

Effect of Alkali on Filaments of Poly(ethylene Terephthalate) and Its Copolyesters

KESHAV V. DATYE and BHARAT H. PALAN, *Nirlon Synthetic Fibres and Chemicals Ltd., Goregaon East, Bombay 400 063, India*

Synopsis

The alkali hydrolysis of poly(ethylene terephthalate), anionic copolymer of poly(ethylene terephthalate), and block copolymer of poly(ethylene terephthalate)-poly(ethylene glycol) is investigated under a variety of conditions of alkali concentration in aqueous bath, additives, time, and temperature. Measurements of loss in weight, linear density, breaking load, tenacity, elongation to break apart from intrinsic viscosity, fiber density, COOH-end group content, diameter of filaments, and scanning electron micrographs have been analyzed to identify the differences in the action of alkali on these polymer materials.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is susceptible to hydrolysis under strong alkaline conditions at elevated temperatures when hydroxyl anion attacks the electron deficient carbonyl carbon atom of the ester group and, in turn, with a scission of the bond in the polymer chain.^{1,2} The PET material loses its weight when the polymer chains break down and dissolve in the alkaline bath. The attack of highly ionized aqueous sodium hydroxide is limited essentially to the surface of the PET material as the nonpolar PET disfavors diffusion of ionic bodies inside the polymer phase.³ Thus the diameter of PET filaments decreases with the loss of polymer on the surface.² However, the molecular weight and tenacity of the slimmed filaments remain essentially unchanged.²

The rate of hydrolysis is accelerated with the replacement of water with alcohols to get alkali solutions² or with the addition of a quaternary ammonium salt to aqueous alkali solution because of the transport of hydroxyl anions into the polyester phase.⁴⁻⁷ Ammonium hydroxide and aliphatic amines also penetrate the PET phase during their action, which is thus not restricted to the PET surface but continued deep into the polymer phase with the formation of amides.^{3,5-9}

Controlled alkali hydrolysis of PET materials is used commercially to get slimmed lightweight textiles with silklike soft feel.^{1,4} Additionally the weight-reduction finishing process improves the dimensional stability, resistance to abrasion damage, soil-release property, and wettability as well as reducing the development of static charge and pilling tendency of the PET textiles.^{5,9} However, these finishes cannot be used when copolyesters are present in the fabrics as these copolyesters get destroyed during the alkali treatment with excessive uncontrolled loss in weight.¹⁰ In model experiments^{11,12} using dihydroxyethyl terephthalate (PET monomer) and dihydroxyethyl-5-sulfoisophthalate (CDP monomer), it has been shown that the anionic group in the

comonomer for cationic dyeable polyester does not accelerate the rate of alkali hydrolysis of the ester. Furthermore, the comonomer in cationic dyeable polyester (CDP) is only about 2–3 mol %. Thus the mechanism of hydrolysis of copolyesters vis-à-vis PET needs to be elucidated to understand the high rate of alkali hydrolysis of copolyesters.

Scope of the Present Work

The action of aqueous sodium hydroxide solutions on PET and two copolyesters, CDP, and EDP (easy dyeable polyester) filaments is investigated under a variety of conditions of concentration, pH, additives, time and temperature. For this purpose, loss in weight (%), linear density (dtex), breaking load, tenacity, % elongation to break, —COOH end-group concentration, intrinsic viscosity, fiber diameter, and density as well as scanning electron micrographs of the three polymer filaments are studied.

The effect of addition of quaternary ammonium salt-alkyl (C_{12} – C_{14})-dimethyl-benzyl-ammonium chloride to alkali solution on the attack on PET and copolyesters has been discussed in the second part of the investigation.

EXPERIMENTAL

Materials

The polymeric materials have been specified in Table I. Yarns with same number of filaments and similar yarn denier were produced on a commercial high speed spinning unit and the POY thus produced is draw-twisted in the conventional manner. The yarn was knitted in a hose for easy handling during the experiments. The spin finish on the yarn was removed by scouring with dilute solution of a nonionic detergent at 97°C, rinsing with distilled water, and drying at 60°C. The cleaned yarn was conditioned at 65% RH/28–30°C. The boiling water shrinkage of these yarns was not the same for the three polymers and that created small differences in the yarn deniers (as well as in the diameters of filaments) which are ignored. For the study of denier effect, a CDP yarn with significantly different yarn denier and number of filaments was specially spun and used as CDP-yarn B. The actual yarn deniers were used while presenting the data.

TABLE I
Polymers

PET = Poly(ethylene terephthalate)
CDP = Cationic dyeable poly(ethylene terephthalate) having 2 mol % sodium-5-sulfoisophthalate
EDP = Easy dyeable poly(ethylene terephthalate) having 2.5 mol % poly(ethylene glycol)-600 block polymer
<i>Filament yarns</i>
Nominal denier: 95 dtex (for B-yarn: 56 dtex)
No. of filaments: 34 (for B-yarn: 24)
(Other specifications are given in Table IV)

The reagents were of chemically pure grade with 97% or more purity. Freshly distilled water was used for making solutions and for washing the treated materials.

Reaction with Alkali

The conditioned, cleaned polymer-filament hose was weighed accurately and placed in a beaker having an alkali solution at desired temperature. The temperature was accurately maintained by the surrounding constant-temperature thermostatic waterbath. The material to liquor ratio was 1:50. The sample was occasionally moved (to remove gas bubbles and the creases) within the liquor by a glass rod. However, vigorous movement of liquor or the sample was avoided. (These conditions are closed to those practiced in the technical weight reduction treatment of PET textiles.³⁻⁹) In the absence of vigorous stirring of the bath, a thin boundary layer on the fiber surface may remain stationary and, in turn, influence the kinetics of the process. However, this effect was found to be very small, e.g., the loss in weight of PET with 1*N* NaOH at 97°C after 40 min was 10.7% on vigorous stirring and 10.1% without any stirring. Thermal convection of liquor, loose construction of hose, occasional movement of liquor and the sample, and large material to liquor ratio appear to minimize the boundary layer effect.

The beaker was covered for the desired length of time. The sample was then removed from the alkali solution, rinsed in dilute alkali solution (to avoid redeposition of hydrolyzed polymer on the filament surface), followed by distilled water until free from alkali, dilute acetic acid solution, and again distilled water until free from acid. The treated sample was then dried and conditioned as before and used for determining properties.

Properties

The conditioned hose was weighed before (W_1) and after (W_2) the treatment with alkali solution. The loss in weight (%) was given by the following expression:

$$\text{Loss in weight (\%)} = \frac{(W_1 - W_2) \times 100}{W_1}$$

The yarn was wound on a wrap reel from the hose and definite length of yarn was weighed in grams to get dtex (0.9 dtex = den). Linear density (%) was calculated by normalizing the denier (original cleaned yarn = 100).

Breaking load, tenacity, and % elongation to break were determined using Zwick 1510 machine, 500 mm traverse length, and 18–21 s breaking time (speed is adjusted). The average breaking load was divided by the observed denier of the yarn to get the tenacity of the yarn.

RESULTS AND DISCUSSION

Rate of Hydrolysis

The three polymer filaments were treated with 1*N* NaOH at 97°C for different lengths of time. The results are graphically shown in Figures 1–3.

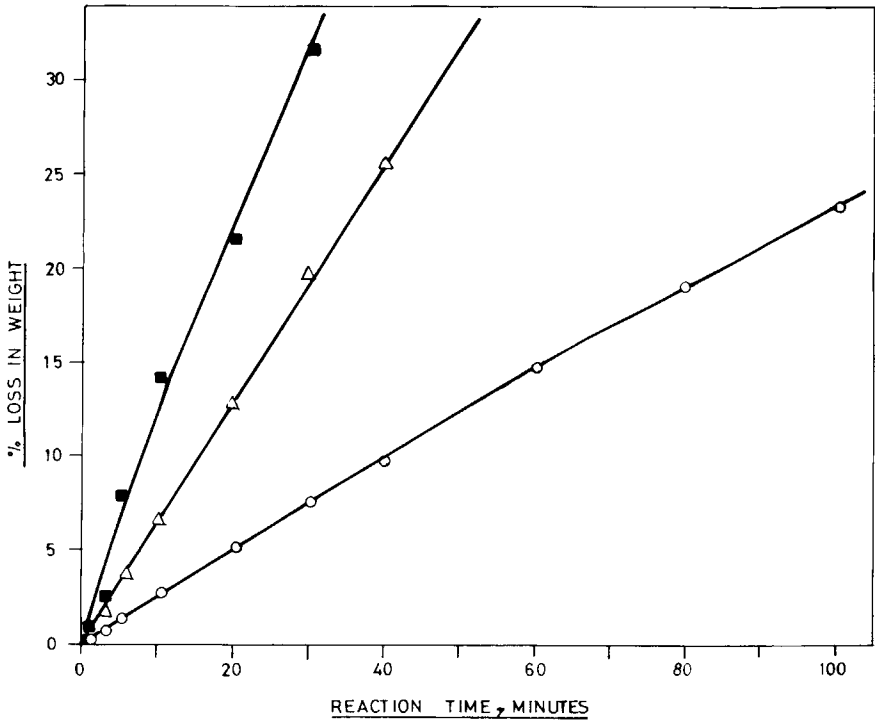


Fig. 1. Loss in weight (%) with time of reaction with 1N NaOH at 97°C: (○) PET; (Δ) EDP; (■) CDP.

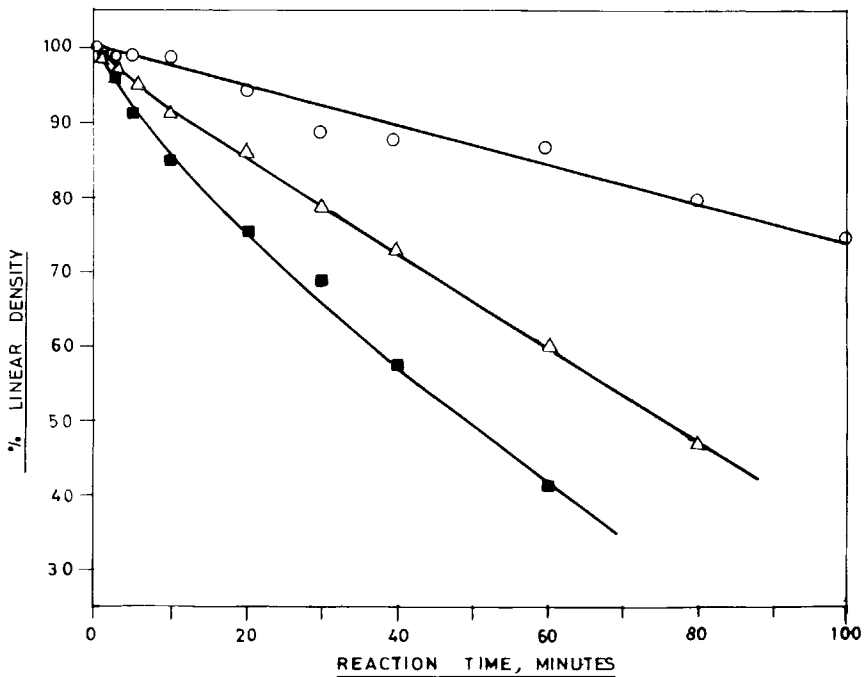


Fig. 2. Relationship of linear density (dtex) of the filaments yarns with time of reaction with 1N NaOH at 97°C: (○) PET; (Δ) EDP; (■) CDP (original linear density is taken as 100).

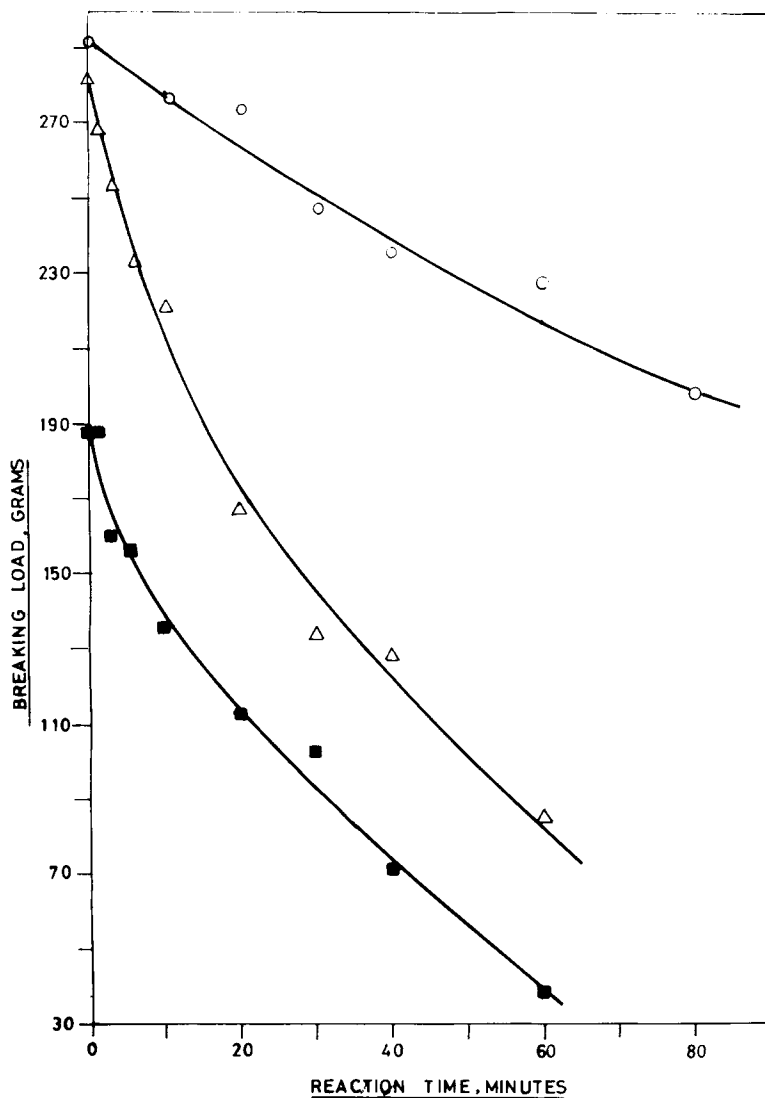


Fig. 3. Breaking load (g) of filament yarns on treatment with 1*N* NaOH at 97°C for different lengths of time: (○) PET; (Δ) EDP; (■) CDP.

The rate of hydrolysis increases in the order PET < EDP < CDP, CDP yarn showing highest loss in weight (%) and drop in linear density. Usually 10–25% loss in weight is aimed at in the commercial deweighting finishes. The three polymer materials need widely different lengths of alkali treatment to get the desired deweighting, e.g., as shown in Table II. It is obvious that PET and copolyesters cannot give similar loss in weight (%) from a given bath under identical conditions of time. The copolyesters lose their strength (measured as breaking load) very rapidly (Fig. 3). If the initial breaking load is normalized for the three polymers as 100, it is seen that within an hour of treatment, the copolyesters lose their 70–80% strength. Typical normalized breaking load values are shown in Table III. EDP yarn shows almost similar loss in strength

TABLE II
Duration of Alkali Treatment for the Given Dewatering of Polymeric Filament Materials

Loss in wt	10%	20%	25%
	Time (min) at 97°C		
PET	40	84	92
EDP	15	31	36
CDP	8	17	19

(10% and 20% from Fig. 1, 25% from Fig. 2)

as CDP yarn even though it has lower loss in weight (%) than the CDP yarn at a given time. The tenacity (g/den) of the yarn is correlated with the loss in weight (%) in Figure 4. The drop in tenacity of CDP yarn is low and slowly increases over the reaction time. On the other hand, PET and EDP yarns exhibit a drop in tenacity with the loss in weight (%) from the beginning which is higher for a given weight loss (%) than that of CDP yarn.

The properties of original and typical treated yarns are given in Table IV. The intrinsic viscosity, COOH end-group concentration, and density of the filaments show no change on alkali treatment. Thus the polymer remaining in the slimmed filaments after alkali treatment is almost identical to the original polymer in its molecular weight, DP, and crystallinity for the fiber. This confirms that the alkali attacks only the fiber surface and removes the hydrolyzed polymer from the surface.² The filaments show loss in thickness and their diameters are smaller than those of the original filaments, in agreement with the above mechanism. The filament continuity remains over a wide range of loss in weight (%) which also supports the mechanism of alkali reaction. Furthermore, as there is no change in the crystallinity (or density) of filaments, it may be said that the alkali attack does not leach out preferentially noncrystalline regions in the fiber.

Effect of Fiber Thickness

Loss in weight (%) with reaction time (with 1N NaOH) at 97°C for CDP-yarn A and yarn B is graphically shown in Figure 5. The yarn A with 2.77 dtex/filament shows a lower rate of loss in weight (%) than the yarn B with 2.315 dtex/filament. The surface area per unit weight of a filament is inversely proportional to the square root of the filament denier when density is same. When this factor is considered by multiplying the weight loss (%)

TABLE III
Normalized Breaking Load of Treated Polymeric Materials

Reaction time (min)	PET	EDP	CDP
0	100	100	100
10	94.6	75.4	75.9
20	90.0	61.4	62.2
40	81.3	43.5	38.9
60	74.0	29.1	20.2

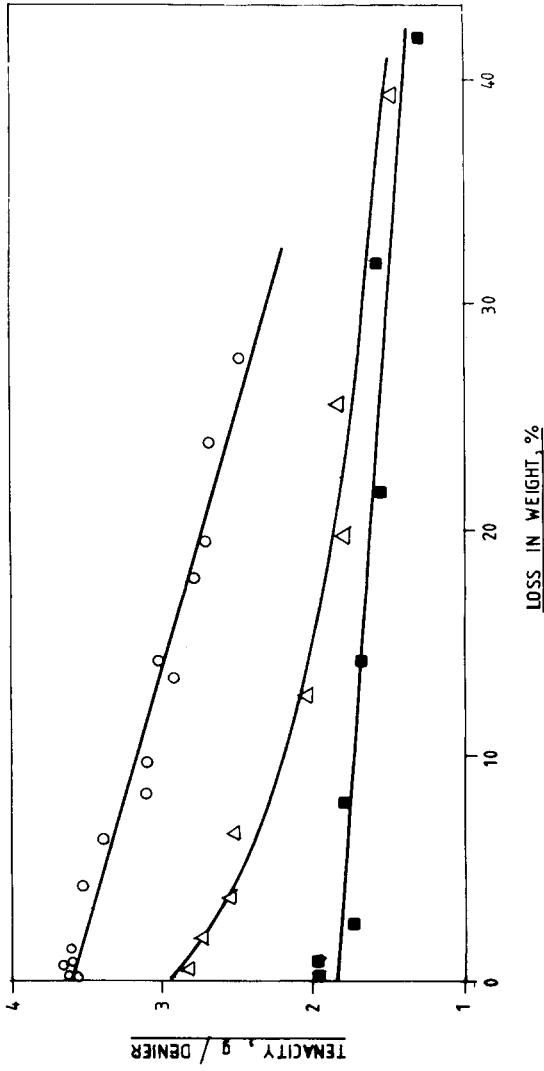


Fig. 4. Tenacity of filaments (g/den) vs. loss in weight (%) of the yarn on treatment with 1N NaOH at 97°C: (○) PET; (△) EDP; (■) CDP.

TABLE IV
 Properties of Filament Yarns^a

Property	Sample	PET	CDP	EDP
Loss in weight (%)	I	0	0	0
	II	9.63	31.3	25.6
Intrinsic viscosity (dL/g) phenol-tetrachloroethane (60:40), 25°C	I	0.6212	0.5029	0.6205
	II	0.6205	0.5004	0.6221
COOH end groups (eq/g × 10 ⁶)	I	44.8	47.7	33.3
	II	44.2	50.0	33.6
Filament diameter (μm)	I	16.46	15.02	17.33
	II	15.30	12.71	14.15
Density (g/cc) (floatation method)	I	1.382	1.382	1.370
	II	1.382	1.385	1.374

^aReaction conditions: 1N NaOH, 97°C, 40 min (30 min for CDP). Yarn before treatment: I sample. Yarn after treatment: II sample.

with the square root of the filament denier (dtex), the rate curves of the two yarns should merge into one plot if surface area is influencing the rate. The filament deniers at each stage of reaction were determined and the weight loss (%) values were multiplied by the square root of these deniers. The results of these corrections are shown in Figure 6 wherein it is seen that the plots for two yarns merge into a single plot. (It was not possible to measure deniers on heavy weight loss and those data are ignored.) Thus, it appears that the fiber

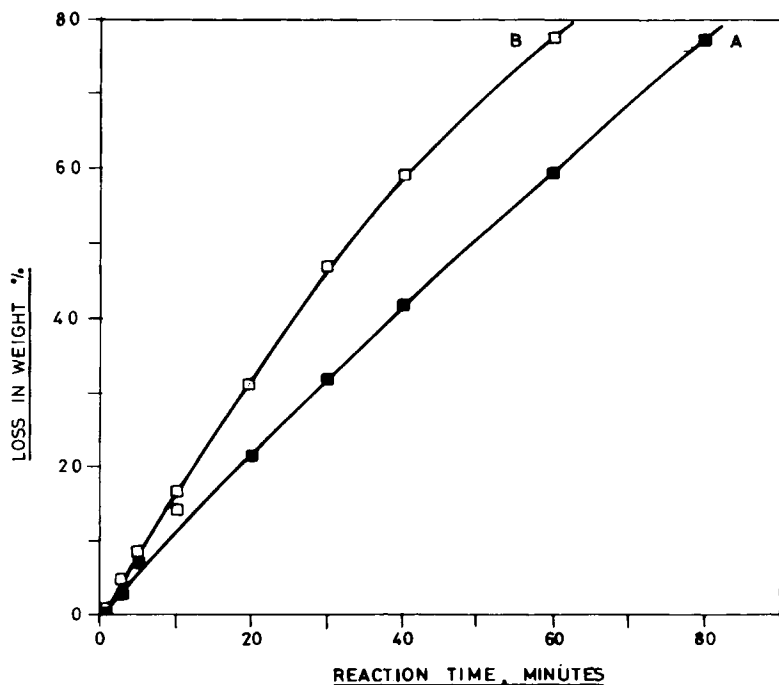


Fig. 5. Comparison of rate of hydrolysis of two CDP yarns: (□) CDP-yarn B (55.5 dtex/24 fil), (■) CDP-yarn A (99.4 dtex/34 fil).

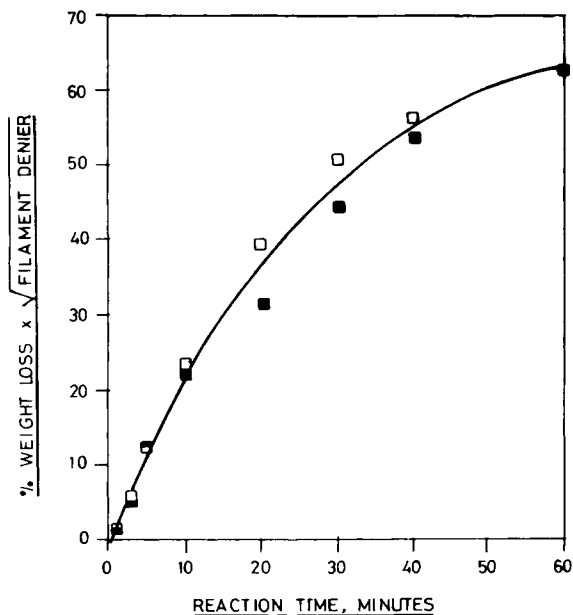


Fig. 6. Rate plot after correction for surface area of the filaments in two CDP yarns (signs same as in Fig. 5).

thickness or the surface area per unit weight is a factor influencing the rate of alkali hydrolysis of polyester yarns.

The filaments maintain the shape of their cross section and with time of reaction; they become thinner and thinner, i.e., the surface area per unit weight of filaments increases with the hydrolysis of the polymer. The rate of hydrolysis would therefore increase with time of reaction. The cumulative loss in weight (%) does not indicate this effect as it does not consider the actual weight of yarn at a given time and it takes the original weight of yarn for calculating the integral loss in weight (%).

The data are calculated to find the average rate of loss in weight (%) per minute over the intervals of time using the following expressions:

$$R = \frac{W_2 - W_1}{100 - W_1} \times \frac{100}{t_2 - t_1}$$

where R = rate of weight loss (%) per min from time t_1 and W_1 and W_2 are cumulative weight losses (%) at times t_1 and t_2 . Typical results of these computations are shown in Figure 7. It is observed in all the cases that the rate of hydrolysis increases with loss in weight (%) of yarn as per expectations as the filament becomes thinner and thinner with time. It may therefore be concluded that the alkali reaction is influenced by the surface area of the filaments of polyester and copolyesters.

Effect of pH

The effect of the anion concentration in the reaction mixture on the action on PET and CDP filament yarns was examined with and without varying

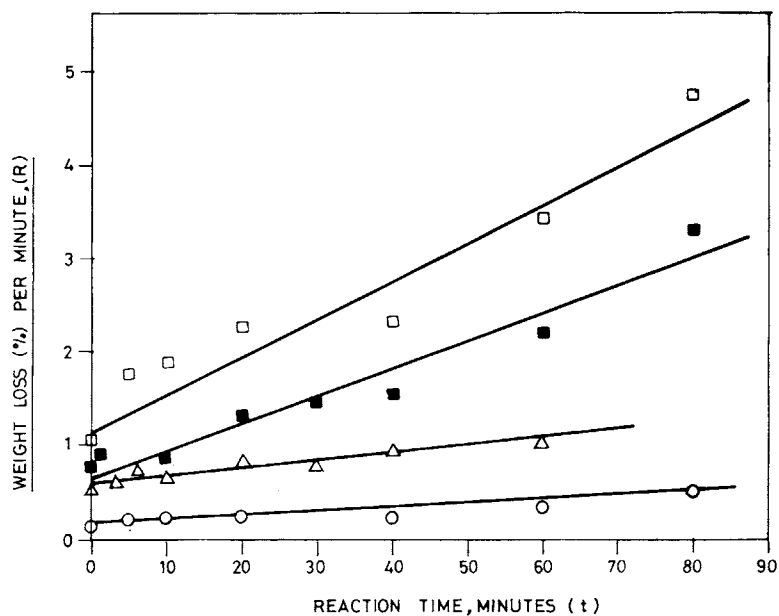


Fig. 7. rate of hydrolysis at intervals of reaction time (for details, see text): (○) PET; (△) EDP; (■) CDP-yarn A; (□) CDP-yarn B.

sodium ion concentration. Thus 1N NaOH was diluted with (a) water and (b) 1N Na_2CO_3 to get different solutions. 1N Na_2CO_3 was used as such as a solution with infinite dilution (NaOH-nil). The treatment was carried out under identical conditions (97°C , 40 min, M:L ratio = 1:50, etc.) and loss in weight (%) and pH of the solution at the beginning were recorded. The results are graphically presented in Figure 8 using appropriate scales for PET and CDP. The rate of hydrolysis of PET and CDP decreases rapidly as the pH of the solution drops on dilution, reaching a very small value when NaOH concentration is zero. The data for PET with and without variation in Na^+ concentration are represented by the same curve. The presence of sodium carbonate does not help the process of hydrolysis of PET with NaOH. However, this is not the case with CDP where the rate of hydrolysis increases when water is replaced by 1N Na_2CO_3 . Thus, even though the pH is slightly lower for NaOH of a given concentration CDP exhibits more loss in weight (%) (when water is replaced by 1N Na_2CO_3 in the bath). The presence of the sulfonic acid group in the comonomer probably helps in dissolving the product of hydrolysis in the sodium carbonate solution, thus facilitating the process. This is supported by the data on hydrolysis in the presence of sodium salts in NaOH bath as follows. In the absence of NaOH, sodium carbonate does not hydrolyze the CDP or PET material to a significant extent.

Effect of Salt

Sodium salt of mono-, di-, and tribasic acids was added to get 0.1N salt in 1N NaOH, which was used as a reaction mixture at 97°C for 40 min. The nominal concentration of Na^+ was thus 1.1M. The pH of the reaction mixture

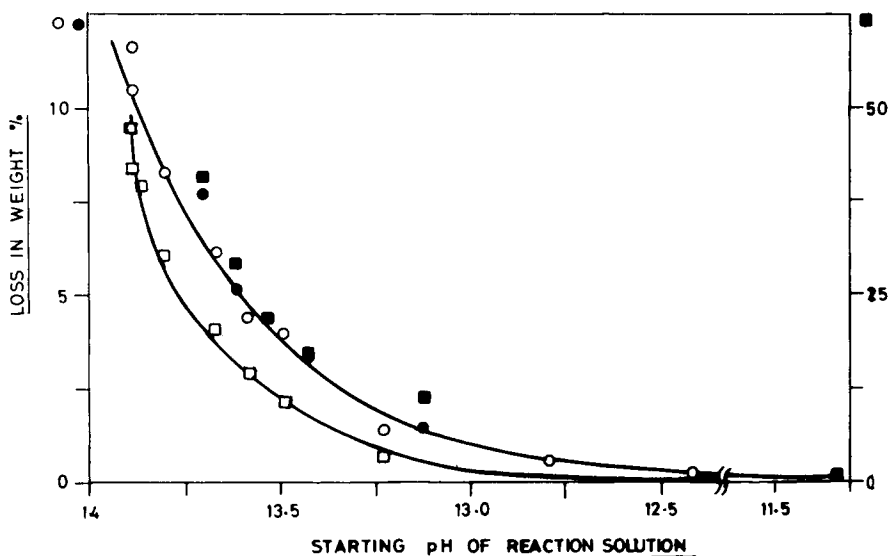


Fig. 8. Effect of pH of the reaction-solution on the loss in weight (%) of PET and CDP yarns (97°C, 40 min). Y-axis scale for CDP is fivefold (as shown on the right side). (□) CDP and (○) PET: NaOH with varying dilution with water. (■) CDP and (●) PET: NaOH/Na₂CO₃, 1*N* (total concentration).

and loss in weight (%) of PET and CDP are recorded in Table V. The pH of the reaction mixture is suppressed by the addition of salts. However, a drop in the weight loss (%) is small as compared to that observed for similar drop in pH on dilution (Fig. 8). The loss in weight (%) for both the polymers is lowest when trisodium phosphate was present when a drop in pH was the highest among the series of solutions with salts. Increase in Na⁺ concentration from 1*M* to 1.1*M* has not increased the rate of hydrolysis, confirming that the sodium-ion concentration has no role in the alkali reaction with PET and copolymers. The hydroxyl anions get consumed when they react with the polymer and the amount of NaOH lost from the reaction mixture matches well with the gravimetric determination of weight loss of polymer.⁴ When the reaction mixture is a dilute sodium hydroxide solution, there will be a further drop in the concentration of NaOH and, in turn, pH as the reaction proceeds. On the other hand, when the ionization is suppressed by the common ion effect of sodium salt, NaOH will dissociate to regain the starting anion

TABLE V
Effect of Salts on Alkali Hydrolysis of PET and CDP (1*N* NaOH, 0.1*N* Salt, 97°C, 40 min)

Additive	pH	Loss in weight (%)	
		PET	CDP
Nil	13.86	11.65	47.39
Sodium formate	13.70	11.51	44.27
Sodium chloride	13.70	9.75	44.26
Sodium sulfate	13.61	10.87	42.05
Trisodium phosphate	13.41	8.23	35.99

concentration during the reaction as Na^+ and OH^- ions are consumed in the reaction, and the reaction may proceed without much drop in pH or ion concentrations. This mechanism explains the difference in the loss in weight (%) at similar pH under the two conditions.

Addition of 1% alkyl (C_{12} – C_{14})-dimethyl-benzyl-ammonium chloride to 1N NaOH accelerates the reaction and within 15 min at 97°C CDP yarn disintegrates and PET yarn loses more than 60% of its weight. This catalytic behavior of quaternary ammonium salt has been exhaustively studied separately.

Effect of Temperature

The alkali hydrolysis was carried out with 1N NaOH at different temperatures in the range of 25–100°C for 40 min. The properties of treated yarns are correlated with temperature in Figures 9–12. All the properties show discontinuity in the plots and there is a sudden change when the temperature is increased beyond a point. The apparent transition temperatures from these breaks in the plots are determined and given in Table VI. The transition temperatures from loss in weight (%) (Fig. 9) and the linear density (dtex) of the yarns (Fig. 10) for the three polymers are between 76 and 78°C, i.e., they are not much affected by the nature of the polymeric materials. On the other hand, the tenacity (Fig. 11) and % elongation to break (Fig. 12) show transition temperatures in the range of 50–67°C, which are significantly different for the three polymeric materials, the EDP showing minimum transition temperatures.

Polyester and copolyesters show transition temperatures in many other properties. On heating, the glassy polymer changes to a rubbery elastic state at a temperature range when concerted segmental mobility of polymer chains begins. This temperature, T_g , varies with the conditions under which the polymer is heated. For comparison, the transition temperatures of the three polymeric materials were determined by dyeing, with a disperse dye (1%) for 10 min. The dye on the fiber is correlated with temperature in Figure 13 to arrive at the T_g values which are included in Table VI. It is seen that the transition values by dyeing are almost similar to those obtained by the alkali-hydrolysis and are in between those obtained from loss in weight (%) or linear density data and those from the mechanical properties. EDP has the lowest T_g among the three polymers and shows lowest transition temperature for the mechanical properties as well. This is not the case with PET and CDP yarns, which show no correlation between T_g and transition temperature for the mechanical properties.

Results in Table VI and Figures 9–13 are explained as follows. The adsorption of dye is controlled by the diffusion of dye inside the polymer phase. Therefore, the transition in rate of dye uptake is related to the glass transition (and T_g) of the polymer filament. The attack of anions in alkali hydrolysis of PET and copolyesters probably does not involve any diffusion process in the polymer phase to control the kinetics of the reaction. The removal of polymer fragments after hydrolysis also appears not to have any diffusional process inside the fiber phase since anions do not diffuse deep into the polymer phase and the hydrolysis is essentially taking place on the fiber

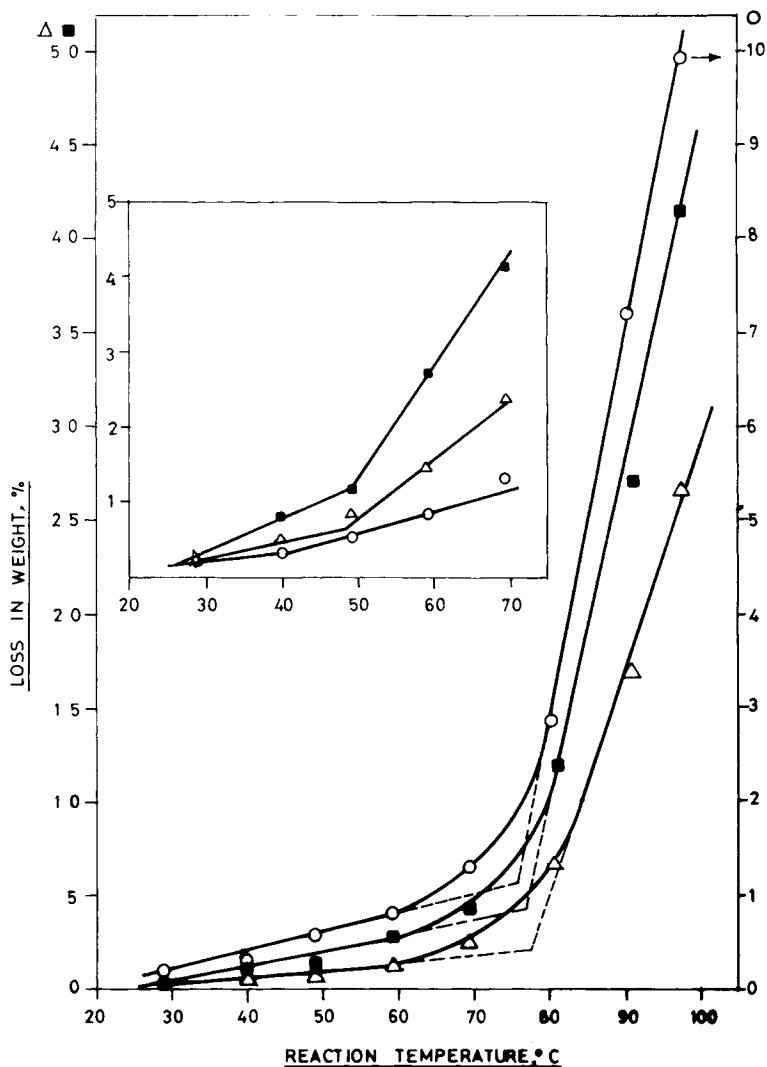


Fig. 9. Loss in weight (%) with temperature of reaction with 1N NaOH for 40 min: (○) PET; (Δ) EDP; (■) CDP. [The Y-axis has two scales, one for PET and a fivefold bigger one for copolyester. The inset figure shows the initial part of the curves (up to 70°C) before the transition.]

surface. Because of this, three polymers show similar transition temperature for loss in weight (%) and linear density. This transition is around the T_g of these polymer yarns. The segmental movement of polymer chains above T_g helps in leaching out the hydrolyzed polymer, giving a sudden jump in the rate of reaction.

The attack of anions on the fiber surface is at some places severe enough to develop ditches, holes, and weak spots along the length of the filaments. The filament becomes locally thinner at these spots. Such places are easily seen under the optical microscope. The contribution of such deep attacks to the loss in weight (%) is not very high to influence its total value. However, such

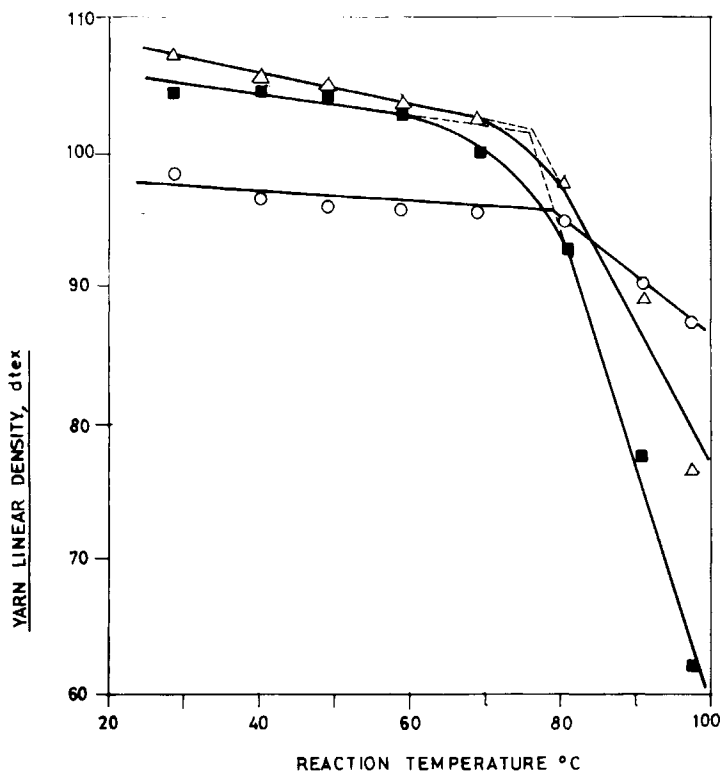


Fig. 10. Relationship of linear density (dtex) of filament yarns with temperature of reaction with 1*N* NaOH for 40 min: (○) PET; (Δ) EDP; (■) CDP.

defects bring down the mechanical properties of the yarn. With rise in temperature, the damage increases rapidly and, just before T_g , shows a sudden increase with a corresponding drop in the mechanical properties. The T_g of EDP yarn is the lowest among the three polymers and the transition temperature for the mechanical properties of EDP yarn is also the lowest.

Apparent Activation Energy of Hydrolysis

Arrhenius type plots of log (weight loss % in a fixed time) vs. reciprocal absolute temperature (K) are constructed in Figure 14. The plots are not continuous but show a break around T_g when apparent energy of activation ΔE (from the slopes) almost doubles (Table VII). The ΔE for diffusion process in PET is of the order of 35–40 kcal/mol.¹³ Present low ΔE values thus suggest that there is no diffusion process in the fiber material, which controls the rate of hydrolysis even after T_g . Furthermore, apparent activation energy is less below T_g than above T_g while, in the diffusion process, the activation energy below T_g is very high (ca. 100 kcal/mol).¹³

Ingamells et al.¹² found, on the basis of elemental analysis, that probably a trimer with one comonomer residue in the chain molecule is leached out from CDP during the hydrolysis in water (at neutral pH). In the alkali hydrolysis also probably the sodium salt of the 5-sulfoisophthalic acid facilitates the

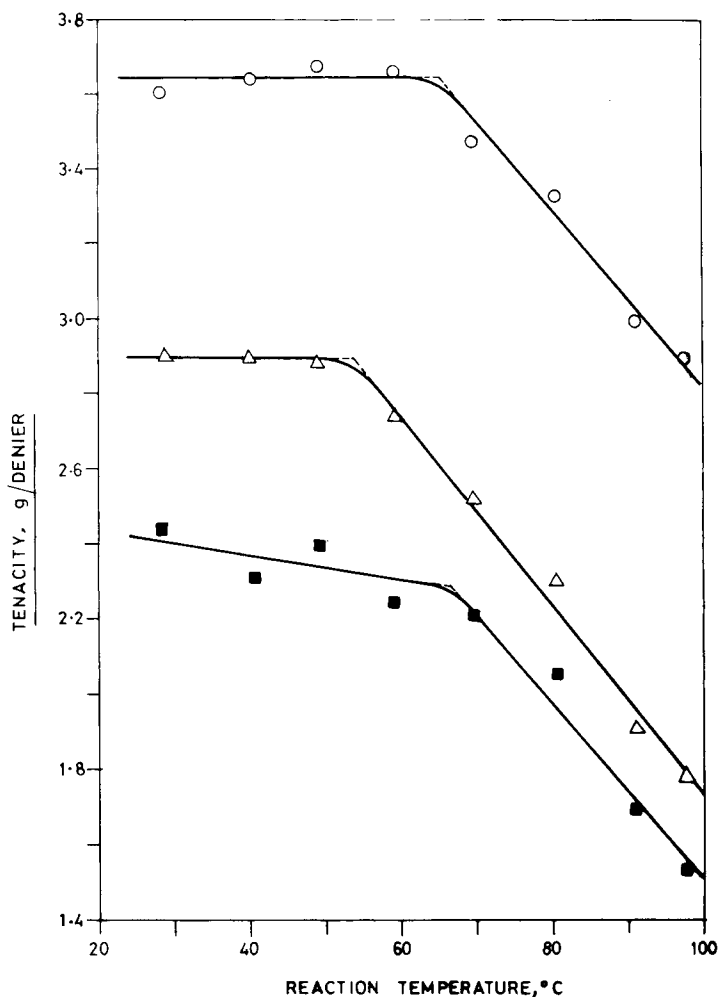


Fig. 11. Tenacity of filaments (g/den) in relation to the temperature of reaction with 1*N* NaOH for 40 min: (○) PET; (△) EDP; (■) CDP.

dissolution for the hydrolyzed polymer fraction. The chains where comonomer is present will have a solubilizing group and with a scission of an ester bond the two groups may bring down the chain segment into the alkali solution. The character of the surface in CDP yarn will be less hydrophobic in nature than that in PET, which may allow the approach of anions to the carbonyl carbon atoms on the surface easily. The mol weight of Na-5 sulfoisophthalic acid in CDP is higher than terephthalic acid by 103 (ca. 50%) and, when it is leached out as a trimer (mol wt 679), the loss in weight will be higher. All these factors contribute to the high rate of alkali action on CDP yarn.

Statistical Treatment

To confirm that the mechanism of alkali attack on polyester fiber is the same under various conditions employed in different experiments, all the data

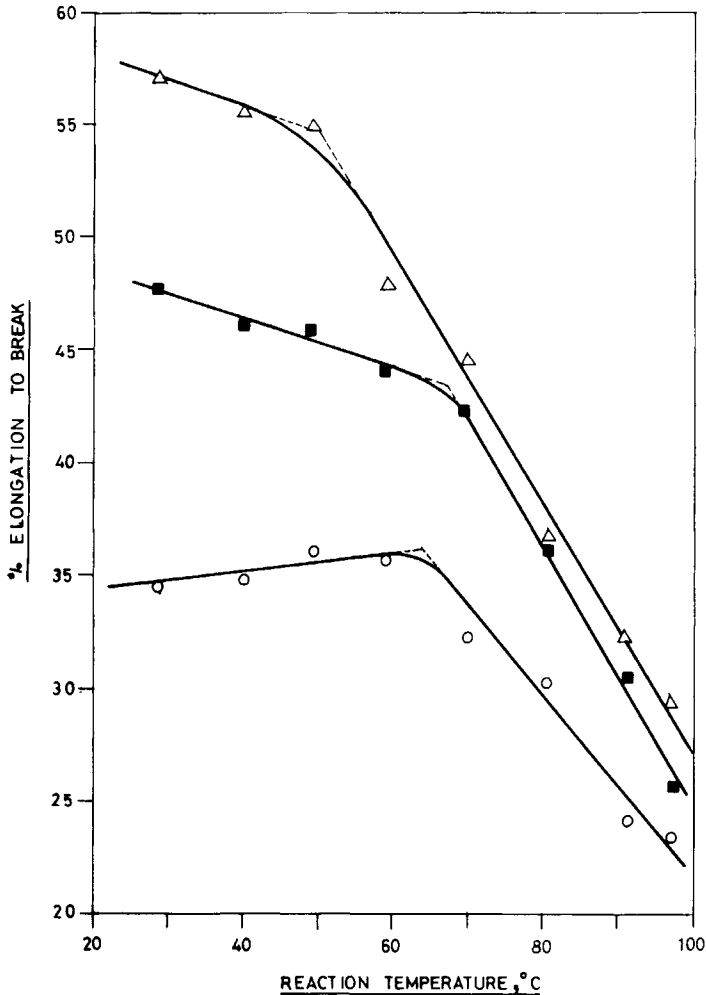


Fig. 12. Elongation (%) to break of filament yarns in relation to the temperature of reaction with 1*N* NaOH for 40 min: (○) PET; (Δ) EDP; (■) CDP.

are considered for tenacity–weight loss relationship. The data are fed into the computer to find the best fitting line, intercept (C), slope (M), and coefficient of correlation (regression) (R). Results are plotted in Figure 15 for PET and CDP yarns. The following expressions are used¹⁴:

$$C = \frac{\sum X^2 \sum Y - \sum X \sum XY}{n \sum X^2 - (\sum X)^2}$$

$$M = \frac{n \sum XY - \sum X \sum Y}{n \sum X^2 - (\sum X)^2}$$

$$R = \left(\frac{C \sum Y + M \sum XY - \bar{Y} \sum Y}{\sum Y^2 - \bar{Y} \sum Y} \right)^{1/2}$$

TABLE VI
Transition Temperature from Various Properties

Property	Transition temperature (°C)		
	PET	CDP	EDP
Loss in weight (%) (Fig. 9)	76	76.5	77
Linear density (dtex) (Fig. 10)	78	76.5	76.5
Tenacity (g/den) (Fig. 11)	65	67	54
% Elongation to break (Fig. 12)	64	67	50
Dye adsorption (Fig. 13)	73	71	66

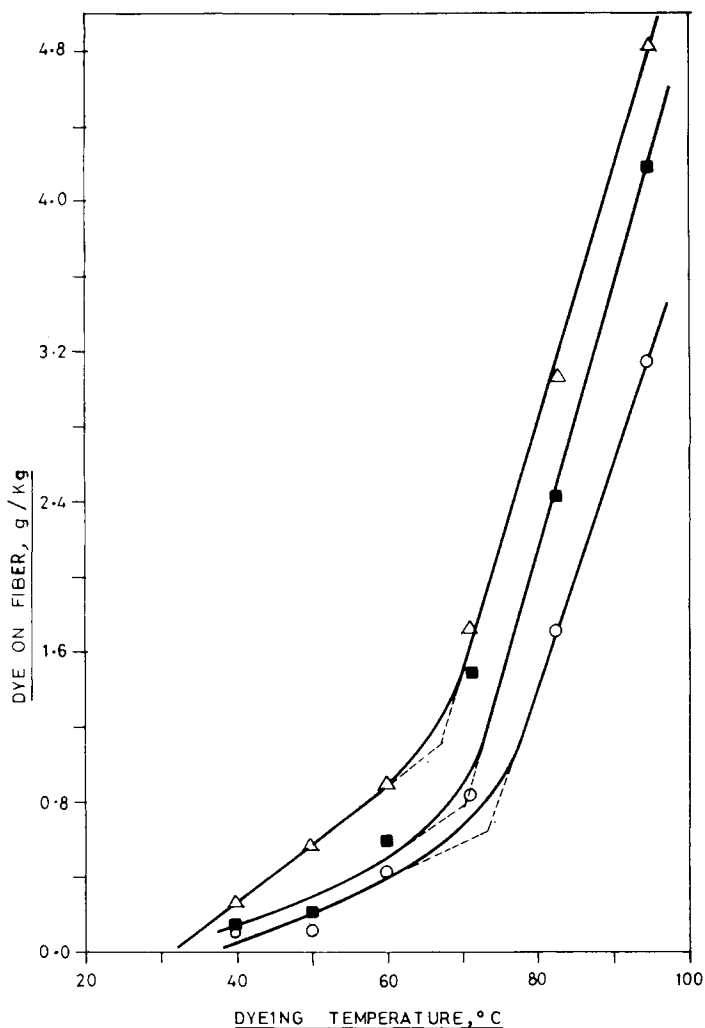


Fig. 13. Dye uptake of the polymer yarns at different temperatures (1% dye, 10 min): (○) PET; (Δ) EDP; (■) CDP.

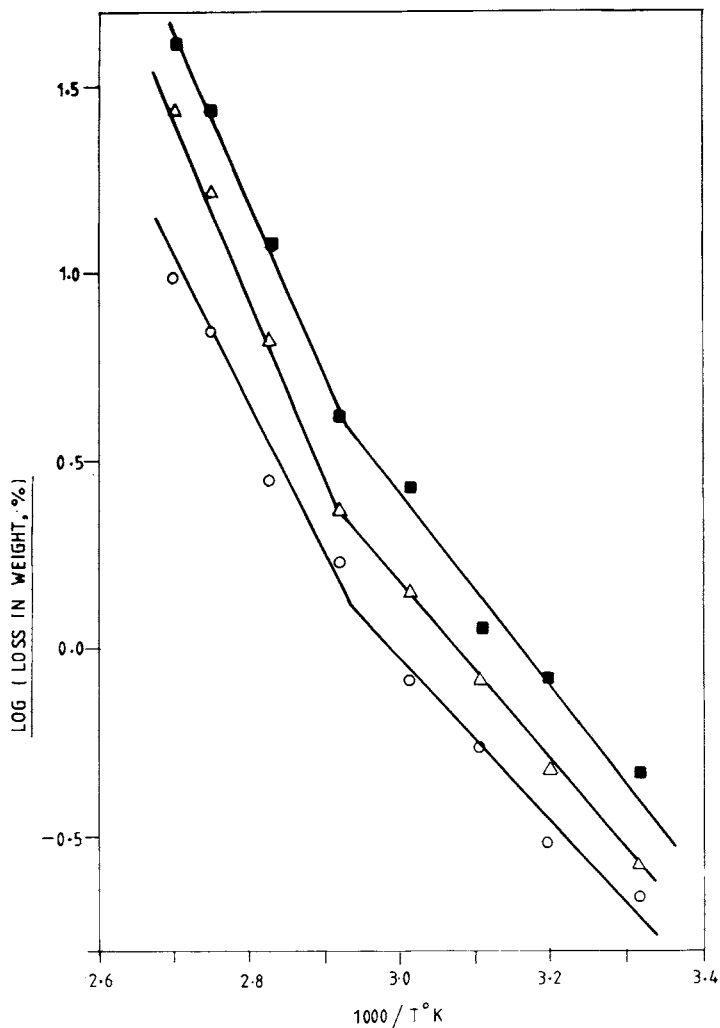


Fig. 14. Arrhenius plots for the reaction of NaOH with PET (○), CDP (□), and EDP (Δ) yarns (details from Fig. 9).

TABLE VII
Apparent Activation Energy (ΔE) for Alkali Hydrolysis of PET, CDP,
and EDP Fiber Materials (Fig. 14)

Material	ΔE (kcal/mol)	
	Below T_g	Above T_g
PET	9.84	18.13
CDP	11.53	20.41
EDP	10.68	21.77
Avg.	10.68	20.13

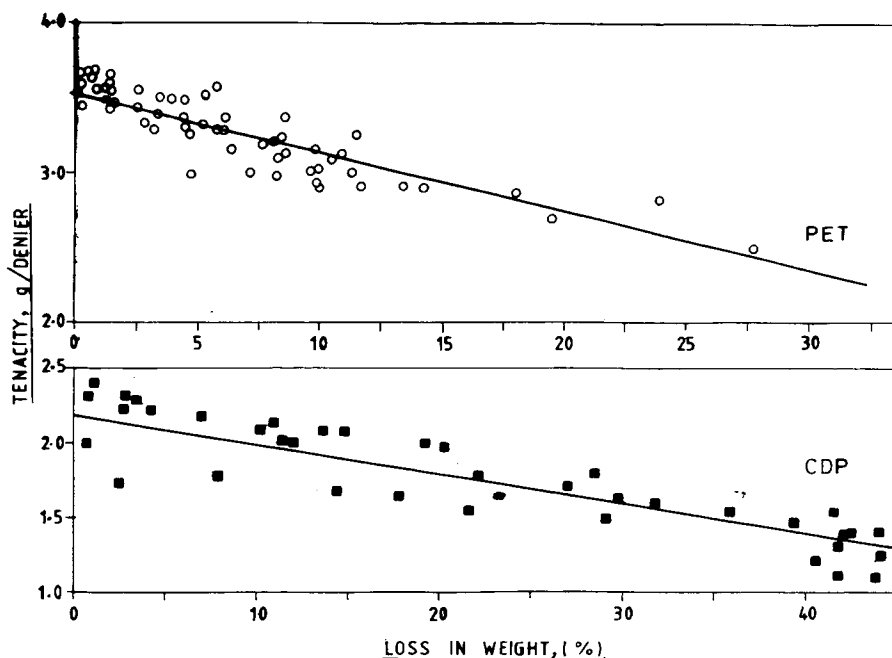


Fig. 15. Tenacity vs. loss in weight (%)—under a variety of reaction conditions for PET and CDP yarns.

where X is loss in weight, \bar{X} = avg loss in weight, Y is tenacity, \bar{Y} = avg tenacity, and n = number of readings. The results are shown in Table VIII. It is seen that all the experimental data can be represented by a single plot for each fiber.

Scanning Electron Micrographs

The polyester and copolyester fibers were examined under scanning electron microscope. With loss in weight, the fibers were becoming thinner and thinner. On high loss in weight, copolyester fibers exhibit deep etching at many places. The ditches thus formed are along the fiber axis in the case of CDP yarns and are radial in direction in the case of EDP yarns. Typical ESM are shown in Figure 16. The micrographs are in agreement with the observed tenacity drop with weight loss. The easy dyeable polyester fiber (EDP) shows rapid loss in

TABLE VIII
Tenacity-Weight Loss (%) Relationship

	PET	CDP
Slope	-0.03936	-0.1992
Intercept	3.535	2.19
Coefficient of correlation	-0.8527	-0.8997
No. of readings	64	40

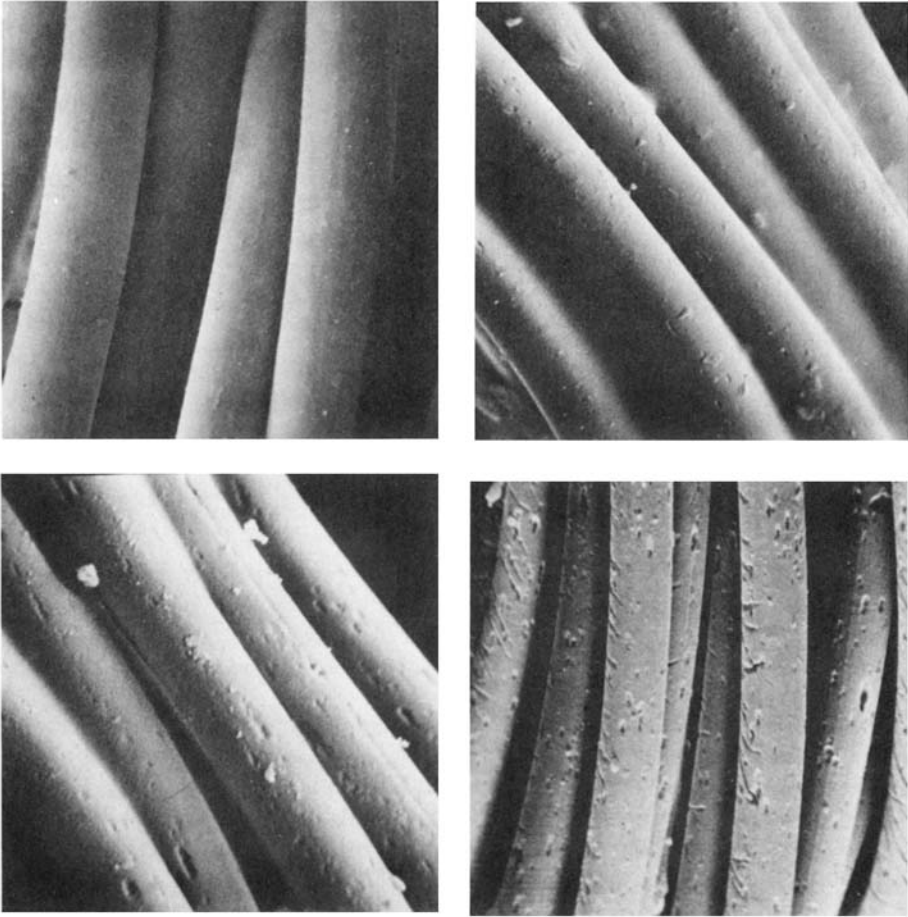


Fig. 16. Scanning electron micrographs of fibers: (a) original; (b) after alkali treatment (PET, CDP, EDP).

tenacity as the ditches are radial in direction and tensile stress concentrates on the uncut small areas, bringing the fracture of filament at low tensile force. On the other hand, cationic dyeable polyester fiber shows cuts parallel to the fiber axis, which does not bring down the tenacity. All the fibers become thinner in diameter showing a drop in breaking load but PET and CDP fiber shows a slow drop in tenacity (see M-values in Table VIII).

CONCLUSION

The rate of hydrolysis of PET, CDP, and EDP filament yarns with aqueous caustic soda varies considerably, and loss in weight (%) is in order PET < EDP < CDP. All the materials remain in filament form even after a considerable loss in weight. The diameter of filaments decreases with the loss in weight with matching drop in breaking load of the yarn. EDP yarn shows higher drop in breaking load for initial small loss in weight. The tenacity

(g/den) drop for the three fibers is, however, low, indicating that the attack is restricted mainly to the fiber surface. This is further seen from the properties of the polymer—viscosity, end-group concentration, and density—which remain essentially unaffected by the alkali attack. Furthermore, the higher rate of hydrolysis of finer denier filaments (original or formed by loss in weight during the reaction) supports this conclusion.

The attacking species is the hydroxyl ions and lowering its concentration by drop in alkali concentration, pH, or adding sodium ions lowers the rate of hydrolysis. Except the common-ion effect, sodium ions play no role in the hydrolysis process. The reaction product dissolves in the reaction mixture leaving the residual polymer free of low mol wt hydrolyzed product. The anionic comonomer probably accelerates the dissolution process. The attack is facilitated with lower T_g and open structure of the polymer, particularly EDP.

Reaction rates increase with temperature of reaction in a discontinuous manner, exhibiting sudden jump around the glass transition temperature of polyester fiber. Mechanical properties and apparent activation energy of reaction also show a sudden break with temperature around T_g , EDP yarn showing the break at much lower temperature. The relationship between tenacity and loss in weight of PET and CDP remains unaffected by temperature and other variations in the reaction conditions.

Under the optical microscope, the surface of copolyester fibers shows etching, ditches, cuts, and holes with increasing loss in weight. The scanning electron micrographs show distinct difference between the two copolymer fiber surfaces. In EDP, the damage to the surface is more and the cuts are radially directed while, in CDP, the damage to the surface appears to be less and the cuts are axially oriented (directed). PET shows very few surface defects. This probably explains the mechanical behavior of EDP vis-à-vis the other two fiber materials, and may have its origin in the fine structure of the polymeric materials.

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