

The Decomposition Kinetics of Polyester Microfiber Fabrics by Sodium Glycerolate/Glycerol Solution

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ABSTRACT: Polyester microfiber fabrics were alcoholized at 120, 140, and 160°C in 0.5, 1.0, and 1.5% (w/w) sodium glycerolate/glycerol solutions (NaGR) and the decomposition kinetics was studied in comparison to the hydrolysis done by a 5% aqueous sodium hydroxide solution (NaOH) at temperatures 80, 90, and 100°C. The activation energy and the Arrhenius pre-exponential factor of the alcoholysis found from this study were 30.57 kcal/mol and $2.04 \times 10^{14}/M \text{ s}^{-1}$, respectively. In comparison to the hydrolysis case, these values are much higher. The activation energy and the preexponential factor of the hydrolysis found from this study were 14.48 kcal/mol and $1.947 \times 10^6/M \text{ s}^{-1}$, respectively. The resulting surface morphologies observed by a scanning electron microscope showed that the NaGR-decomposed PET fiber surfaces were distinguished from the NaOH-decomposed PET fiber surfaces by a uniformly developed fine structure of microcraters. It is believed that such a fine microcrater structure of the NaGR-decomposed fiber surface is due to the greater pre-exponential factor as well as to the higher activation energy of the alcoholysis. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1217–1223, 1997

INTRODUCTION

Along with the improvement in spinning technology to produce a finer denier polyester (PET) fiber, various PET microfibers have appeared since the mid-1980s.^{1,2} The appearance of the microfibers is believed to be a great step toward manufacturing a silklike fiber with PET. However, it is also true that various problems arise due to the finer denier feature of the PET microfibers, particularly in the softening treatment, which is an essential process to give a silklike touch to PET fabrics.² Much the same as in the softening of regular

PET fabrics,^{3–5} the softening of microfiber PET fabrics has been accomplished using hot aqueous sodium hydroxide solutions. It has been known that hydroxide anions in a sodium hydroxide solution hydrolyzes PET fabrics on the surface. This results in the PET fabric being able to tolerate some weight loss but gives a soft and silky hand to the fabric. Although it has been known that the more the weight loss the more the silky hand that can be obtained, in practice, the weight loss ratio does not exceed more than 30–40% for regular PET fiber fabrics and 10–15% for most PET microfiber fabrics. In excess of the weight loss ratios, the mechanical properties of the PET fabrics are known to be severely deteriorated. Many studies have shown that this deterioration is due mainly to the irregularity of the hydrolysis caused by the

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preferential attack of hydroxide anions in the amorphous region of the PET surface.⁵

Recently, Huh⁶ as well as Cho et al.⁷ alcoholized PET films, using sodium glycerolate/glycerol (NaGR) solutions. They successfully decomposed the PET films to reach weight loss ratios over 80% without any significant physical deterioration. It is believed that this is due to the lack of the preferential attack of the glycerolate anions in the amorphous region of the PET surface, unlike the hydroxide anions. Further, they also found that the hygroscopicity of the NaGR-treated PET film increased by up to five times compared with that of the original PET film. If so, the use of the alcoholysis may improve the major drawbacks of PET fabrics, such as the static and the dyeability problems originating from the hydrophobic nature of PET.

Inspired by this, we applied the alcoholysis method directly to PET microfiber fabrics to examine the PET fabric decomposition kinetic behavior and to observe the characteristic decomposition pattern of the alcoholized fabric surface. More specifically, we derived a general form of the PET decomposition kinetic equation and calculated the activation energies and the Arrhenius preexponential factors of the NaOH–PET and the NaGR–PET decomposition reactions. Further, by using the calculated results, the surface appearance of the alcoholized PET microfiber fabrics in comparison to that of the hydrolyzed PET microfiber fabrics is also discussed.

EXPERIMENTAL

The PET microfiber fabrics used were a conjugated microfiber fabric (warp: 75d/72f, semi-dull; weft: 150d/288f, semidull) supplied by Kolon Co. They were cut into sheets of sizes of 10 × 12 cm and were prepared by drying them in a desiccator over silica gel overnight. GR (first grade, Junsei Chemical Co., Japan) was used after removing the contained water by distillation. NaOH (first grade, Junsei Chemical Co.), NaH (first grade, Junsei Chemical Co.), and acetic acid (first grade, Kanto Chemical Co., Japan) were used without further purification. As a cleaning solution, Sunmorl BK-20T (industrial use, Korea Fine Chemical Co., Korea) was used.

For the preparation of NaGR stock solutions, GR was poured under nitrogen into a three-necked round flask equipped with a drying tube. A calculated amount of NaH powder was added

successively in small portions to the GR. Similarly, a 5% NaOH solution was prepared by dissolving NaOH powder in distilled water.

The prepared PET microfiber fabrics samples, approximately 1.5 g, were weighed accurately. Then, the treatment was carried out in a 2000 mL cylindrical flask equipped with a reflux condenser for the time periods of 20, 40, 60, 80, and 100 min with the use of 0.5, 1.0, and 1.5% concentrations of the NaGR solution and 5% NaOH solution at the bath ratio of approximately 250 : 1. During the treatment, the temperature was maintained constant by immersing the flask into a constant temperature bath. The treatment temperatures used were 120, 140, and 160°C for the NaGR treatment and 80, 90, and 100°C for the NaOH treatment. After the treatments, the samples were washed with excess distilled water and neutralized with 0.5% acetic acid. Then, the samples were scoured with 80°C aqueous BK 20T cleaning solution (2 mL/L) and washed again with distilled water. After suction extraction of water, the samples were collected and dried at 80°C in a vacuum dry oven for at least 48 h to complete the dryness and kept on dehydrated silicagel in a desiccator.

RESULTS AND DISCUSSION

Derivation of Rate Equation

In the NaOH solution, PET is known to decompose via the hydrolysis mechanism, while in the NaGR solution, PET is known to decompose via the base-catalyzed ester exchange reaction mechanism. Although the details of these two decomposition reactions are not the same, the main chemical kinetic schemes can be depicted in the same way. In Figure 1, the schematics of the chemical kinetics is shown.⁸ In both cases, a preequilibrium step is established between the intermediate complex and the reactants. In general, such a preequilibrium arises when that rate of the formation of the complex (k_1) and the rate of its decay back into the reactants (k_{-1}) are much faster than its rate of formation of the products (k_2), so that we may write the overall PET decomposition rate equation for both hydrolysis and alcoholysis as

$$\frac{d[p]}{dt} = -\frac{d[\text{PET}]}{dt} = k[\text{PET}][S] \quad \text{with } k = k_1k_2/k_{-1} \quad (1)$$

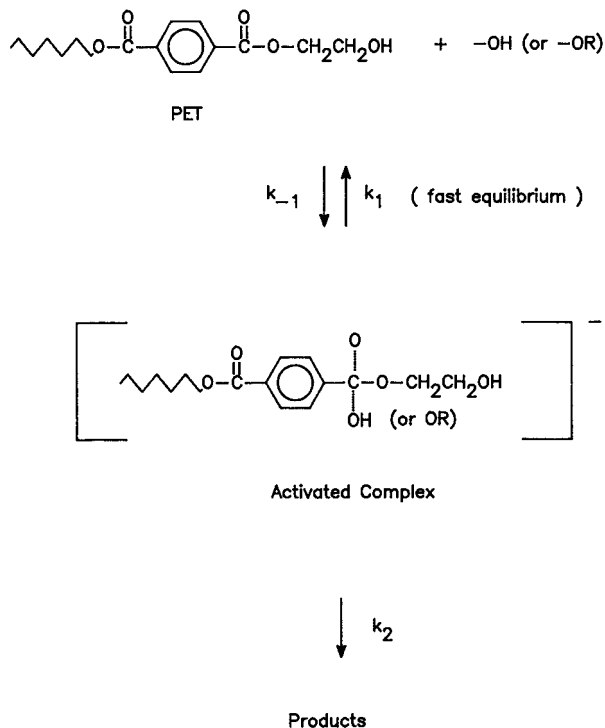


Figure 1 Kinetic scheme of the hydrolysis and the alcoholysis of PET.

where p , t , k , and $[]$ stand for the product, the reaction time, the overall reaction rate constant, and the concentration, respectively. The term S denotes the hydroxide or alkoxide anion. Here, one has to notice that $[S]$ is approximated to be constant throughout the reaction. In practice, the bath ratio 250 : 1 used is enough to keep the anion concentrations constant during the decomposition. Then, eq. (1) is solved as

$$[PET]_t = [PET]_0 \exp(-k[S]_0 t) \quad (2)$$

where the subscripts 0 and t are the initial and the final reaction times, respectively. Rewriting eq. (2) in the power series form, we have

$$[PET]_t = [PET]_0 - [PET]_0 k[S]_0 t + \frac{1}{2} [PET]_0 (k[S]_0 t)^2 - \dots \quad (3)$$

Each term in the series may be interpreted as follows: The first term is the initial PET concentration, the second term is the complex concentration changed to the products via the forward reaction after time t , and the third term is the complex concentration back to the reactants via the re-

verse reaction after time t , \dots and so on. Further, by assuming that in the product formation step there is no reverse reaction, the terms higher than the second term were truncated to obtain

$$\frac{[PET]_0 - [PET]_t}{[PET]_0} = k[S]_0 t \quad (4)$$

By noticing that the concentration ratio can be converted to the weight ratio, the familiar weight loss equation is obtained⁹:

$$\frac{W_0 - W_t}{W_0} = k[S]_0 t \quad (5)$$

Calculation of Rate Constants

In Figures 2 and 3, the weight loss rates of the PET microfiber samples in 5% NaOH solution and in 0.5, 1, and 1.5% concentrations of NaGR solutions at various temperatures are plotted. As can be seen in Figures 2 and 3, the weight loss ratios are linearly proportional to the treatment time and the initial base concentration. This indicates that the PET decomposition reactions are indeed first-order reactions to the reaction time, as was predicted by eq. (2). Accordingly, the rate constants were calculated by obtaining the slopes from Figures 2 and 3. In Table I, the calculated

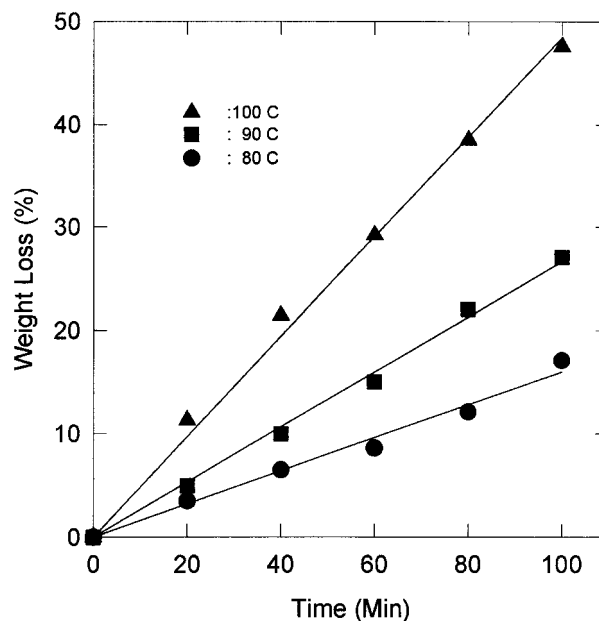


Figure 2 Weight loss ratios of PET microfiber fabric by 5% NaOH at various temperatures.

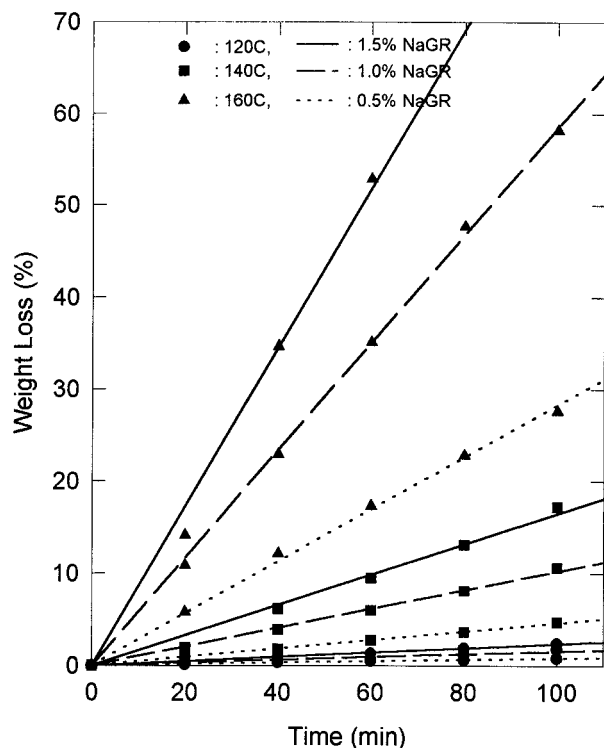


Figure 3 Weight loss ratios of PET microfiber fabric by NaGR at various temperatures and concentrations.

rate constants at the temperatures and the concentrations examined are listed. By examination of Table I, one may easily notice that the rate constants are dependent on temperature but are kept nearly constant with the concentration change. In fact, this corresponds to the theory of chemical kinetics which states that reaction rate constants are exponentially dependent on temperature but are independent of concentration. In this study, to keep the concentration independent, the rate constants used are averaged over all the concentrations examined.

Arrhenius Parameters

Since the rate constant increases exponentially with increasing temperature, we now apply the Arrhenius equation to obtain the activation energy of the PET decomposition reactions. The usual form of the Arrhenius equation is

$$\ln k = \ln A - E_a/RT \quad (6)$$

where A , E_a , and R are the preexponential factor, the activation energy, and the gas constant, re-

spectively. In Figures 4 and 5, the Arrhenius plots of the hydrolysis and the alcoholysis are shown, respectively. In both cases, $\ln k$ vs. $1/T$ plots show good linear relations. The activation energies and the preexponential factors calculated from the slopes and the intercepts of the Arrhenius plots are given in Table II. As can be seen in Table II, the activation energy of the hydrolysis obtained in present work (14.48 kcal/mol) is comparable with those reported by others (≈ 15 – 19 kcal/mol).^{10,11} However, the activation energy of the alcoholysis (30.57 kcal/mol) obtained is much higher than that of the previously reported value from the PET film system by Cho et al.⁷ (19.4 kcal/mol). The activation energy of the alcoholysis obtained by Cho et al. lies essentially in the range of those reported for the hydrolysis. Although the definitive reason is not known, their low activation energy seems due to the water moiety in their GR solution. So far, since the activation energy of the alcoholysis is higher than that of the hydrolysis, it becomes obvious that the alcoholysis needs more heat than does the hydrolysis. On the other hand, the preexponential factors of the hydrolysis and the alcoholysis were 1.947×10^6 and $2.04 \times 10^{14}/M \text{ s}^{-1}$, respectively. The physical significance of the preexponential factor is that it represents the random collision frequency between the reactants irrespective of their energy states. Since the present PET decomposi-

Table I The Rate Constants of the Hydrolysis and the Alcoholysis of PET Microfiber Fabric

Reactant	Temperature (°C)	Reaction Rate (/M s ⁻¹)
NaOH (5.0%)	80	0.0021
	90	0.0036
	100	0.0065
NaGR (0.5%)	120	0.0021
	140	0.0122
	160	0.0749
NaGR (1.0%)	120	0.0021
	140	0.0135
	160	0.0774
NaGR (1.5%)	120	0.0021
	140	0.0146
	160	0.0763
NaGR (average)	120	0.0021
	140	0.0134
	160	0.0762

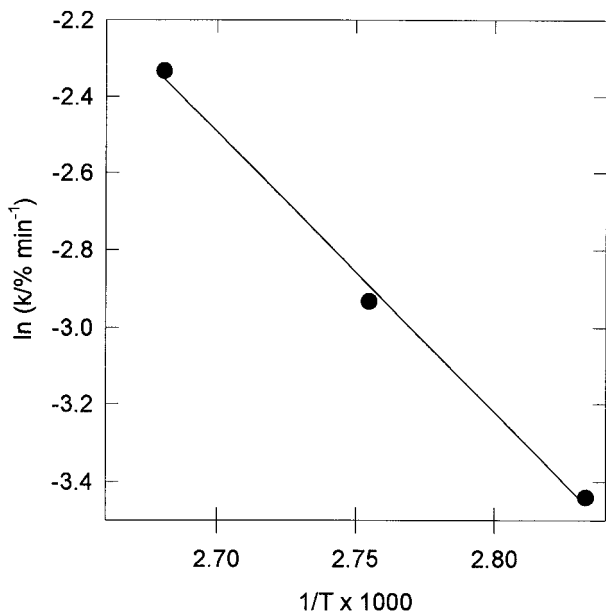


Figure 4 Arrhenius plot of PET decomposition by NaOH.

tion reactions occur in dense liquid media, the preexponential factors obtained are not necessarily the true random collision frequencies. However, here, we freely interpret that the preexponential factors obtained are the random collision frequencies so as to state that the random colli-

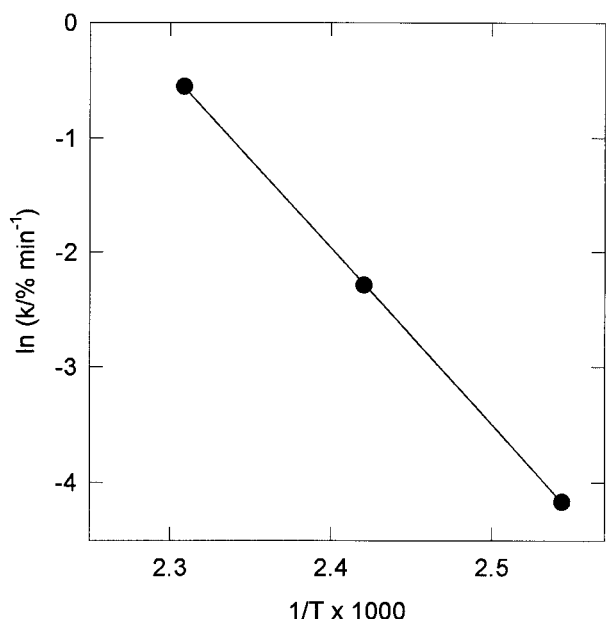


Figure 5 Arrhenius plot of PET decomposition by NaGR.

Table II The Arrhenius Parameters

System	E_a (kcal/mol)	A ($/M s^{-1}$)
PET/NaOH	14.48	1.947×10^6
PET/NaGR	30.57	2.040×10^{14}

sion frequency of the alcoholysis is much higher than that of the hydrolysis. Since the more the random collisions the less the preferential attack, it is expected that the alcoholysis would occur much more uniformly on the entire PET fiber surface than would the hydrolysis.

Surface Appearance

The surface morphologies of the PET microfiber fabrics treated with the NaGR and the NaOH solutions were observed by a scanning electron microscope (SEM). In Figure 6, the SEM pictures of the NaOH- and the NaGR-treated fabric surfaces at similar levels of the weight losses are shown. The microcraters are the results of the alcoholysis or the hydrolysis.¹² The larger ditchlike craters are due to the dislodging of TiO₂ particles and are not our major concern. A close examination of these SEM pictures shows that in both the hydrolysis and the alcoholysis cases the number of microcraters increases with increasing weight loss. The distinguishing feature of the alcoholysis from the hydrolysis compared at similar levels of weight loss is that the microcraters on the alcoholized fiber surface are much more abundant and uniformly developed than are those on the hydrolyzed fiber surface as can be seen in Figure 6. Such a more abundant and uniform feature of the craters on the alcoholized fiber surface seems due to the greater preexponential factor as well as to the higher activation energy of the alcoholysis, as predicted from the Arrhenius parameter calculations.

CONCLUDING REMARKS

The uniformly developed microcrater feature of the alcoholysis may have some advantage for the softening finishing of PET fabrics, particularly PET microfiber fabrics. This feature of the alcoholysis might prevent sudden physical deterioration of PET fabrics and may improve the tactility of PET fabrics. Moreover, this feature is likely to

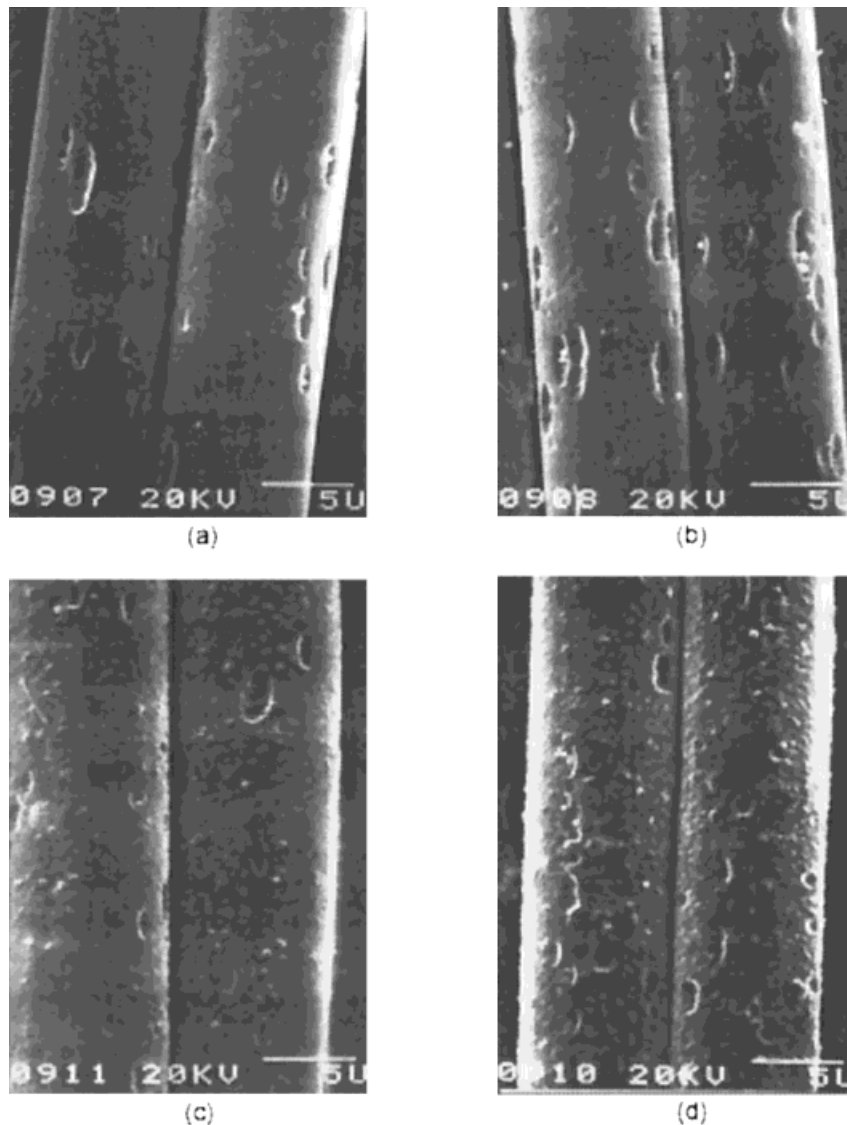


Figure 6 SEM photos of NaOH and NaGR treated PET microfiber fabric surfaces at similar levels of weight loss ratio; (a) 29.2% by NaOH, (b) 47.6% by NaOH, (c) 34.3% by NaGR, and (d) 47.7% by NaGR.

change the coloration of the fabrics by increasing the dispersed light reflections from the fabric surfaces, i.e., some deep-color effect in NaGR-treated PET microfiber fabrics in dyeing is expected.¹³ Apart from this, since NaGR may reform PET by introducing the hydrophilic glycerol residues each with two hydroxyl groups to PET chains, one may increase the hygroscopicity of the PET fabric with the NaGR treatment, as shown by Cho et al.⁷

All these features discussed are believed to be essential to make PET fabrics more silklike. We feel that experiments covering a wider range of PET–alcohol systems are needed to gain a more

detailed understanding of this phenomenon. Such experiments are in progress.

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