Effect of Alkali on Filaments of Poly(ethylene Terephthalate) and Its Copolyesters. II. Presence of Quaternary Ammonium Salt in the Alkali-Bath

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Synopsis

Influence of alkyl (C_{12}–C_{14})-dimethyl-benzyl ammonium chloride in the solution of sodium hydroxide on the hydrolysis of poly(ethylene terephthalate) (PET), anionically modified poly(ethylene terephthalate) copolyster (CDP), and block polymer of poly(ethylene terephthalate)-poly (ethylene glycol) (EDP), has been studied under a variety of proportions, concentrations, time and temperature of reaction, M : L ratio, etc. Mechanical properties of treated polymeric materials are evaluated. Hydrolysis of two polymers in the same bath is compared with that in separate baths.

INTRODUCTION

Polyester textile materials are treated with sodium hydroxide solution for weight reduction, silklike soft handle, and improved properties.[1]

The hydrolysis reaction of PET, CDP, and EDP filament materials with aqueous sodium hydroxide is studied in an earlier report.[1] Quaternary ammonium salts in the alkali bath are known to accelerate the rate of hydrolysis. DeMaria[2] examined the process in the presence of different quaternary ammonium salts and found alkyl (C_{12}–C_{14})-dimethyl-benzyl ammonium chloride to be the most effective compound. The loss in the weight of PET material rapidly increased with the concentration of the quaternary salt up to a point, and its concentration in the bath was more important than the total amount (on weight of fiber) in deciding the extent of reaction. High weight loss matched with high loss in tensile strength of the material.

Hydrolysis of CDP and EDP materials in the presence of quaternary salts has not been reported so far. Many commercial fabrics contain unions and blends of polyesters PET, CDP, and EDP. It was observed in the first part of this work[1] that the rates of hydrolysis of these materials differ from each other, and under conditions of the alkali treatment, similar rate and extent of hydrolysis were obtained. It is not known how these materials will behave when combined simultaneously in the bath.

SCOPE OF PRESENT WORK

The reaction of PET, CDP, and EDP fiber materials with aqueous alkali solutions containing alkyl (C_{12}–C_{14})-dimethyl-benzyl-ammonium chloride is studied under various reaction conditions. The reaction is carried out using PET and CDP yarns together in the same reaction bath.

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EXPERIMENTAL

Materials and methods are described in Part I.[1] Alkyl (C_{12}–C_{14})-dimethyl-benzyl-ammonium chloride (92% purity) is used without purification. PET, CDP, and EDP yarns (nominal 95 d.tex/34 filaments) are purified, knitted in a hose, and conditioned before the reaction and evaluation.[1] Aqueous sodium hydroxide solution containing the quaternary salt is freshly prepared as the reaction medium.

RESULTS AND DISCUSSION

Typical results of pilot experiments are given in Tables I and II. These results clearly elucidate the effect of concentrations of reactants on the three fiber materials. It appears that weight loss (%) of PET decreases while that of CDP increases when they are treated in the same bath compared with that when placed in separate baths. Copolyesters show very high weight loss in all cases in comparison with PET.

TABLE I
Alkali-Hydrolysis of PET, CDP, and EDP Yarns in the Presence of Quaternary Salt

NaOH	I = 0.025*N*,	II = 0.01*N*,	III = 1*N*
Alkyl-dimethyl-benzyl-ammonium chloride			10 g/L
M : L ratio			1 : 50
Temperature			97°C
Time			30 min
(at 1*N* NaOH = 15 min)			
	Weight loss (%)		
Polymer	I	II	III
PET	7.94	20.89	60.08
CDP	12.32	36.67	Disintegrates
EDP	12.08	37.02	Disintegrates

TABLE II
Alkali Hydrolysis of PET and CDP in Same (Together) and Different Baths (Alone)

Conditions	A	B
NaOH (*n*)	0.025	0.2
Quaternary salt (g/L)	10	0.1
M : L ratio	1 : 50	1 : 25
Temperature and time		97°C/30 min

	Weight loss (%)			
	PET		CDP	
Bath	Alone	Together[a]	Alone	Together
A	7.94	5.91	12.32	13.15
B	6.50	2.76	5.40	5.78

[a] PET and CDP materials in the same bath.

Effect of Quaternary Salt Concentration

PET and CDP yarns are treated with a solution of NaOH (0.2 *N*) containing 0.01 to 10 g/L quaternary salt, at material to liquor ratio of 1 : 25 and 1 : 50 and temperature of 97°C for 30 minutes. The loss in weight (%) is correlated with the concentration of quaternary salt (log scale) in the bath in Figure 1.

The weight loss (%) slowly increases up to 0.05 g salt/L, then very rapidly up to 1 g salt/L, after which it increases slowly until reaching a steady value. Thus the concentration range of 0.1–1.0 g salt/L is very critical. Except at very low salt concentration (see insert in Fig. 1), CDP shows higher weight loss than PET. The weight loss for both fibers is similar at 0.1 g salt/L.

The weight loss in both materials is higher at M : L ratio of 1 : 50 than that at 1 : 25 at any concentration of the quaternary salt. CDP yarn shows higher sensitivity to M : L ratio than PET yarn in the concentration range above 0.1 g salt/L.

This is the case even when the curves in Figure 1 have tapered off. This clearly shows that the effect of material-liquor ratio is not due to the "quantity" (on weight of fiber) of the quaternary salt under the two conditions. For example 10 g/L at M : L ratio of 1 : 25 and 5 g/L at M : L ratio of 1 : 50 will have same quantity of quaternary salt on weight of fiber. Sodium hydroxide in the bath is consumed during the course of reaction, and therefore its quantity is important in deciding the available NaOH in the bath during the reaction. At M : L ratios of 1 : 25 and 1 : 50, it is 20% and 40% on weight of fiber, respectively. Thus, when the liquor ratio changes, the quantity of NaOH and, in turn, the maximum loss in weight (%) also change. A + 40 g, NaOH can dissolve 96 g PET while 20 g NaOH can dissolve only 48 g PET. Therefore

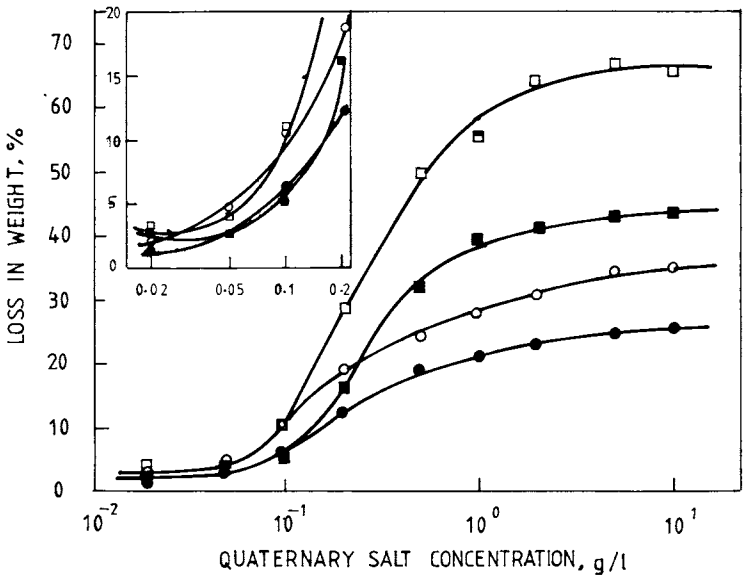

Fig. 1. Loss in weight (%) vs. concentration of quaternary ammonium salt in the bath (log scale). Reaction bath: NaOH 0.2 N; salt varied; temperature 97°C; time 30 min; M : L ratio 1 : 50 (○, □), 1 : 25 (●, ■); PET ○, ●; CDP □, ■.

the quantity of NaOH (normality and M : L ratio) becomes the deciding factor. If NaOH quantity is more, that is, if M : L ratio is higher, the concentration of NaOH will drop at a slower rate during the reaction, giving a correspondingly higher rate of hydrolysis. This is clearly illustrated by varying the concentration of NaOH at fixed quaternary salt concentration in the bath.

Effect of Alkali Concentration

The reaction mixtures now contain fixed concentrations of quaternary salt (0.05 g/L where rates of PET and CDP are similar in Fig. 1) and 0 to 40 g/L (1*N*) sodium hydroxide. The reaction is carried out at 97°C for 30 min, using the M : L ratio of 1 : 50. The results are graphically presented in Figure 2. The loss in weight (%) of PET is slightly higher than that of CDP material at very low concentration of NaOH (see insert figure) which appears almost equal at the concentration of 0.2 NaOH. On further increase in NaOH concentration, the weight loss (%) increases very rapidly; CDP material showing greater loss

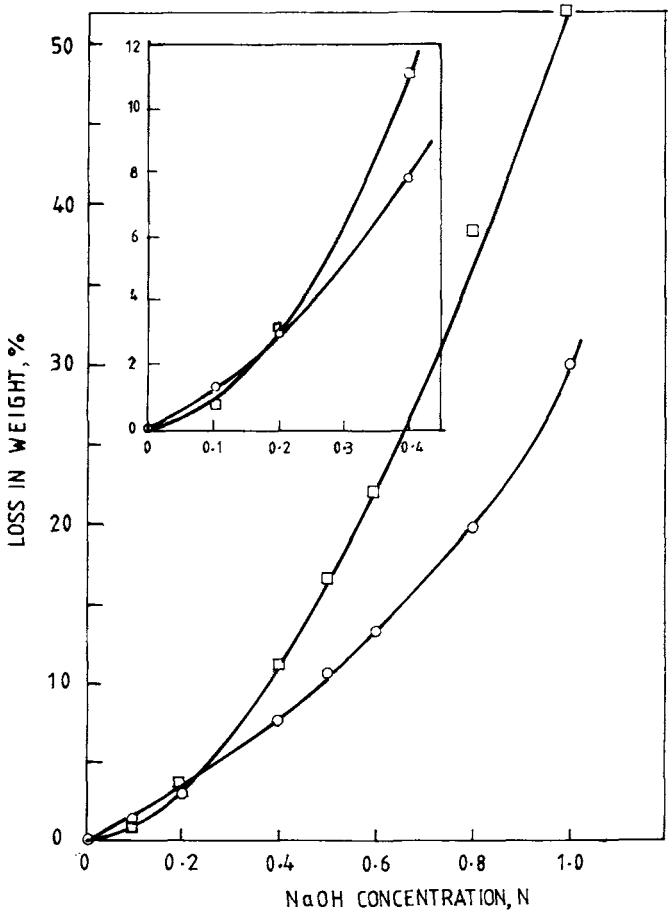

Fig. 2. Loss in weight (%) vs. concentration of alkali in bath. Reaction bath: NaOH 0.1*N*; salt 0.05 g/L; temperature 97°C; time; 30 min; M : L ratio 1 : 50; PET ○; CDP □.

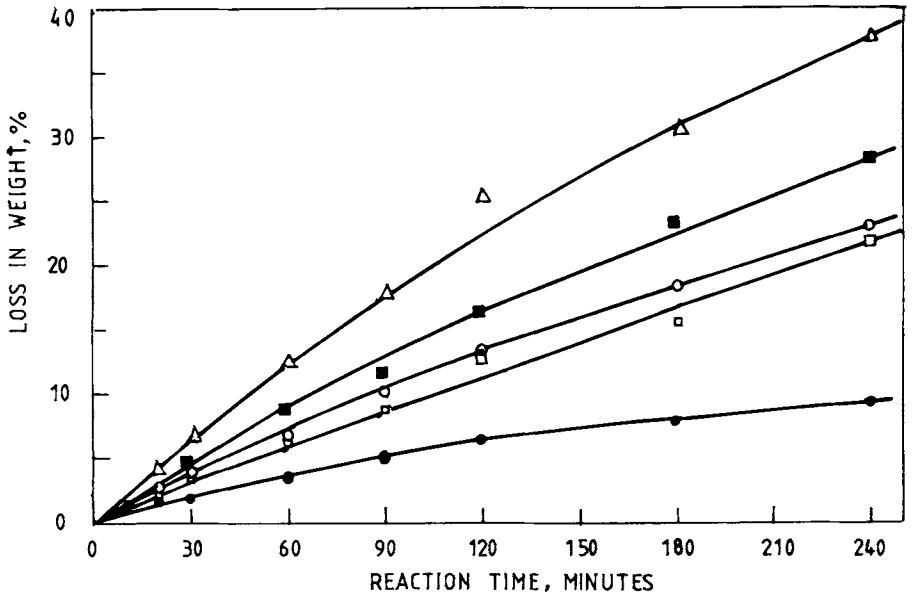

Fig. 3. Loss in weight (%) vs. reaction time at 97°C. Reaction bath: NaOH 0.2*N*; salt: 0.05 g/L; M : L ratio 1 : 50; PET ○; CDP □; EDP Δ; PET ● and CDP ■ in union in same bath.

than PET material. Thus the reaction mixture having 0.02 *N* NaOH and 0.05 g/L salt (when both the polymers show similar loss in weight) is used for the study of rate of reaction. The reaction is carried for different lengths of time using PET, CDP, EDP, and union of PET-CDP (in the same bath). The plots of weight loss (%) versus time are shown in Figure 3. The rate of hydrolysis increases in the following order. PET (in union with CDP)〈PET, CDP〈CDP (in union with PET)〈EDP.

The rate plots of PET and CDP are close, confirming that their rates of reaction under the bath conditions are similar. However, when the two polymers are treated together in the same bath (as union), CDP shows far greater loss in weight (%) than PET at any time of reaction. The rate of reaction of PET in union drops considerably. EDP polymer shows maximum rate of hydrolysis.

On hydrolysis of polyesters, disodium terephthalate is formed from one repeat unit (Mw 192) of the macromolecule. Thus the amount of NaOH present in the reaction mixture during the course of the reaction can be calculated from the loss in weight (192 g will consume 80 g NaOH),[2] knowing the initial concentration of NaOH and M : L ratio. In the present case, 40 g NaOH in the bath per 100 g polymer will form disodium salt with 96 g loss in weight (i.e., 96%). Thus by subtracting the loss in weight (%) from 96, the equivalent concentration of NaOH remaining in the bath can be determined. The plots of log residual (equivalent) concentration versus time are shown in Figure 4. All the rate plots are linear, confirming the first-order kinetics with respect to NaOH concentration. Furthermore, it appears that the moiety lost by the fiber material is one repeat unit at a time throughout the course of the reaction and not big chunks of polymer. In the single-bath–two-polymer

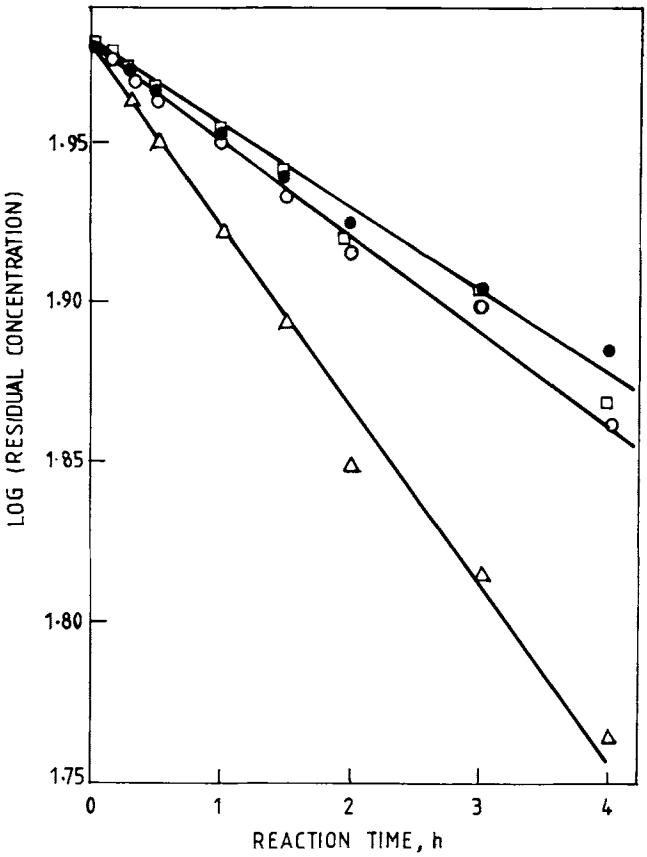

Fig. 4. First-order kinetics with respect to NaOH concentration in the bath (see text for details). Legend same as in Figure 3.

reaction, the loss in weight of both the polymers is added together for the calculation of equivalent concentration of NaOH in the bath. For all the fibers, the weight of losing repeat unit is taken as 192. In union, even though CDP has shown enhanced rate of hydrolysis (Fig. 3) the overall rate of alkali consumption has dropped, giving the lowest slope of the rate plot. This behavior of the PET–CDP union may be explained if we consider the M : L ratio with respect to individual fibers. CDP and PET in union are in the ratio 1 : 1, the M : L ratio with respect to each polymer thus is 1 : 100. For higher M : L ratio, CDP material shows much higher loss in weight than PET material (Fig. 1) The effect of higher ratio on PET is much less. This initial difference in the rates of the two polymers increases further as CDP yarn becomes thinner with loss in weight as the reaction progresses,[1] consuming more and more NaOH which lowers the rate of hydrolysis of PET. Thus, when two polymers are present together in the bath, reaction of CDP is accelerated while that of PET is retarded (Table II), even when the two fibers exhibit similar rates of hydrolysis when treated individually in separate baths.

The exact role of concentration and quantity of NaOH becomes clear if we carry out the reaction by taking 40% NaOH on weight polymer and diluting it

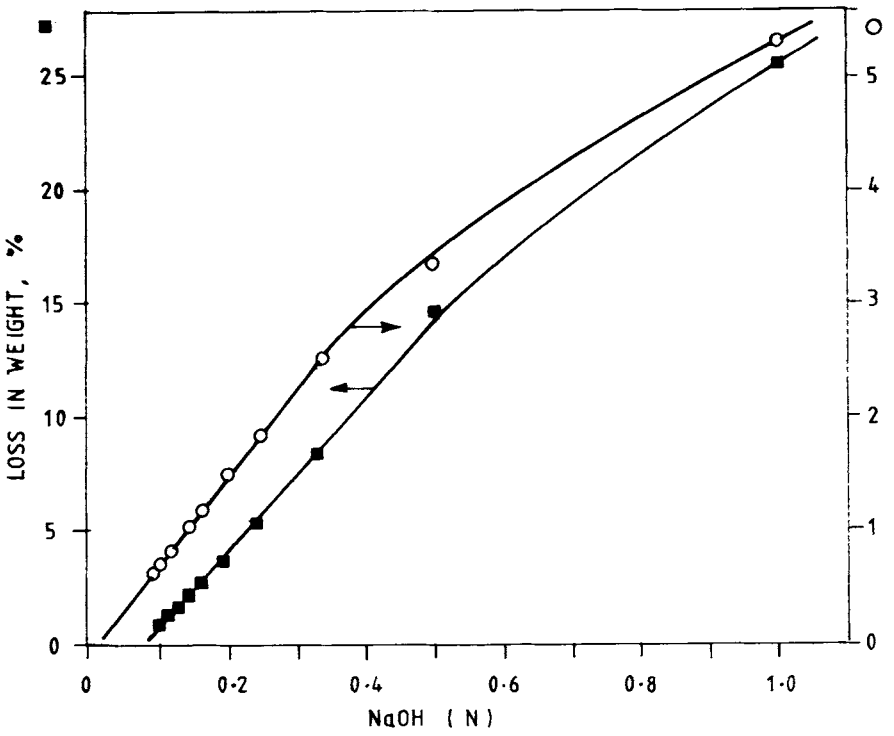

Fig. 5. Loss in weight (%) vs. NaOH concentration in the bath. Reaction bath: NaOH 40% wt/wt of fiber; water varied to get 0.1 to 1*N* NaOH; M:L ratio varies from 1.100 to 1:10; 97°C/40 min; PET ○; CDP ■.

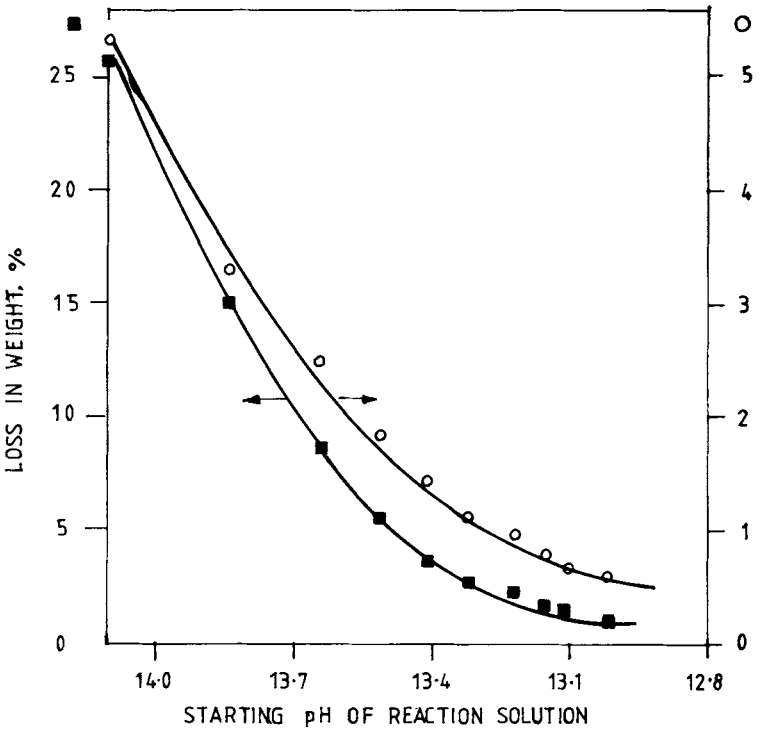

Fig. 6. Loss in weight (%) vs. pH of the bath (conditions and legends same as in Fig. 5).

to various extent to get M : L ratio from 1 : 100 to 1 : 10 when NaOH concentration in the bath is 0.1 *N* to 1*N*. The reaction is carried at 97°C for 40 min. The loss in weight of PET and CDP are correlated with NaOH concentration and pH of the bath in Figures 5–6. The pH of the bath decreases with decreased NaOH concentration and the loss in weight (%) decreases accordingly. Thus, the concentration of NaOH in the bath is the rate-determining factor and the higher amount of NaOH on fiber basis to maintain the concentration at a higher level, giving loss in weight. As the reaction proceeds, NaOH is consumed and there is a drop in its concentration which will lower the reaction rate as seen from the data in Figure 5 for high loss in weight (%).

Effects of Temperature

The reaction is carried out over a range of temperatures up to 100°C. Typical results are shown in Figures 7 and 8 when the reaction bath consists of 0.1*N* NaOH and 10 g salt/L and M:L ratio of 1:100 and the reaction time is 40 min. The data appear to be represented by smooth curves without

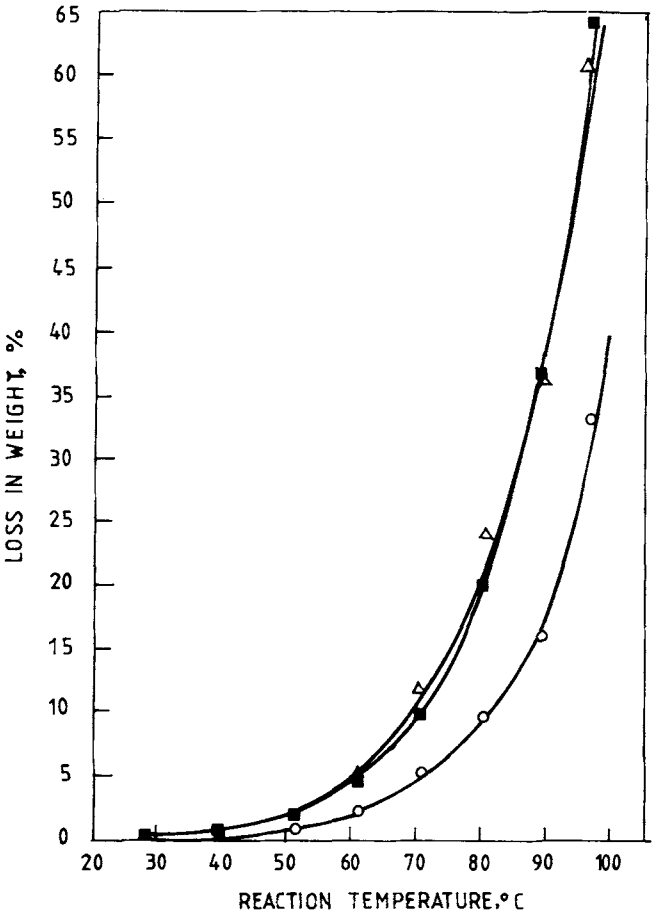

Fig. 7. Loss in weight (%) with reaction-temperature. Reaction bath: NaOH 0.1*N*; time 40 min; salt 10 g/L; M : L ratio 1 : 100; PET ○; CDP ■; EDP Δ.

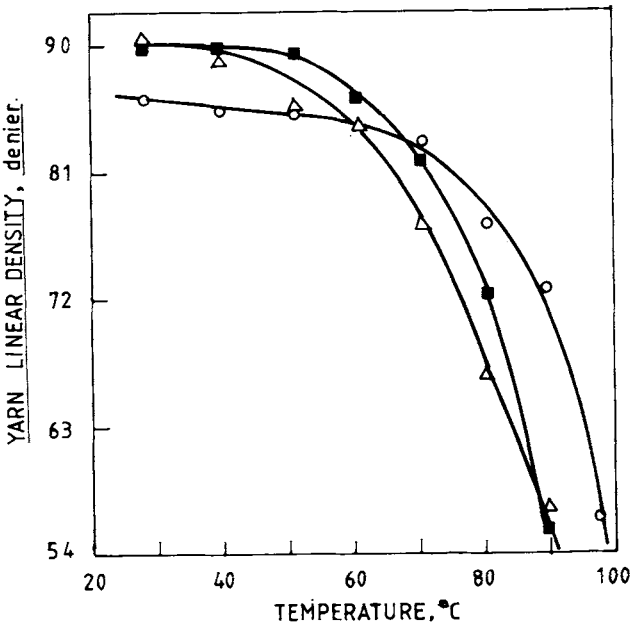

Fig. 8. Yarn linear density (d.Tex) with reaction temperature (legends and conditions as in Fig. 7).

any apparent breaks near glass transition temperature (T_g) as seen in similar curves for the reaction without quaternary salt in the bath (see Ref. 1; Fig.9). Arrhenius plots are constructed assuming the loss in weight (%) in a given time represents the rate of reaction at all temperatures (Fig.9). These plots do not show any break. The linear slope of these plots is calculated by feeding the data to the computer as detailed in the earlier paper.[1] The results are given in Table III. The coefficient of correlation is above 95%. The apparent activation energy for the process is of the order of 15.2 kcal/mol. The process of diffusion into the fiber phase requires higher activation energy[3] and it may be concluded that no rate-determining diffusion process is involved in the reaction of alkali and polyesters. All three fibers show similar magnitude of apparent activation energy though their T_8 values are not the same. The presence of quaternary salt has eliminated the jump in reaction rates after T_g. [1]Since the reaction is probably restricted mainly to the fiber surface, only separation of the repeat unit away from the fiber surface will be involved.

Mechanical Properties

Breaking load, tenacity, and % elongation to break of the treated fibers are correlated with the reaction temperature in Figures 10–12. Though breaking load versus reaction temperature shows no clear breaks in the plots, the tenacity versus temperature plots show distinct breaks at 57°, 62°, and 49°C for PET, CDP, EDP, respectively. Breaks in similar plots in the absence of quaternary salt in the bath were at temperatures higher by 5–8°C.[1] There is another break at each plot at higher temperature, which may be attributed to very heavy damage by the loss in weight. The filament sections with small

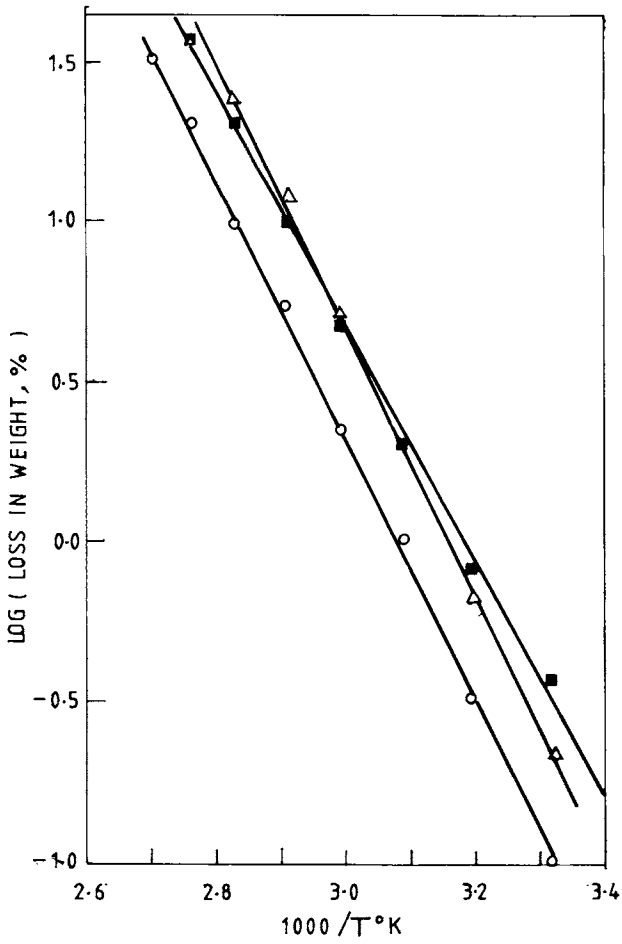

Fig. 9. Arrhenius type of plots. (Legends and conditions as in Fig. 7). (Loss in weight (%) at fixed time is assumed to represent the reaction rate when M : L ratio is 1 : 100.)

local diameters are prone to concentrate the tensile stress during testing of tensile strength. The fiber has become brittle with a large drop in elongation to break (%). The elongation to break (%) shows a linear relationship with temperature without any break for copolyesters and a break at 51°C for PET.

TABLE III
Apparent Activation Energy (ΔE) for Alkali Hydrolysis of PET, CDP, and EDP Filaments in the Presence of Quaternary Salt (Fig. 7)

Polymer material	Slope $\times 10^{-3}$	Degree of correlation (R)	ΔE (kcal/mol)
PET	−3.459	−0.9726	15.8
CDP	−3.143	−0.9733	14.3
EDP	−3.383	−0.9668	15.4
Average	−3.329	−0.9709	15.17

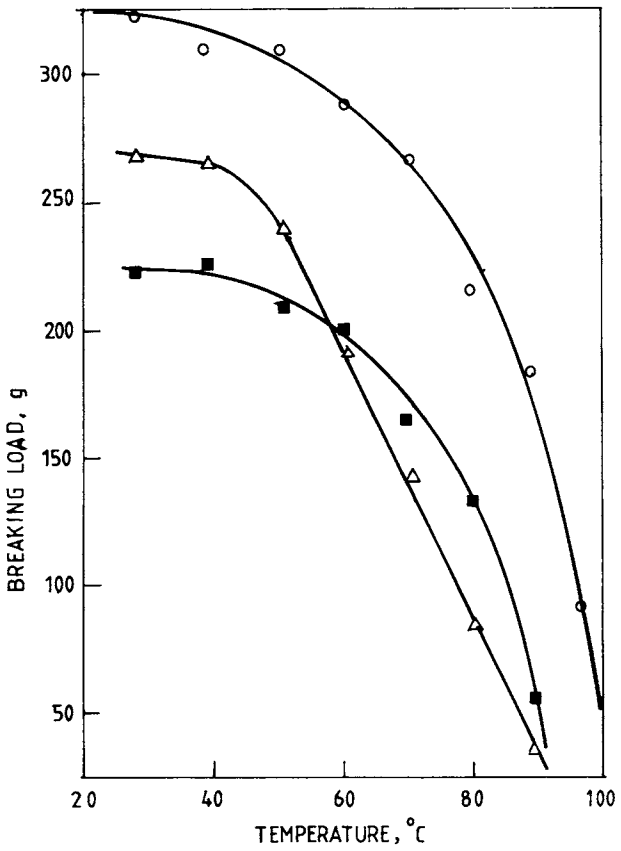

Fig. 10. Breaking load vs. reaction temperature (legends and conditions as in Fig. 7).

The mechanical properties are thus affected to a greater extent when quaternary salt is present in the reaction mixture. The relationship between tenacity and loss in weight (%) at different temperatures is shown in Figure 13. Initially, the drop in tenacity is very high for PET and EDP yarns. Otherwise the relationships are linear. When all the data on tenacity and loss in weight (%) are correlated (Fig. 14) using the computer analysis technique,[1] the observations are confirmed (Table IV). The slopes of the plots for PET and CDP are higher in the presence of salt than in its absence.[1]

Addition of quaternary salt has accelerated the rate of hydrolysis and damage to the fiber. It has eliminated the break in Arrhenius type plots which are clearly seen in the absence of salt in the bath (Ref. 1; Fig. 14). The ΔE value of 15 kcal/mol remains the same over the entire range of temperature. Thus below T_g, ΔE value has increased by about 5 kcal/mol and above T_g it has decreased by similar amount by the addition of quaternary salt to the reaction mixture. (In the absence of quaternary salt, ΔE is 10.68 and 20.13 kcal/mol, respectively below and above T_g.)[1] Shet et al.[4] have suggested that the quaternary salt neutralizes the negative charge on the PET surface thus facilitating the anions' approach to the polyester surface and avoiding repulsion. CDP fiber surface with sulfonic acid groups in the comonomer will be

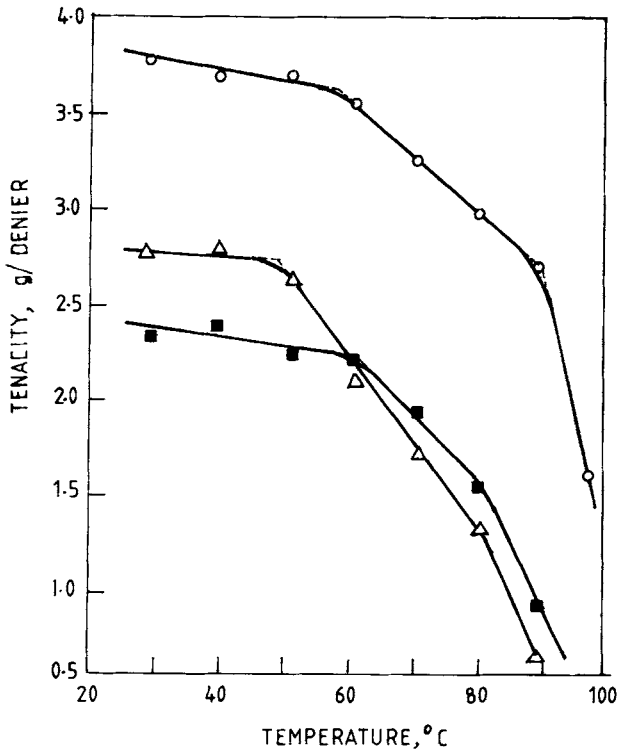

Fig. 11. Tenacity of filaments vs. reaction temperature (legends and conditions as in Fig. 7).

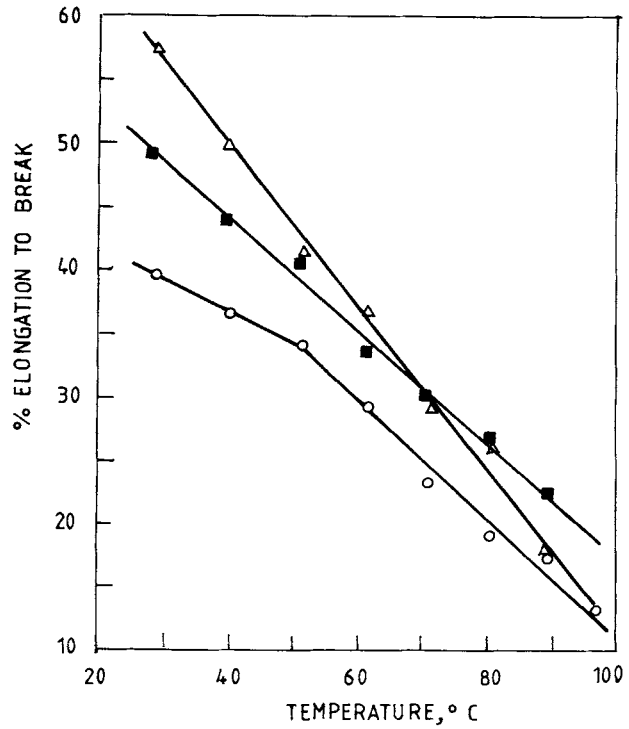

Fig. 12. Elongation to break (%) vs. reaction temperature (legends and conditions as in Fig. 7).

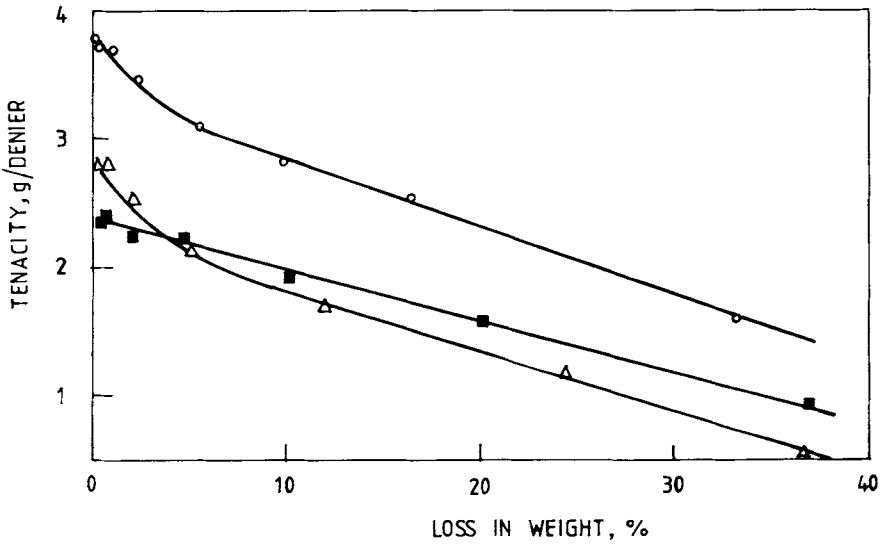

Fig. 13. Relation between tenacity and loss in weight (%) (legends and conditions as in Fig. 7).

more electronegative than PET fiber surface. However, the rate of hydrolysis of CDP material is always greater than that of PET material except when the concentration of quaternary salt is very low and NaOH is 0.2*N*. Probably under these conditions quaternary salt may form a salt with the sulfonic acid groups on the CPD surface and become blocked, rendering itself ineffective in accelerating the rate of hydrolysis. Once the available sulfonic acid groups are saturated with the quaternary salts, the remaining quaternary salt will become available. It is well known that quaternary salts block sulfonic (and sulfate) groups in acrylic fibers and act to retard dyeing with cationic dyes. A

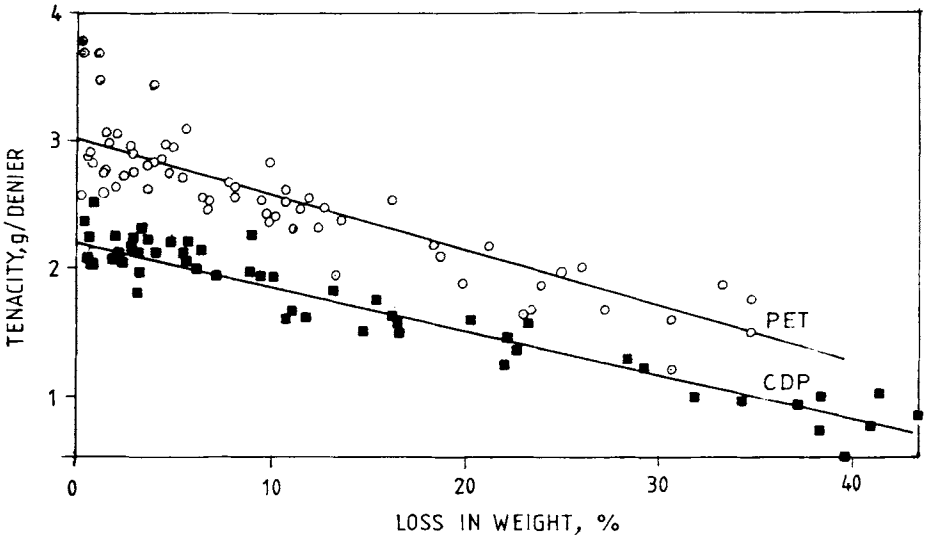

Fig. 14. Tenacity-loss in weight (%) relationships for PET and CDP from all experimental data (computed results in Table IV).

TABLE IV
Tenacity-Weight Loss (%) Relationship[a] (Fig. 11)

	PET	CDP
Slope (M)	−0.0452	−0.0344
Intercept (C) (g/d)	3.010	2.195
Coefficient of correlation	−0.8111	−0.9363
No. of readings	63	57

[a]Samples which were too brittle to measure the denier or mechanical properties are not considered.

similar mechanism is valid at low concentration of quaternary salt in the present case. In PET, the quaternary salt remains free to act, and therefore accelerates the rate of hydrolysis even at low concentration. Furthermore, it is the concentration of quaternary salt and not the quantity which decides its activity in the reaction as discussed earlier (Fig 1).

Thus for acceleration of the reaction, the quaternary salt must be free and not reacted with the fiber. Though the rate of hydrolysis significantly increases in the presence of quaternary salt in the range of 0.1 to 1.0 g/L, there appears to be little uniform penetration, if any, into the fiber phase. The activation energy value is very small for a diffusion process, similar in magnitude for all three fibers, even though the rates of hydrolysis of these fibers are significantly different from each other.

CONCLUSION

The rates of hydrolysis of polyester and copolyesters with NaOH increases when quaternary ammonium salt is present in the reaction mixture. Salt concentration in the range of 0.1–1 g/L is most effective and for a given concentration of NaOH (g/L), higher material to liquor ratio gives higher loss in weight (%). The reaction follows first-order kinetics with respect to NaOH concentration. The rate of loss in weight (%) of PET and CDP in union is significantly different from that in separate baths, CDP shows greater loss and PET shows much less loss in union than when treated individually. The order of loss in weight thus is PET (in union)〈CDP PET〈CDP (in union)〈EDP when bath contains 0.05 g salt/L and 8 g NaOH/L. The polymer loses weight with one repeat unit (Mw 192) in the polymer chain at a time and not in larger segments of polymer macromolecule, and the consumption of NaOH can be equated with the loss in weight as single repeat units. In the case of CDP, if three repeat units (in which one is comonomer) are dissolving together they are hydrolyzed very rapidly into monomer salts.

Arrhenius type plots do not show breaks around T_g of the fibers. The apparent activation energy for the process is 15.2 kcal/mol, which differs by about ± 5 kcal/mol from that for hydrolysis without quaternary salt in the bath (before and after T_g). All the data agree with the topochemical mechanism of the reaction. There is no diffusion process in the rate-determining reaction.

The fiber is damaged to a greater extent in the presence of quaternary salt with loss in tenacity and % elongation to break. There is a break in the tenacity versus temperature plots around T_g at a lower temperature than when quaternary salt is absent. Easy dyeable polyester shows maximum damage among the three materials.

References

1. K. V. Datye and B. H. Palan, *J. Appl. Polym. Sci.*, **38**, 1447 (1989).
2. A. DeMaria, *Am. Dyestuff Reptr.*, **68**, 30-32,51, (October 1979).
3. K. V. Datye and A. A. Vaidya *Chemical Processing of Synthetic Fibers and Blends*, J. Wiley & Sons, New York, 1984 p. 87.
4. R. T. Shet, S. H. Zoronian, and H. L. Needles *Blended Textiles Book of Papers*, All India Textile Conf. M. L. Gulrajani, Ed., Textile Association (India), 1981, pp. 260-268.

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