Action of Alkali on Polybutylene Terephthalate and Polyethylene Terephthalate Polyesters

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ABSTRACT: The two polyesters (polybutylene terephthalate and polyethylene terephthalate) were treated with aqueous as well as alcoholic solutions of sodium hydroxide at varying temperatures for different durations of time. The results were evaluated in terms of the loss in weight of the samples. The fabric samples of polyethylene terephthalate showed a greater degree of weight loss as compared to those of polybutylene terephthalate. The mechanism for the differences in the action of alkali on these two polyesters is explained. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1097–1102, 2000

Key words: polyester; polybutylene terephthalate; polyethylene terephthalate; alkali

INTRODUCTION

Polyethylene terephthalate (PET) is known to be attacked by different alkalis and amines. The treatment with sodium hydroxide solution is a versatile tool for imparting certain desirable properties to the polymer surface since this topochemical degradation causes scission of the surface polyester chains through hydrolysis. In contrast, certain organic amines and ammonia can diffuse into the fiber structure causing in-depth attack to weaken the fiber, the extent of which is proportional to the severity of the treatment.[1] Many workers report that the surface hydrolysis of polyester fiber by sodium hydroxide solution improves its working properties. Thus, the feel, luster, and the soil release properties are improved, reducing at the same time the static charge generation and the pilling tendency, particularly when the level of weight loss is controlled between 15 and 25%.[2–4] Namboori[5] studied the effect of sodium hydroxide on the PET fibers and reported that the alkaline hydrolysis proceeds linearly with respect to time at constant temperature.

The use of alcoholic solutions of alkali[6,7] as well as the use of additives like cationic surfactants to the aqueous alkaline bath[8,9] has been suggested to accelerate the hydrolytic action on polyester. Work carried out in our laboratories also has revealed that the rate of hydrolysis of PET fibers is enhanced by adding certain additives like ethylene diamine to the aqueous solution of sodium hydroxide.[10]

No literature seems to have been reported on the alkaline treatment of polybutylene terephthalate (PBT) fibers, except that the PBT is more resistant to alkali treatment than PET.[11] This "easy-dyeable" PBT polyester is gaining popularity because of the certain advantages it possesses over the commonly used polyester, PET. The most important factor contributing to the enhancement of its popularity and future development is the diversification and ramification of the stretch fabric markets.

The present paper reports the results of the comparative studies on the treatments of the PBT

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and PET fabric samples with aqueous as well as methanolic and ethanolic sodium hydroxide solutions in terms of their loss in weight.

MATERIALS AND EXPERIMENTAL PROCEDURES

Substrates

PBT filament yarn "Finecell" was procured from Teijin Ltd., Japan, having specifications BB, 15 filaments/75 Denier, Type G 300 HP. The fabric with plain weave was woven using this filament yarn with the construction 125 reeds × 76 picks. PET fabric having similar construction was used.

Chemicals

Sodium hydroxide, methanol, and ethanol were of analytical reagent grade. All other chemicals were of laboratory reagent grade.

Treatment with 40% (w/v) Aqueous Sodium Hydroxide

About 2 g of accurately weighed PBT and PET fabric samples were treated with 40% (w/v) aqueous sodium hydroxide solution in an open beaker dyeing machine, keeping the liquor ratio at 100. The treatments were carried out at temperatures between 30 and 60°C for times from 0.5 to 60 min. In the case of treatment with 40% (w/v) aqueous sodium hydroxide solution, the samples were also treated at 97°C. The treated samples were immediately and thoroughly washed with water for complete removal of the alkali. The final washings were checked with a pH paper until neutral. The samples were finally air dried.

Treatment with 10% (w/v) Alcoholic Sodium Hydroxide

Sodium hydroxide was dissolved in pure methanol as well as in pure ethanol to get a 10% (w/v) solution. PBT and PET fabric samples were treated with these reagents as mentioned above for varying temperatures and time periods followed by thorough washing and drying.

Treatment with 10% (w/v) Sodium Hydroxide in Alcohol:Water Mixture

Solutions of sodium hydroxide [10% (w/v)] were also prepared by taking equal volumes of water and alcohol (methanol or ethanol) as solvent medium. PBT and PET fabric samples were then treated with these solutions as mentioned above followed by washing with water and drying.

Measurement of Percentage Weight Loss

The control and the treated PBT and PET samples were dried in an oven at 110°C for 3 h and then cooled in a P_2O_5 desiccator to room temperature. The dry weight of the sample was obtained accurately. The percentage weight loss was determined according to the formula

$$\text{Weight loss, \%} = \frac{w_1 - w_2}{w_1} \times 100$$

where w_1 and w_2 are the weights of the control and the treated samples, respectively.

RESULTS AND DISCUSSION

The process of alkaline weight reduction of PET, mainly in the form of fabric, has gained considerable commercial importance because of a number of advantages associated with the process. Our earlier studies on PET fibers involved the use of aqueous as well as alcoholic solutions of caustic soda for this purpose, including the use of certain additives to enhance the level of action under milder conditions of treatment.[7,10] Since PBT is another polyester fiber of importance, but with different chemical structure, similar studies were conducted on its fabric form and the results were compared with those on the PET fabric.

Table I gives the data on the effect of 40% (w/v) aqueous sodium hydroxide solution on the weight loss of the PET and PBT fabric samples. It may be observed that under identical conditions of alkali treatment, the effect on PET fabric was much higher than that on PBT fabric. Thus, at 60°C and for 60 min treatment time, a weight loss of 12.10% was observed for the PET fabric as against only 2.20% for the PBT fabric. Also, with the rise in temperature of the alkali treatment at equal time periods, the weight loss increased for both the fibers.

Further, the effect of 10% (w/v) solutions of sodium hydroxide in pure methanol and pure ethanol on the weight loss of PBT and PET fabrics was studied. These results, given in Table II, indicate that the weight loss increased almost linearly with the increase in the treatment time and temperature for both the reagents used. Also, for

Table I Effect of 40% (w/v) Aqueous NaOH on Weight Loss of Polyester Samples

Temperature (°C)	Time (min)	Weight Loss (%)	
		PET	PBT
30	30	1.62	0.12
	60	3.47	0.53
50	30	3.20	0.49
	60	6.39	1.00
60	15	3.75	0.51
	30	6.72	1.00
	45	9.42	1.60
	60	12.10	2.20
97	1	7.60	0.58
	3	18.17	1.79
	5	32.00	3.18
	8	—	4.69
	10	—	5.94

a similar level of weight loss, lesser and lesser time was required with increase in the temperature of treatment. The effect of these reagents was extremely high on PET fabric as compared to that on PBT fabric under identical treatment conditions, causing severe degradation of PET. For this reason, the weight loss values for the PET samples treated under such conditions have not been reported.

The results on the use of 10% (w/v) ethanolic sodium hydroxide solution indicate that the action of this reagent also was much more pronounced on PET than on PBT fabric, although marginally lower than that obtained using 10% (w/v) methanolic sodium hydroxide solution. The difference in the actions of the two alcoholic solutions decreased with increase in the temperature of treatment.

When the results on treatment of polyesters using 40% (w/v) aqueous sodium hydroxide solution were evaluated against those using 10% (w/v) alcoholic sodium hydroxide solutions, it was observed that the action of the latter treatments was drastically higher, although the strength of sodium hydroxide in these alcoholic solutions was only one-fourth of that in the aqueous solution. This was, therefore, advantageous from the point of view of reducing the quantity of alkali, the treatment time as well as the temperature.

The 10% (w/v) solutions of sodium hydroxide prepared in equal volumes of alcohol and water were also used for the treatment of the polyester fabrics. The results given in Table III indicate that the effect of these solutions in terms of the weight loss of PBT and PET fabrics was intermediate to that of the aqueous solution and the pure alcoholic solutions of sodium hydroxide. The weight loss values obtained were higher than

Table II Effect of 10% (w/v) Alcoholic NaOH on Weight Loss of Polyester Samples

Temperature (°C)	Time (min)	Weight Loss (%)			
		Methanolic NaOH		Ethanolic NaOH	
		PET	PBT	PET	PBT
30	15	18.10	—	11.00	—
	30	34.00	1.79	18.00	0.79
	60	64.17	3.30	50.30	1.84
40	5	23.40	—	13.17	—
	10	44.10	—	28.44	—
	30	—	15.00	—	2.10
50	2	20.00	—	12.00	—
	4	39.20	—	25.60	—
	15	—	12.86	—	8.19
	30	—	26.43	—	17.70
60	0.5	6.90	—	4.80	—
	1	19.70	—	11.00	—
	2	27.50	—	18.50	—
	10	—	14.62	—	9.53
	15	—	22.90	—	18.04

Table III Effect of 10% (w/v) NaOH in Alcohol/Water Mixture on Weight Loss of Polyester Samples

Temperature (°C)	Time (min)	Weight Loss (%) NaOH in Methanol : Water PET	PBT	NaOH in Ethanol : Water PET	PBT
40	15	5.00	—	3.19	—
	30	9.36	—	7.57	—
	60	20.15	—	15.93	—
50	15	7.77	1.00	5.11	—
	30	13.00	1.32	9.64	0.90
	60	25.40	2.03	21.00	1.30
60	15	9.00	2.61	7.32	2.31
	30	15.70	5.01	13.08	4.50
	60	32.20	10.03	26.46	8.97

those obtained by the aqueous solution but far less than those by pure alcoholic solutions.

The bar chart in Fig. 1 indicates the action of different sodium hydroxide solutions on PET and PBT fabric samples in terms of weight loss. It clearly indicates the lower receptivity of PBT to the alkaline hydrolysis.

The different levels of action shown by the different alkali solutions may be explained in the following manner.

Sodium hydroxide forms different hydrates with water depending on its concentration in the aqueous solution. A number of water molecules surround a sodium hydroxide molecule in such hydrate and its size decreases with increase in the concentration of sodium hydroxide. For example, at nearly 10% (w/v) aqueous sodium hydroxide concentration, about 20 water molecules are associated with one molecule of sodium hydroxide having a hydrodynamic diameter of the hydrated ion pair of about 10–15 Å.[12]

The comparative solubility of sodium hydroxide at room temperature is maximum in water followed by that in methanol and still lower in ethanol.[13] For the hydrolysis of polyester to take place, it is essential that the molecules of sodium hydroxide have good access to the fiber surface. It should also be noted that polyester is a hydrophobic fiber due to which the highly polar water molecules (those associated with sodium hydroxide to form a hydrate) will be greatly repelled. On the other hand, the two alcohols viz., methanol and ethanol—are less polar than water, and hence these molecules will experience less repulsion by the polyester fibers.

The smaller size of the solvated sodium hydroxide molecules in alcohols (much smaller than the hydrates) and lesser repellence of those solutions from polyester due to less polarity perhaps may be responsible in providing them more easy access to the fiber surface leading to increased weight loss of polyesters. Among the two alcohols, although ethanol is somewhat less polar than methanol, its molecular size is bigger. For sodium hydroxide in ethanol, therefore, the access to the fiber is reduced due to the steric hindrance caused by the larger size of these solvent molecules associated with the sodium hydroxide molecules and hence the action on the fiber is somewhat reduced.

The intermediate level of weight loss by the sodium hydroxide solution prepared in equal volumes of water and alcohol may be attributed to the larger amount of water present in the solution, which makes the solution much more polar than the purely alcoholic solution.

As regards the lower action of any of the sodium hydroxide solutions on PBT, the reason is based on the structural differences between PET and PBT. Goodman and Rhys[14] were of the opinion that the constituent structural features of polymers have more impact on their chemical behavior rather than their physical state such as the crystalline and amorphous portions. The susceptibilities of polyesters of different structural types toward hydrolysis differ greatly. The two ester bonds in the chemical structures of the polyesters, which are sensitive to decomposition reactions, are spaced much farther apart in PBT than in PET, so that their interaction is reduced. In

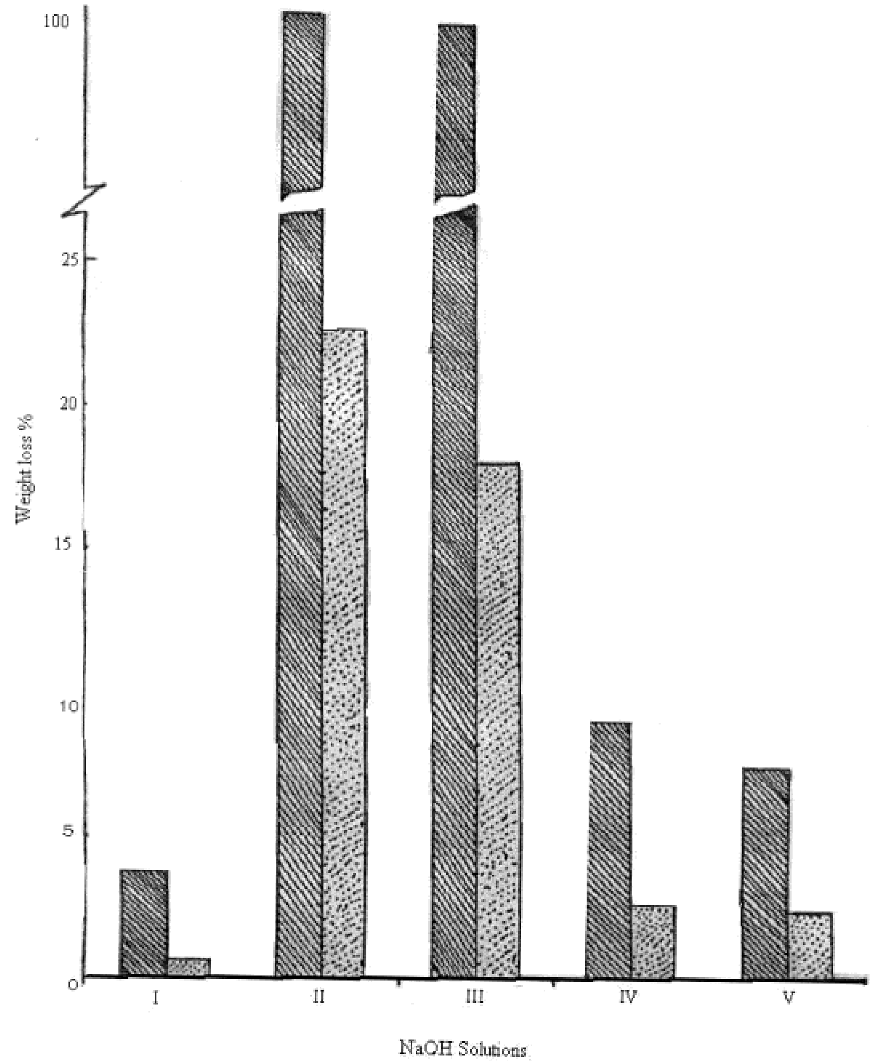

Figure 1 Percent weight loss of polyester fabrics treated with different NaOH solutions at 60°C for 15 min. I: 40% (w/v) NaOH in water; II: 10% (w/v) NaOH in methanol; III: 10% (w/v) NaOH in ethanol; IV: 10% (w/v) NaOH in (1:1) methanol:water; V: 10% (w/v) NaOH in (1:1) ethanol:water. Hatched bar: PET; stippled bar: PBT.

polyesters, the methyl groups are present in the proximity of ester linkages, making them considerably stable toward hydrolysis. In the case of PBT, the number of such methylene groups is double that in the case of PET. Further, the molecular chains in the normal α form of PBT are in a relaxed state. Due to this, the orientation of the chains, and hence that of the chain portions containing four methylene groups, is less perfect, causing significant steric hindrance to the action of alkali to hydrolyze the ester linkage. All these factors contribute to the much lesser action of different sodium hydroxide solutions on PBT as compared to that on PET.

Thus, it has been observed during these studies on alkali treatment that due to the differences in the chemical structures of the two polyesters, the supermolecular structures also possess marked differences, due to which PBT is much less sensitive to the action of alkali. Less polar solutions of alkali are more effective in hydrolyzing polyester fibers topochemically. The fabrics treated to effect a weight loss of about 20–25% could give a smooth feel. Also, with increase in the level of weight loss, the breaking load of the fabrics reduced whereas the moisture regain showed a marginal increase. The action was nonlinear and more severe with increase in either time or temperature of treatment.

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