

# Effects of Pretreatment Reagents on the Hydrolysis and Physical Properties of PET Fabrics

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**ABSTRACT:** The effects of pretreatment reagents on the hydrolysis and physical properties of PET fabrics were investigated under various alkaline hydrolysis treatment and pretreatment conditions. Before alkaline hydrolysis, solvent treatment with pretreatment reagents, including benzyl alcohol (PET-b) or 2-phenyl ethanol (PET-p), modified the structure of the PET fabric, thus affecting the hydrolysis and physical properties of the PET fabrics. Fabric weight loss increased with increasing hydrolysis time. The rate constant ( $k$ ) increased markedly with increasing methyl groups in the pretreatment reagents. The activation energy ( $E_a$ ) of untreated fabrics was higher than those of the treated fabrics. The crystallinity of the PET fabrics increased with increasing hydrolysis times ( $t$ ) and methyl groups in the

pretreatment reagents. The weight loss of PET-b increased with increasing pretreatment temperature ( $T$ ). However, the weight loss of PET-p increased up to 100°C but decreased above 120°C. The shrinkage of all samples increased with increasing hydrolysis times ( $t$ ). Shrinkage of PET-b and PET-p was greater than that of untreated fabrics. PET-b displayed greater shrinkage than PET-p because byproducts polluted the PET fibers. Both the initial and maximum water absorption of the fabrics increased with increasing hydrolysis times ( $t$ ). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3071–3078, 2009

**Key words:** PET; alkaline hydrolysis; pretreatment reagent; alcohols

## INTRODUCTION

Generally available poly (ethylene terephthalate) (PET) is a very useful fiber because of its excellent processibility at low cost and its good mechanical properties. However, it has low water absorption properties and softness compared with those of natural fibers. Alkaline hydrolysis has been studied extensively to overcome these problems because alkaline hydrolysis improves the water absorption properties and softness of the PET fiber to give it a character similar to that of natural fibers. The patent for the alkaline hydrolysis of PET fiber was granted in 1949. The mechanism of alkaline hydrolysis was identified in 1958 by Hashimoto.<sup>1</sup>

The alkaline hydrolysis of PET fibers is usually carried out with an aqueous alkaline solution, such as sodium hydroxide (NaOH). In the alkaline hydrolysis process, PET undergoes a nucleophilic substitution and is hydrolyzed with NaOH solution.<sup>2</sup> Chain scission of PET occurs, resulting in a considerable weight loss and the formation of hydroxyl and carboxylate end groups, which improves the handling of the fabric and its moisture retention, and allows the fabric to

drape like silk.<sup>3–5</sup> However, hydrolysis is expensive because of the long treatment time, high temperature, and high alkali concentration required. To reduce the processing costs, an accelerating reagent is used in the process. Extensive research into the accelerating reagent, such as how the addition of an organic solvent or cationic surfactant affects the weight loss of the PET fabric, has been undertaken by many researchers.<sup>6–8</sup> Teli and Purkayastha studied the effects of solvent pretreatments on weight-reduced fabrics.<sup>8</sup> Solvent pretreatment is an important technique that induces extensive structural modification of the PET fibers.<sup>9</sup> Chemical modification of the PET fibers by solvent pretreatment results in changes in weight loss, degree of crystallinity, shrinkage behavior and water absorption properties.

In this study, the alkaline hydrolysis of PET fabric was investigated using pretreatment reagents such as benzyl alcohol and 2-phenyl ethanol under various conditions. We also investigated the effects of pretreatment on the alkaline hydrolysis and the structural modifications of PET, and we characterized its weight loss, degree of crystallinity, shrinkage behavior, water absorption properties, and morphology.

## EXPERIMENTAL

### Preparation of PET fabrics

PET fabric of ISO 105 standard was purchased from the Korea Apparel Testing and Research Institute

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(Korea). A high-pressure dyeing machine was used for the pretreatment and alkaline hydrolysis processes. The pretreatment solvents used were benzyl alcohol and 2-phenyl ethanol (Aldrich, WI). The PET fabric samples ( $10 \times 15 \text{ cm}^2$ ) were immersed in benzyl alcohol or 2-phenyl ethanol at various temperatures (80, 100, 120, or  $140^\circ\text{C}$ ) for 4 h. The samples were coded according to the pretreatment reagent: b for benzyl alcohol (PET-b) and p for 2-phenyl ethanol (PET-p). After pretreatment, the solvent-treated fabrics were dried at  $30^\circ\text{C}$  for 24 h. The alkaline hydrolysis of the pretreated PET fabrics was performed under various conditions: bath ratio (50 : 1), alkaline concentration (4 wt %), hydrolysis time (20, 40, 60, 80, or 120 min), pretreatment temperature (80, 100, 120, or  $140^\circ\text{C}$ ), and hydrolysis temperature (80, 100, or  $120^\circ\text{C}$ ). Sodium hydroxide was used as the alkaline hydrolysis reagent and acetic acid was used to adjust the pH. After the hydrolysis, the PET fabrics were neutralized with 1 wt % acetic acid solution for 10 min and then washed with distilled water at a bath ratio of 50 : 1.

#### DSC measurements

The degree of crystallization of the PET fabrics was investigated using a differential scanning calorimeter (DSC; TA Instruments). The specimens were heated from 30 to  $300^\circ\text{C}$  at a scanning rate of  $20^\circ\text{C}/\text{min}$  in a nitrogen atmosphere. Crystallinity was calculated with eq. (1).

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100, \quad (1)$$

where,  $X_c$  is the degree of crystallinity evaluated by the DSC method,  $\Delta H_m$  is the measured melting enthalpy of the polymer obtained directly from the DSC trace, and  $\Delta H_m^0$  is the melting enthalpy of the completely crystallized polymer.  $\Delta H_m^0 = 99.4 \text{ J/g}$  was assumed for PET.<sup>10</sup>

#### XRD measurements

The degree of crystallization of the PET fabrics was examined with a wide-angle X-ray diffractometer (Rigaku Denki) with nickel-filtered  $\text{CuK}\alpha$  radiation at 40 kV and 100 mA. The scanning experiment was carried out at the equator over a  $2\theta$  range from 5 to  $40^\circ$  at a scan speed of  $5^\circ/\text{min}$ . Crystallinity was calculated with eq. (2).

$$X_c = \frac{A_c}{A_c + A_{am}} \times 100, \quad (2)$$

where,  $A_c$  is the area of the diffraction peak for crystallinity and  $A_{am}$  is the area of the amorphous diffraction halo.<sup>11</sup>

#### Shrinkage measurements

The percentage shrinkage of the PET fabric was calculated with eq. (3).

$$\text{Shrinkage}(\%) = \frac{I_0 - I}{I_0} \times 100, \quad (3)$$

where,  $I_0$  is the length of the sample before treatment and  $I$  is the length of the sample after treatment.<sup>12</sup>

#### Water absorption measurements

The water absorption properties of the alkaline-hydrolyzed PET fabric after treatment with either pretreatment solvent were measured with the water absorption system described in our previous publications.<sup>13–15</sup> The intrinsic water absorption capacity at 10 s and the maximum water absorption capacity in weight loss (%) were measured and calculated.

#### Surface morphology

Field emission scanning electron microscopy (FE-SEM; JEOL JSM 9701F) observations were made on the surfaces of the PET fabrics at 15 kV.

## RESULTS AND DISCUSSION

#### Effects of hydrolysis time on weight loss and crystallinity

The 100% PET fabrics treated with pretreatment under different conditions were hydrolyzed with various conditions to study the effect of pretreatment reagent on the alkaline hydrolysis of the PET fabric. Weight loss is plotted against hydrolysis time ( $t$ ) at various hydrolysis temperatures in Figure 1. Sodium hydroxide causes weight loss in PET fabrics because terephthalic acid and ethylene glycol are separated by the hydrolysis of the ester group in the PET chains. The terephthalic acid is neutralized to disodium terephthalate (DST) and this reaction results in weight loss in the PET fabrics. The weight loss increases with increasing  $t$  because DST is water soluble and the reaction is not at equilibrium.<sup>7</sup> Moreover, the weight loss increases with increasing hydrolysis temperature. It implies that the movements of the polymer chains improved with increasing temperature. Furthermore, the weight loss increases when pretreatment reagents are introduced and the methyl groups of these reagents are increased. This means that the pretreatment reagents improve the efficiency of the hydrolysis. This suggests that the pretreatment reagents swell the amorphous region because of the interpenetration of the hydroxyl groups of the pretreatment reagents ( $-\text{OHa}$ ), and  $-\text{OHa}$  increases with increasing methyl groups. The

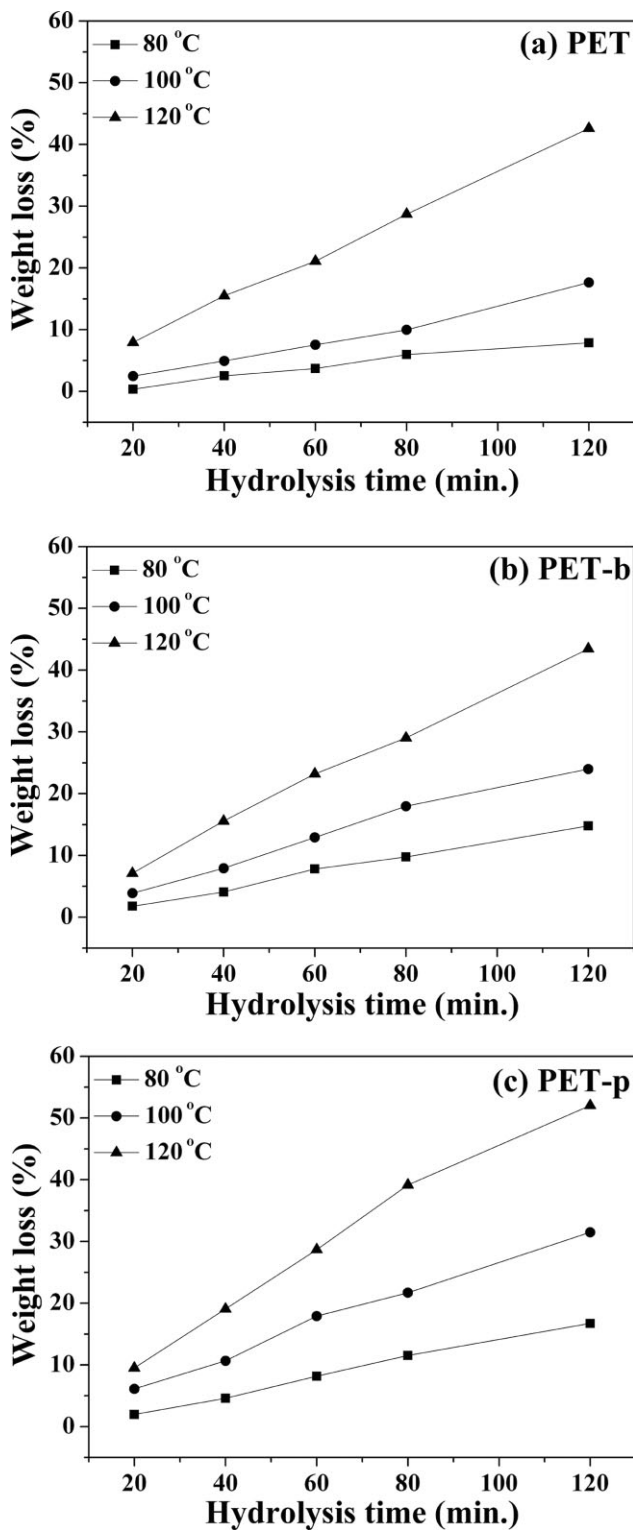


Figure 1 Effects of hydrolysis time ( $t$ ) on weight loss in pretreated PET fabrics at various hydrolysis temperatures.

swelling of the amorphous region increases with increasing -OHa because the increased -OHa moieties have many more chances of interpenetration. After the removal of the reagents, the increased amorphous region absorbs many more hydroxyl

groups from NaOH (-OHb) and so the hydrolysis reaction is more active in this region.  $(1 - x)^{1/2}$  is plotted against hydrolysis time ( $t$ ) at various hydrolysis temperatures in Figure 2. The rate constant ( $k$ ) of the hydrolyzed PET fabrics at  $t$  is calculated with eq. (4). The equation was suggested by Kuriyama.<sup>16</sup>

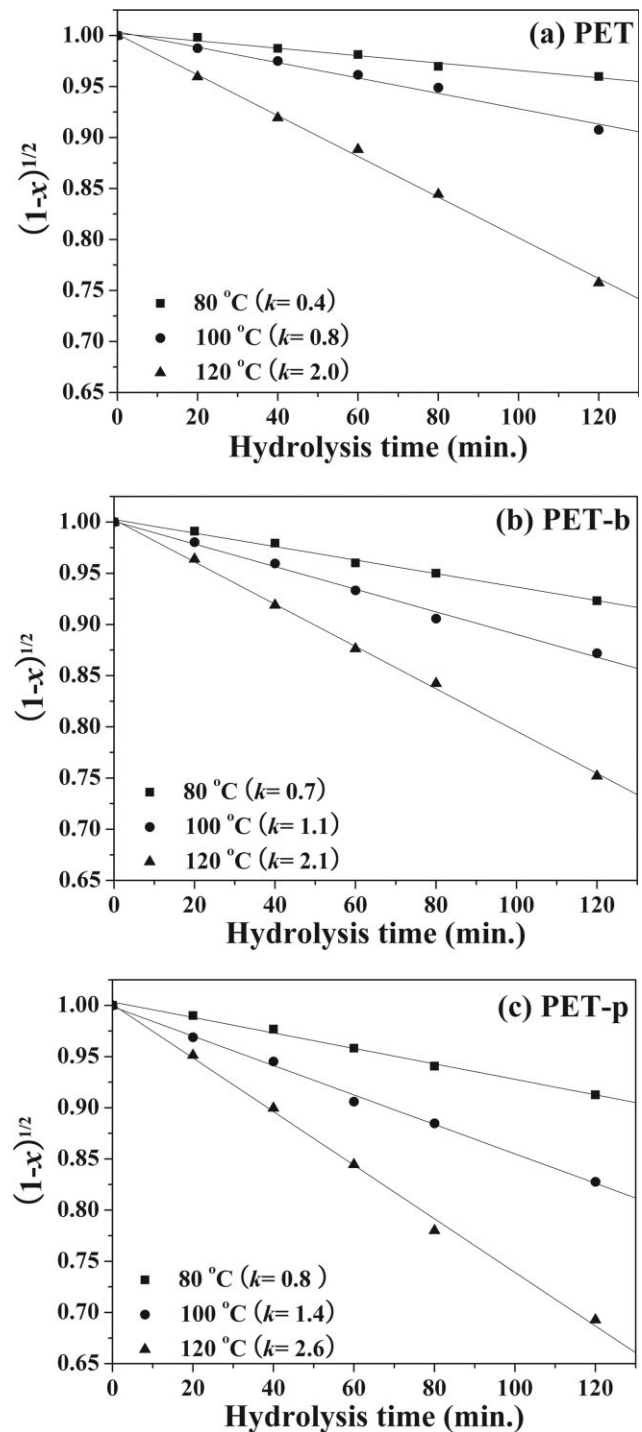
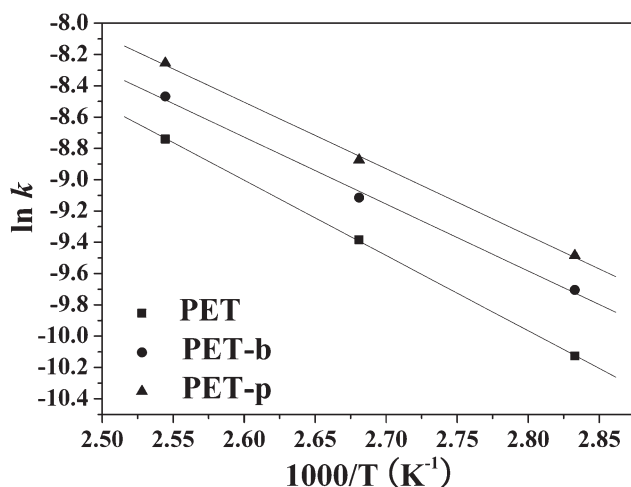


Figure 2 The relationship between the value  $(1 - x)^{1/2}$  and hydrolysis time for pretreated PET fabrics at various hydrolysis temperatures.



**Figure 3** Arrhenius plot for the hydrolysis of PET fabrics with pretreatment reagents.

$$(1 - x)^{1/2} = 1 - \frac{kt}{r_0\rho}, \quad (4)$$

where,  $x$  is the weight loss (%) at hydrolysis time ( $t$ ),  $r_0$  is the radius of the PET filament without NaOH treatment, and  $\rho$  is the density of the PET filament. After the pretreatment,  $k$  ( $\times 10^{-8}$  g/cm<sup>2</sup>·sec) is markedly increased with increasing methyl groups in the pretreatment reagents. Arrhenius plot for the hydrolysis of PET fabrics is shown in Figure 3. The  $k$  of the hydrolyzed PET fabrics at hydrolysis time is calculated by eq. (5) and eq. (6).

$$k = A \exp[-E_a/(RT)], \quad (5)$$

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

where,  $k$  is rate constant of hydrolysis,  $A$  is pre-exponential factor,  $E_a$  is activation energy and  $R$  is gas constant.<sup>17</sup> In Figure 3, when it occurs in the hydrolysis of PET fibers by 4 wt % NaOH,  $\ln k$  of hydrolysis is a linearly consistent with  $1/T$  at various temperatures. The activation energy ( $E_a$ ) value of the hydrolysis of PET, PET-b and PET-p is 95.9, 85.4, and 83.1 kJ/mol, respectively. That obtains from the slope of line in Figure 3. The PET has slightly higher  $E_a$  than pretreated samples. However, weight loss of pretreated PET samples is remarkably higher than

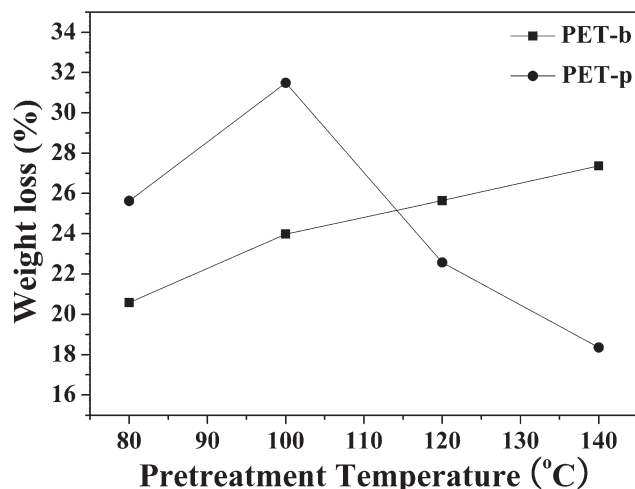
**TABLE I**  
Crystallinity of PET Fabrics at Different Hydrolysis Times ( $t$ ) as Determined by XRD

		Hydrolysis time ( $t$ )				
Sample		20 min	40 min	60 min	80 min	120 min
Xc (%)	PET	35.9	38.8	42.5	43.8	44.1
	PET-b	46.1	47.6	49.1	58.8	61.3
	PET-p	58.6	59.4	60.2	61.1	63.5

**TABLE II**  
Crystallinity of PET Fabrics at Different Hydrolysis Times ( $t$ ) as Determined by DSC

Sample	Hydrolysis time ( $t$ )	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub> (%)
PET	20 min	257.5	37.7	39.9
	40 min	257.5	49.8	50.1
	60 min	257.3	51.6	51.9
	80 min	257.0	52.0	52.3
	120 min	257.9	53.4	53.7
PET-b	20 min	257.0	49.7	50.0
	40 min	256.4	51.1	51.4
	60 min	257.0	52.9	53.2
	80 min	257.2	53.3	53.6
PET-p	20 min	257.3	53.6	54.0
	40 min	258.6	50.6	50.9
	60 min	257.4	52.0	52.3
	80 min	256.6	54.3	54.6
	120 min	257.5	55.2	55.5
	120 min	256.8	56.1	56.4

the one of PET. This suggests that the pretreatment reagents affect  $E_a$  of PET samples. The XRD results for all the samples are summarized in Table I. The crystallinity of the PET fabrics increased with increasing  $t$ , regardless of the pretreatment reagent. Moreover, the treated samples had crystallinity values higher than those of the untreated samples. The crystallinity of PET-p was higher than that of PET-b. The increase in crystallinity is caused by the elution of the amorphous region and the elution is increased by the activity of both -OH<sub>a</sub> and -OH<sub>b</sub>.<sup>7</sup> The increase in crystallinity further verifies their effects. The crystallinity of PET, PET-b, and PET-p is summarized by DSC in Table II. The crystallinity of the PET fabrics increased with increasing  $t$  and increasing methyl groups in the pretreatment reagents. This is in good agreement with the XRD results.



**Figure 4** Effects of pretreatment temperature ( $T$ ) on weight loss in pretreated PET fabrics.



**TABLE III**  
Crystallinity of PET Fabrics at Different Pretreatment Temperatures (*T*) as Determined by XRD

Sample	Pretreatment Temperature ( <i>T</i> )			
	80°C	100°C	120°C	140°C
Xc (%)				
PET-b	49.9	61.3	62.5	62.8
PET-p	58.1	63.5	63.0	57.9

**Effects of pretreatment temperature on weight loss and crystallinity**

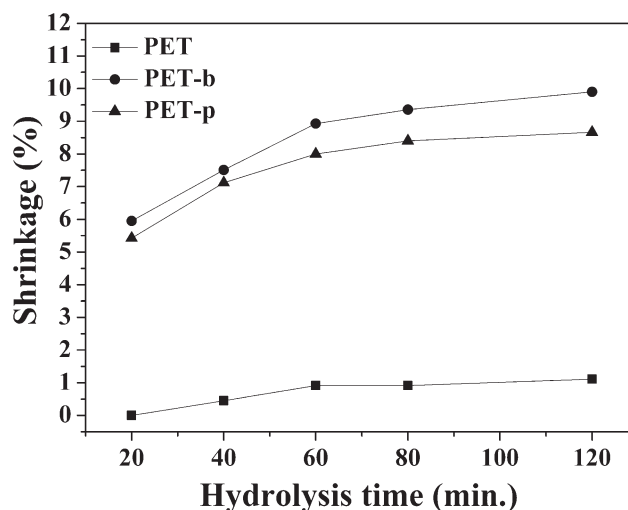
The weight loss in the PET fabrics is plotted against the pretreatment temperature (*T*) in Figure 4. In the case of PET-b, the weight loss increased with increasing *T*. However, the weight loss of PET-p increased up to 100°C but decreased above 120°C. We can infer that the movements of the polymer chains and the pretreatment reagent molecules improved with increasing temperature and then, under hydrolysis at high temperatures, the samples produced byproducts with the accelerated degradation of the PET fabrics.<sup>18</sup> These phenomena suggest that the PET fabrics are polluted by these byproducts. Hence, the weight loss is reduced. The effect of *T* on the crystallinity of the samples was investigated by XRD in Table III. The crystallinity of PET-b increased over the range of *T*. However, the crystallinity of PET-p increased up to 100°C but decreased above 120°C. Toda<sup>19</sup> and Cho et al.<sup>20</sup> proposed that the hydrolysis causes initial swelling in the amorphous region. The effect of *T* on the crystallinity of the samples was investigated by DSC in Table IV. The DSC results are similar to the results of XRD.

**Shrinkage behavior**

Figure 5 shows the shrinkage of the PET fabrics with *t*. The shrinkage of all the samples increased with increasing *t*. The maximum shrinkage of the untreated fabrics was about 1%. PET-b and PET-p displayed greater shrinkage than did the untreated

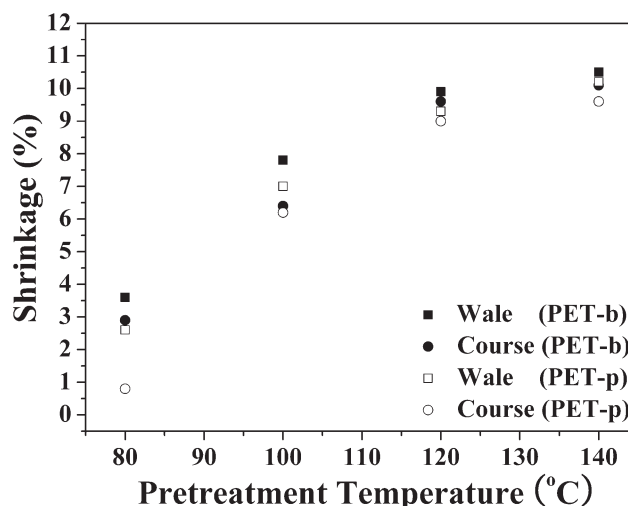
**TABLE IV**  
Crystallinity of PET Fabrics at Different Pretreatment Temperatures (*T*) as Determined by DSC

Sample	Pretreatment Temperature ( <i>T</i> )	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub> (%)
PET-b	80°C	257.7	46.1	46.4
	100°C	257.3	53.6	54.0
	120°C	256.5	53.9	54.2
	140°C	257.3	54.1	54.4
PET-p	80°C	258.9	50.2	50.5
	100°C	256.8	56.1	56.4
	120°C	256.7	54.3	54.6
	140°C	257.0	45.6	45.4

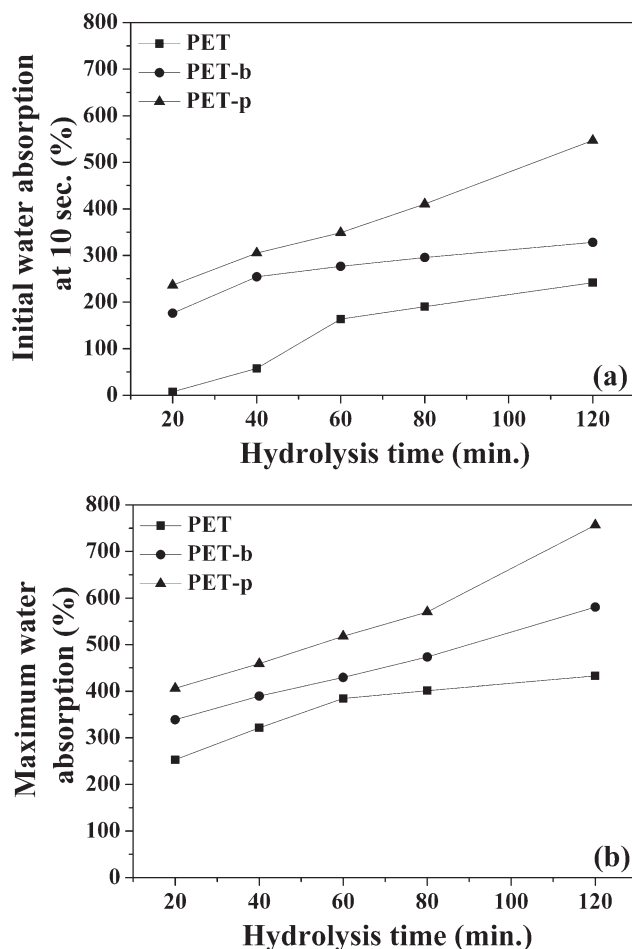


**Figure 5** Effects of hydrolysis time (*t*) on shrinkage behavior in pretreated PET fabrics.

fabrics. The pretreatment reagents swell the PET chains by diffusion and the mobility of the swelled PET chains increases with increasing -OH activity. The PET chains are thermodynamically stable because the pretreatment reagents can have alternative interactions.<sup>7</sup> In other words, the swelled amorphous region changes to crystal by recrystallization. Hence, the shrinkage of the PET fiber increases because of the structural relaxation of the amorphous region. However, PET-p displayed lower shrinkage than did PET-b, regardless of *t*. Figure 6 shows the shrinkage of the PET fabrics with *T*. The shrinkage of wale and course increased with increasing *T*, regardless of sample type. Furthermore, the shrinkage of PET-b was higher than that of PET-p.



**Figure 6** Effects of pretreatment temperature (*T*) on the shrinkage behavior of pretreated PET fabrics.



**Figure 7** Effects of hydrolysis time ( $t$ ) on the water absorption properties of pretreated PET fabrics.

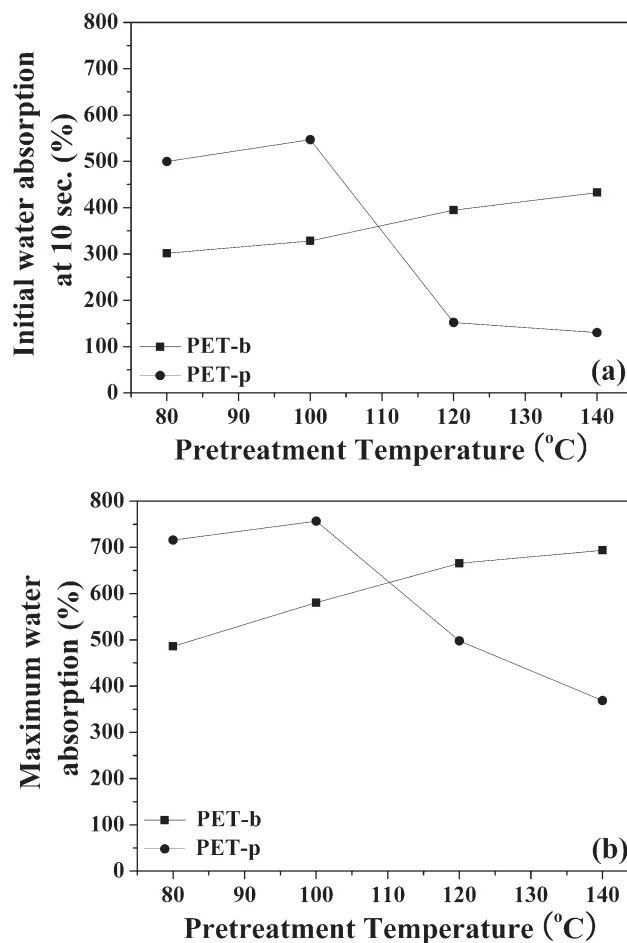
### Water absorption

Figure 7 shows the water absorption properties of the samples plotted against  $t$ . Both the initial and maximum water absorption increased with increasing  $t$ . The water absorption properties of the pretreated samples were higher than those of the untreated samples. Under the same conditions, the water absorption of PET-p was the highest of all the samples. This implies that the microvoid of the PET surface captures water molecules and the hydrophilicity of surface increases because the decomposition of the end groups is accelerated by the pretreatment reagent. Figure 8 shows the water absorption properties of the samples plotted against  $T$ . Both the initial and maximum water absorption of PET-b increased with increasing  $T$ . However, both the initial and maximum water absorption of PET-p increased up to 100°C but decreased above 120°C. The increase in  $T$  increased the reaction between 2-phenyl alcohol and the PET chain. The reaction pollutes the PET fabric with byproducts such as ethylene glycol, PET oligomer, and sodium terephthalate.<sup>18</sup> As a result of this pollu-

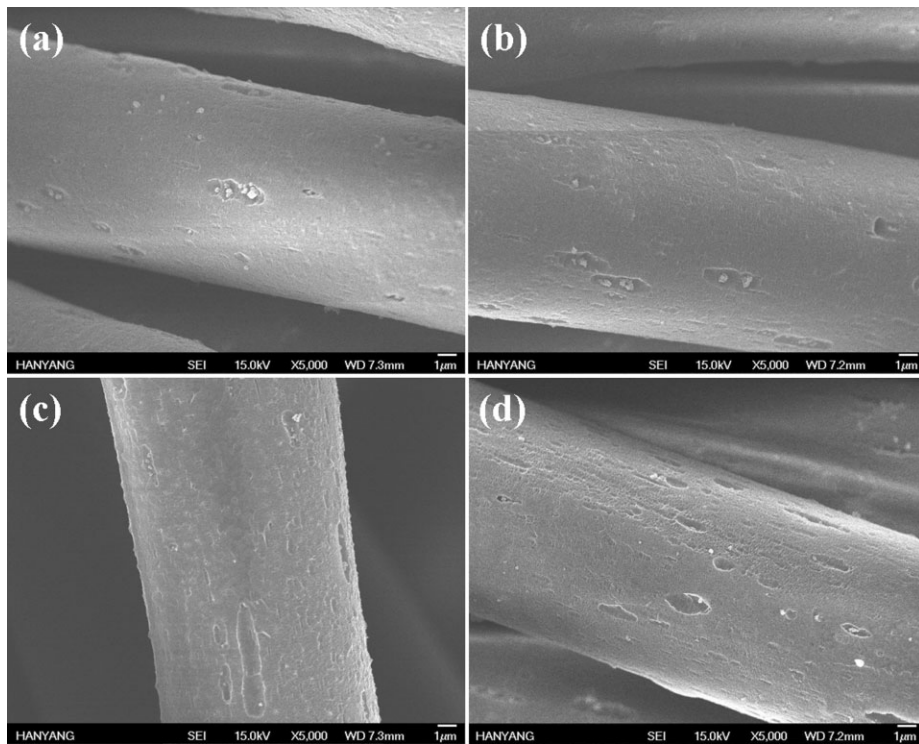
tion, the microvoid and hydrophilic end groups are reduced in the PET fabrics.

### Surface morphology

Figure 9 shows the effects of different  $T$  on the hydrolysis of the PET-b surface. In Figure 9(a), the fiber is thick, round, and smooth. As  $T$  increases, it appears that the pretreatment reagent attacks almost the entire surface of the fiber, causing erosion. As the erosion progresses, it propagates inside the fiber, resulting in the formation of elongated pits or cavities on the surface. Both the depth and frequency of the pits increase with increasing weight loss during pretreatment.<sup>12</sup> Figure 10 shows the effects of different  $T$  on the hydrolysis of the PET-p surface. The pits increased in number and craters began to appear at 80 and 100°C. In Figure 10(a,b), many transverse cracks, which developed inside the fiber, are evident. Bigger craters can also be seen. These stages are mainly the results of the synergistic actions of alkaline hydrolysis and the pretreatment reagents. The migration of the byproducts to the surface of the fiber can be seen in Figure 10(c,d). This means that the byproducts affect



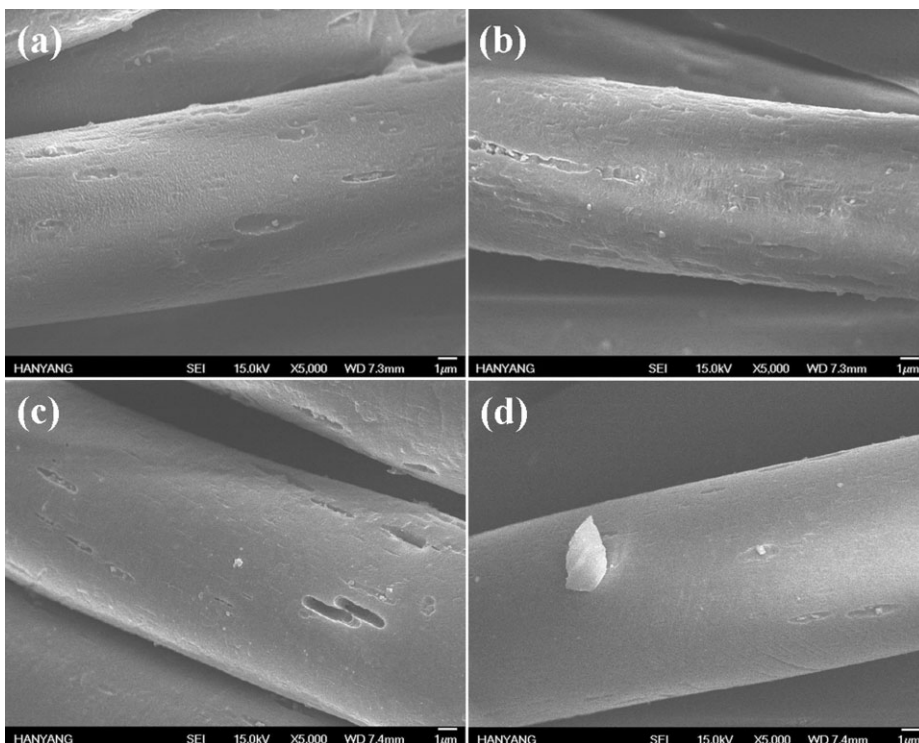
**Figure 8** Effects of pretreatment temperature ( $T$ ) on the water absorption properties of pretreated PET fabrics.



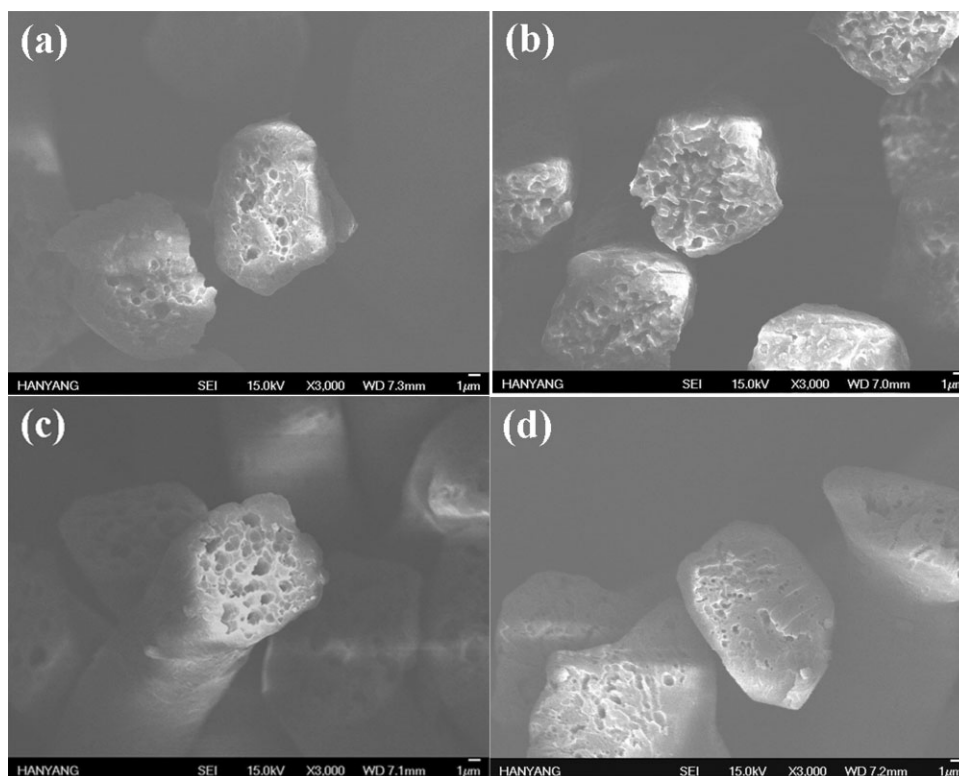
**Figure 9** FE-SEM images of PET-b at different pretreatment temperatures (T): (a) 80°C, (b) 100°C, (c) 120°C, and (d) 140°C.

the weight loss, degree of crystallinity, shrinkage behavior, and water absorption properties of the PET fibers. Figure 11 shows the cross-sectional shape of PET fabrics by different pretreatment reagents. In

case of the pretreatment reagents used, the number of pits is increased, and the size of craters is increased. Under the same conditions, the pits and craters of the PET-p are the deepest of the all samples. On the other



**Figure 10** FE-SEM images of PET-p at different pretreatment temperatures (T): (a) 80°C, (b) 100°C, (c) 120°C, and (d) 140°C.



**Figure 11** FE-SEM images of the cross-sectional shape of PET fabrics: (a) PET at 100°C, (b) PET-b at 100°C, (c) PET-p at 100°C and (d) PET-p at 140°C.

hand, the number of pits and crater of the fiber are decreased in Figure 11(d). This is in good agreement with the Figure 10(c,d). Weight loss relates to both the depth and the number of the pits. Furthermore, crystallinity relates to the weight loss of fiber.<sup>3,7</sup>

## CONCLUSION

The weight loss in alkaline-hydrolyzed fabrics is proportional to the alkaline hydrolysis temperature, time, and the type of pretreatment reagent used. The pretreatment reagents, including benzyl alcohol and 2-phenyl ethanol, affect the hydrolysis and physical properties of the PET fabrics. This investigation has shown that benzyl alcohol and 2-phenyl ethanol treatments modify the structural and morphological characteristics of PET fibers. Therefore, the activity of the hydroxyl groups in the pretreatment reagents affects the morphology and physical properties of the PET fibers. When PET fibers are treated with benzyl alcohol or 2-phenyl ethanol reagent, a disorientation of the amorphous phase and dissolution of the amorphous region occur in the treated fibers. 2-Phenyl ethanol contributed more effectively to the weight loss and crystallization of PET than did benzyl alcohol. These effects on weight loss, crystallinity, shrinkage, and water absorption caused by 2-phenyl ethanol can be attributed to pollution with

byproducts at pretreatment temperatures above 120°C.

## References

1. Hashimoto, T. *J Soc Fiber Sci Technol Japan* 1958, 14, 510.
2. Yongzhe, Y.; Hongchen G. *J Appl Polym Sci* 2006, 102, 3691.
3. Wei, Z.; Gu, Z. *J Appl Polym Sci* 2001, 81, 1467.
4. Niu, S. H.; Wakida, T.; Ueda, M. *Text Res J* 1993, 63, 346.
5. Xiao, W. Z.; Yu, H. M.; Han, K. Q.; Yu, M. H. *J Appl Polym Sci* 2005, 96, 2247.
6. Gawish, S. M.; Mosleh, S.; Ramadan, A. M. *J Appl Polym Sci* 2002, 85, 1652.
7. Kim, A. S.; Kim, G. J. *J Korean Fiber Soc* 1990, 27, 23.
8. Teli, M. D.; Purkayastha, A. *Am Dyestuff Rep* 1991, 80, 22.
9. Chidambaram, D.; Venkatraj, R.; Manisankar, P. *J Appl Polym Sci* 2003, 89, 1555.
10. Berndt, H. J.; Bossmann, A. *Polymer* 1976, 17, 241.
11. Lu, Y. H.; Lin, H.; Chen, Y. Y.; Wang, C.; Hua, Y. R. *Fibers Polym* 2007, 8, 1.
12. Muralidharan, B.; Mathanmohan, T.; Ethiraj, J. *J Appl Polym Sci* 2004, 91, 3871.
13. Kim, S. H.; Lee, J. H.; Lim, D. Y. *Text Res J* 2003, 73, 455.
14. Kim, S. H.; Kim, S. J.; Oh, K. W. *Text Res J* 2003, 73, 489.
15. Park, M. J.; Kim, S. H.; Kim, S. J.; Jeong, S. H.; Jaung, J. Y. *Text Res J* 2001, 71, 831.
16. Kuriyama, S.; Koremaysu, M. *J Soc Fiber Sci Technol Japan* 1960, 16, 110.
17. Goje, A. S.; Mishra, S. *Macromol Mater Eng* 2003, 288, 326.
18. Park, H. S. *J Kor Inst Chem Eng* 1995, 33, 113.
19. Toda, T. *Jap Res Assn Text End-Uses* 1980, 21, 473.
20. Cho, H.; Lee, S. Y.; Chang, D. S.; Choi, S. H. *J Korean Fiber Soc* 1979, 19, 11.