for reaction due to the deposition of the product TPA is reduced and proportional to the radius of the unreacted core. The activation energy obtained is 135 kJ/mol.

References

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