

Studies on Modification of Polyester Fabrics I: Alkaline Hydrolysis*

JAYSHREE DAVE, RAJ KUMAR,[†] and H. C. SRIVASTAVA,[‡]
*Ahmedabad Textile Industry's Research Association (ATIRA),
Ahmedabad-380 015 India*

Synopsis

Hydrolysis of polyester fabrics with sodium hydroxide has been studied with a view to imparting hydrophilicity and other comfort-related properties to polyester textiles. Effect of reaction parameters such as treatment time, concentration of alkali, and temperature on the extent of hydrolysis is examined and the modified fabrics are evaluated for their important physical, mechanical, and physicochemical properties. The mechanism of hydrolytic degradation of polyester fabrics, as determined by the weight loss, has also been ascertained. Alkali progressively degrades polyester by saponification of its ester linkages and results in a loss in weight of the fabric. Weight loss increases linearly with treatment time and nonlinearly with alkali concentration and reaction temperature. A linear correlation exists between strength loss of the fabric and its weight loss. By alkaline hydrolysis, surface hydrophilicity and feel of the fabric are considerably improved, whereas such properties as moisture regain, crease recovery angle, etc., remain practically unchanged. Attempts have been made to explain the results in terms of modifications in the surface characteristics of polyester fabrics.

INTRODUCTION

Polyester possesses several desirable properties such as high strength, attractive handle, dimensional stability, easy-care properties, and suitability for blending with other types of fibers. However, it has certain undesirable qualities such as lack of hydrophilicity, generation and accumulation of static electric charge, and oleophilicity, which have prevented it from enjoying a reputation for comfort.

Various attempts have been made to impart hydrophilicity and other comfort-related properties to polyester textiles.^{1,2} Alkaline hydrolysis, which is one of the ways of modifying polyester, has received considerable attention recently mainly because of its simplicity and implementability on a manufacturing scale without capital investment. A survey of the pertinent literature indicates that alkaline hydrolysis of polyester textiles has been studied extensively with the objective of imparting silk-like properties and improving comfort.³⁻¹⁰ Studies dealing with basic and other aspects of the modification are relatively few,¹¹⁻¹⁴ and in some cases conflicting views have been expressed,^{8,9,12,15,16} particularly regarding moisture regain and dyeing behavior of the hydrolyzed fabrics. Shenai and Nayak⁹ observed that moisture regain of

* This paper forms part of the doctoral thesis submitted by Miss Jayshree Dave to the Gujarat University, Ahmedabad.

[†] Present Address: Research Centre, Indian Petrochemicals Corporation Ltd., Baroda.

[‡] To whom inquiries should be addressed.

polyester fabrics increases with increased concentration of alkali in the presence of quaternary ammonium compounds, whereas Sanders and Zeronian¹² are of the opinion that it remains practically unchanged. Mackawa¹⁶ believes that with an increase in causticizing percentage, the disperse dye exhaustion percentage increases. On the other hand, the work of Padhye and Singhi⁸ indicates that polyester fabrics exhibit a fall in dye uptake as a result of alkali treatment and that by Waters¹⁵ reports no increase in dyeability other than that expected from the increase in surface area of the hydrolyzed fabrics. In view of the conflicting reports by different workers in the field, it was thought worthwhile to carry out a systematic investigation on the alkaline hydrolysis of polyester and to characterize and correlate its various physical, mechanical, and physicochemical properties.

EXPERIMENTAL

Materials

Polyester

Polyester materials used in the present investigation were poly(ethylene terephthalate), PET. Spun/filament polyester fabric was obtained by carbonization of a polyester-cotton (80 : 20) blend fabric containing polyester-cotton (67 : 33) spun yarn and polyester multifilaments in warp and filling directions, respectively, with 70% (w/w) aqueous sulfuric acid. Care was taken to ensure complete removal of cotton component of the blend. Melinex polyester film, used in the study, had a thickness of 15 μm . Polyester fabric having polyester multifilaments in both warp and filling directions was also used for comparison. Important physical characteristics of fabrics, determined following ASTM standard test procedures^{17,18} are summarized in Table I.

Chemicals

Sodium hydroxide and acetic acid used in the present investigation were of laboratory reagent grade. All the solutions were prepared in distilled water having a specific conductance of the order of $1-2 \times 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$. Sodium dodecyl sulfate (SDS), obtained from Koch-Light Laboratories Ltd. (United Kingdom) was used as such without further purification.

TABLE I
Physical Characteristics of Fabrics

Characteristic	Spun/ filament	Filament/ filament
Weight (g/m^2)	71	69
Ends/picks	106/90	106/86
Tex (weft)	9.7	8.6
Count	61.4	—
Air permeability ($\text{cm}^3/\text{cm}^2/\text{s}$)	74.0	—
Thickness (mm)	0.137	0.132
Moisture regain (%)	0.41	0.40

Treatment Procedure

Reaction of polyester with aqueous alkali solutions was carried out by batchwise method. Alkali solution of desired concentration was placed in a round-bottom flask connected to a water condenser having a soda lime guard tube. The flask was attached to a shaker which was kept in a constant temperature ($\pm 1^\circ\text{C}$) oil bath. The flask was left for an hour to attain the temperature of the bath before starting the reaction. Fabric sample (6×6 in.) in duplicate was then immersed in the solution for different spans of time. The material to liquor ratio was 1 : 150. Following the reaction, the samples were washed repeatedly with running water, immersed in 1% (v/v) aqueous acetic acid solution followed by thorough rinsing with distilled water. The samples were air dried and after drying in an oven at $110 \pm 2^\circ\text{C}$ for 2 h, were weighed. The control fabric samples were treated under identical conditions with distilled water instead of aqueous sodium hydroxide solution. Polyester film samples were extracted with carbon tetrachloride before use. All weighings were carried out on a balance having an accuracy of $\pm 5 \mu\text{g}$.

Characterization of Products

Control and treated polyester fabrics were evaluated for important physical, mechanical, and physicochemical properties. Experiments were repeated several times to get a coefficient of variation within $\pm 5\%$.

Physical Properties

Weight Loss

Percent loss in the weight of fabric due to treatment was calculated from oven-dry weights of the fabric, before and after reaction, as follows:

$$\% \text{ Weight loss } (W) = \left[\left[\frac{D - T}{D} \right]_{\text{Sample}} - \left[\frac{D - T}{D} \right]_{\text{Control}} \right] \times 100 \quad (1)$$

where, symbols D and T represent constant oven-dry weights of the fabric before and after the reaction.

Denier and Diameter

The denier of the filament (from weft direction of the fabric) was measured using the standard procedure and the diameter of the single filaments was measured by an optical microscope.

Air Permeability and Openness

Openness, a measure of inter yarn capillary spaces in the fabric was measured on Projectina. The air permeability of the fabric was measured by Air Permeability Tester (Toyo Seiki, Seisaku-Sho Ltd., Japan). All measurements were carried out under a constant air pressure adjusted by maintaining a constant water level (2") in the capillary.

Mechanical Properties

Breaking Strength, Elongation, Tenacity, and Initial Modulus

Before starting the experiment, the fabric samples were conditioned for 24 h in an atmosphere maintained at $65 \pm 2\%$ relative humidity and at 27°C , a secondary standard prescribed for tropical countries. Polyester filament yarns were obtained from the weft direction of the fabric and testing was performed on Instron (Instron Engineering Company, Quincy, MA) at a constant sample length of 5 cm, cross-head speed of 20 cm/min, and a chart speed of 3 cm/min. Values of breaking strength and percentage elongation at break were then read from the curves. The effect of reaction parameters such as treatment time, alkali concentration, and temperature on strength loss was examined. Tenacity was calculated from the data on breaking strength and denier of the multifilaments. The initial modulus of the treated and control polyester samples was estimated from stress-strain curves obtained at a cross-head speed of 1 cm/min and a chart speed of 20 cm/min.

Flexural Rigidity

Flexural rigidity, a measure of bending modulus, and hence, stiffness of the fabric as it is experienced between fingers, was measured using a single Cantilever test.¹⁹ The overall effect of warp and weft is reported as the flexural rigidity value of the fabric.

Flex Abrasion Testing

Flex abrasion testing of the control and modified polyester fabrics was carried out following the ASTM standard test method.²⁰ Rectangular fabric strips (6×1 in.) were cut in warp and weft directions and the number of abrasive cycles required to break the strip under a known tension was measured. An average of values obtained with strips cut parallel to the warp and weft directions is considered as a measure of flex abrasion resistance.

Crease Recovery Angle

The dry crease recovery angle of fabrics was measured using Monsanto Crease Recovery Tester following the ASTM standard test procedure.²¹

Physicochemical Properties

Critical Dissolution Time

Time required to break polyester multifilaments hung vertically with the help of a constant weight in phenol at $50 \pm 2^\circ\text{C}$ was measured. Each measurement was repeated 25 times and the average value is reported.

Moisture Regain

Bulk hydrophilicity of the fabrics was measured as moisture regain under the conditions of humidity and temperature prescribed for tropical countries following the ASTM²² method. Moisture regain was calculated from the constant oven-dry and moisture-sorbed weights of the fabric.

Vertical Wicking Height

Fabric strips (6 × 1 in.) parallel to warp direction of the fabric were cut and hung vertically. The lower end of the strip was weighted down to prevent floating. A 1 cm section of the lower end of the strip was dipped in a water reservoir and allowed to wick. The height of water travelled after 5 min was measured. The transport of water in the fabric was followed visually and was measured with an accuracy of ±1 mm. The test was repeated four times on the same sample and four times on its duplicate. Average of the eight observations so made is reported as the vertical wicking height of the sample.

Contact Angle

Contact angle measurements on polyester film were carried out by photographic method using a microscope equipped with photographic attachment. Polyester film was mounted horizontally under stretched condition. A known amount of water (0.01 mL) was placed on the film as a drop with the help of a micrometer syringe and photographed. The angle between polyester/water and water/air interfaces at the point of intersection in the water phase was measured from the photographs. Contact angle measurements on single filament/fiber were made following the method of Grindstaff.²³

All the measurements were carried out in an atmosphere maintained at 65 ± 2%RH and 27 ± 1°C.

Molecular Weight

Average molecular weight of the control and treated polyester samples was measured by viscosity method using the equation²⁴

$$[\eta] = 1.7 \times 10^{-4} \bar{M}_n^{0.83} \quad (2)$$

where, $[\eta]$ and \bar{M}_n are intrinsic viscosity of solution and molecular weight of the polyester, respectively. A 1% solution of control and treated polyester filaments was prepared in *o*-chlorophenol (99% pure). Flow times of polymer solutions and pure solvent were measured at 25°C. The intrinsic viscosity was calculated from the specific viscosity of the solution using Huggins viscosity slope constant as determined by Todd.²⁵

Soiling and Soil-Release

Studies on soil-release behavior of polyester fabrics was carried out with lubricating oil (grade SAE 40). It had density and coefficient of viscosity of 0.909 g/cm³ and 275 cps, respectively, at 27°C. Soiling was carried out using Accelerotor (Atlas Electric Device Co., USA) by keeping a known amount of oil on the sample and its duplicate (size 4 × 4 in.) in the soiling chamber of Accelerotor and revolving at 2000 rpm for 2 min.

Washing of soiled fabrics was done using a Terg-o-tometer (Osaka-Tsuruga Electric Works Ltd., Japan) with 1 g/L sodium dodecyl sulfate (SDS) solution at 50°C and 50 oscillatory rotations per minute (stroke = 315°) for 10 min.

Evaluation of soiling value of fabric before and after washing was carried out spectrophotometrically using a Pretema spectrophotometer by converting reflectance values into corresponding Kubelka-Munk functions.

Dyeing Behavior

Studies on dyeing behavior of treated and control fabrics were carried out by the carrier dyeing method. Dye uptake by the fabric was measured using Spectronic-100 spectrophotometer (Bausch and Lomb, USA) at the wave length of maximum absorption of the dye. Dye was extracted from the fabric with dimethyl formamide at 50°C. Dye uptake was also estimated by reflectance measurements using Pretema spectrophotometer. Rate of dyeing was studied by measuring optical density of solutions as a function of time during the course of dyeing.

Scanning Electron Microscopy

Fabric samples previously coated with gold in a vacuum coating unit were viewed under a scanning electron microscope (Cambridge Stereoscan Model S4-10) at different magnifications. Control fabric sample was also examined for comparison.

Thermal Analysis

Control and hydrolyzed polyester fabrics were evaluated for their thermal characteristics using a differential scanning calorimeter model DSC-2C (Perkin Elmer Corporation, USA) under a scanning rate of 40°C/min in nitrogen atmosphere. Area of fusion peaks in the DSC thermogram was estimated using a planimeter with an accuracy of $\pm 0.01 \text{ cm}^2$.

RESULTS AND DISCUSSION

Weight Loss

Alkaline hydrolysis of polyester, as determined by the weight loss, proceeds linearly with time at constant temperature and depends on the initial concentration of the alkali. A representative set of results at 100°C treatment temperature is given in Figure 1. It can be seen from the figure that slope of the straight lines obtained between weight loss and time increases with increasing concentration. A linear dependence of weight loss on treatment time has also been observed by other investigators.¹¹ The relationship between weight loss, W , and treatment time, t , can be expressed as:

$$W = b \cdot t \quad (3)$$

where, b is a constant dependent on temperature and alkali concentration. Values of constant b obtained from the slope of the straight lines using the method of least squares are given in Table II.

A representative set of results on filament/filament polyester fabrics are given in Figure 2. As observed with spun/filament fabric, weight loss varies linearly with treatment time. Slopes of the straight lines are also included in Table II for comparison. Under similar reaction conditions, higher weight loss in the case of spun/filament fabric appears to be due to its higher surface area and a relatively open structure of spun yarns.

Alkaline hydrolysis, measured as weight loss, proceeds nonlinearly with the concentration of alkali and treatment temperature. The extent of nonlinearity

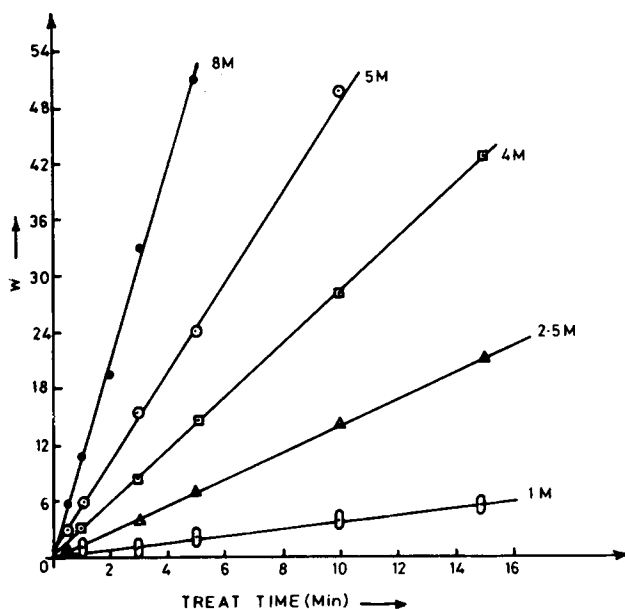


Fig. 1. Dependence of weight loss on treatment time at 100°C with sodium hydroxide solutions of different concentrations for spun/filament fabric.

increases with increasing time and temperature of treatment. Typical curves showing the dependence of weight loss on concentration of alkali are given in Figure 3. A second order relationship,

$$W = aC + dC^2 \tag{4}$$

where, *a* and *d* are constants dependent upon treatment time and temperature, satisfactorily describes the experimental data. Validity of Eq. (4) is checked in Figure 4, wherein *W/C* values have been plotted against *C*. All plots are straight lines as required by Eq. (4). Values of constants *a* and *d*, obtained from the intercept and slope, respectively, of the straight lines, are summarized in Table III. It is clear from the table that in addition to constant *a*, values of constant *d*, a measure of the extent of nonlinearity, are

TABLE II
Values of Constant *b* for Spun/Filament and
Filament/Filament Polyester Fabrics

NaOH concentration (moles)	Spun/filament					Filament/filament
	Temp. (°C): 60	70	80	90	100	Temp. (°C): 100
1.0	0.04	0.10	0.17	0.30	0.38	—
2.5	0.13	0.27	0.54	0.80	1.40	0.96
4.0	0.21	0.45	0.84	1.46	2.81	1.89
5.0	0.35	0.65	1.21	2.01	4.70	2.46
8.0	—	—	—	—	10.21	—

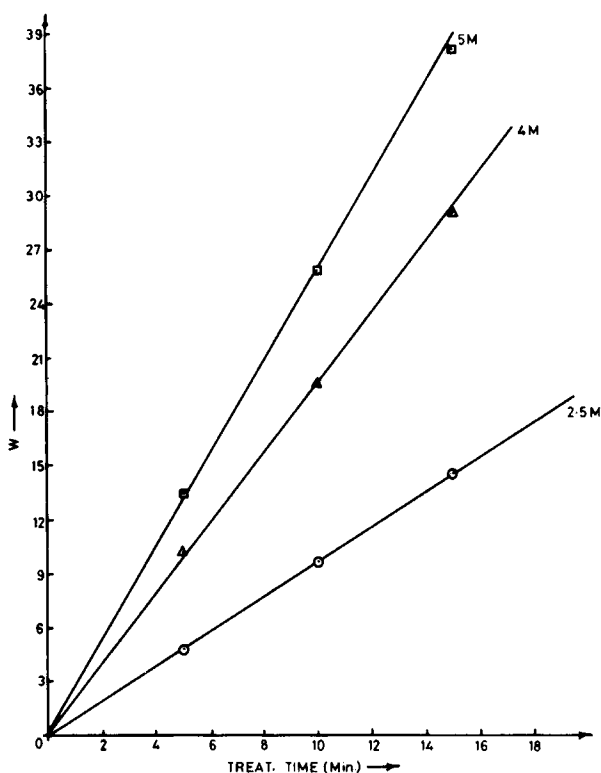


Fig. 2. Dependence of weight loss on treatment time at 100°C with sodium hydroxide solutions of different concentrations for filament/filament fabric.

lower for filament/filament fabrics as compared to that of spun/filament fabrics.

Dependence of weight loss on treatment temperature is shown in Figure 5 for spun/filament fabric. Similar results were obtained with filament/filament fabric. It can be seen from the figure that weight loss increases gradually up to nearly 70°C and then shows a steep rise with further increase in temperature.

According to the reaction mechanism given by Namboori¹¹ for the hydrolysis of polyester there should be no loss in weight of the fiber. On the other hand, it indicates an increase in the weight of the fiber on account of addition of hydroxide anion. It appears, therefore, that in the initial stages of reaction, attack of OH⁻ ions occurs randomly on the fiber surface and results in cleavage of polymer chains. Once a chain is cleaved, further attack of OH⁻ ions occurs mostly on already cleaved chains, produces shorter chains which go into solution, and therefore, in the later stages, reaction is primarily of "unzipping" type.¹³ This mechanism is supported by results on molecular weight, vertical wicking height, and basic dye uptake which will be discussed later.

The observed nonlinear dependence of weight loss on the concentration of alkali and temperature is due to the enhanced dissolution of polymer chains with increasing severity of the treatment. It appears that increasing con-

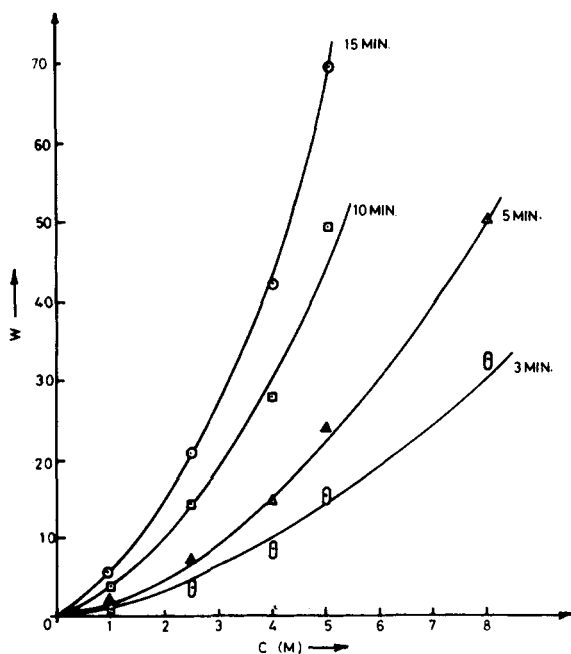


Fig. 3. Dependence of weight loss on concentration of sodium hydroxide solutions for different intervals of treatment time (spun/filament fabric).

centration of alkali increases the frequency of attack of OH^- ions at various places along the length of the chain resulting in relatively shorter chain fragments which can easily go into solution. Increase in temperature further increases the frequency of attack by increasing the kinetic energy of both OH^- ions and fragmented polymer chains causing faster dissolution of the latter in the treatment solution. The steep rise in weight loss at treatment

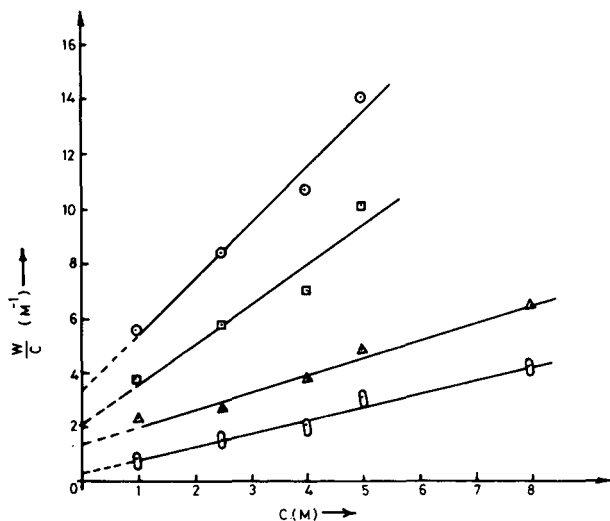


Fig. 4. Test of validity of Eq. (4) for the description of data given in Figure 3.

TABLE III
 Values of Constants a and d for Spun/Filament and
 Filament/Filament Polyester Fabrics at 100°C

Treatment time (min)	Spun/filament		Filament/filament	
	a mol ⁻¹	d mol ⁻²	a mol ⁻¹	d mol ⁻²
3	0.40	0.48	—	—
5	1.48	0.61	1.04	0.37
10	2.16	1.44	1.55	0.64
15	3.42	1.99	3.12	0.84

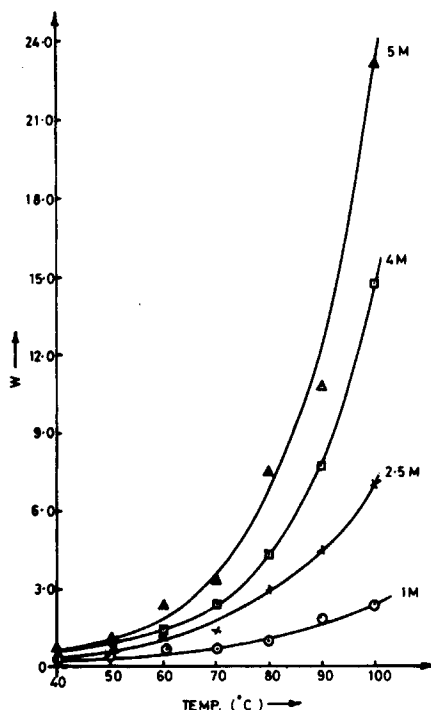


Fig. 5. Dependence of weight loss on treatment temperature for 5 min with sodium hydroxide solutions of different concentrations (spun/filament fabric).

temperatures above 80°C may partly be due to the increased segmental mobility of polymer chains when temperature is increased beyond the glass transition temperature of polyester.

It can be inferred from the above discussion that in the process of alkaline hydrolysis of polyester, the relative effectiveness of different reaction parameters increases in the order:

Treatment time < concentration of alkali < treatment temperature.

Denier / Diameter, Air Permeability and Openness

Denier/diameter of filaments decreases with increasing weight loss in the treatment. It appears that alkaline hydrolysis progressively destroys the outer

skin of the filaments/fibers making them thinner as the reaction progresses. This results in a gradual decrease in denier/diameter of the filament/fibers with increasing severity of the treatment.

Decrease in diameter of filaments/fibers in the process of hydrolysis increases interfiber and interyarn spaces in the fabric. This results in a gradual increase in porosity and consequently air-permeability of the fabric. Interyarn spaces in the fabric is expressed as "openness" in the present investigation.

Data on denier, openness and air-permeability of control and hydrolyzed fabrics, given in Table IV, are in accordance with the findings of other investigators.^{9,10}

Breaking Strength, Tenacity, and Initial Modulus

The degradation of polyester chains results in strength loss of the fiber/ filaments. The dependence of percentage strength loss on weight loss is found to be linear (correlation coefficient = 0.989), having a slope greater than unity indicating thereby that strength loss increases more rapidly than weight loss (Fig. 6). Tenacity also decreases with increasing weight loss in the treatment. However, the rate of decrease of tenacity with respect to weight loss is slower than that of breaking strength. This is expected on the basis of decreasing trend of the denier of the filaments in the treatment. The relatively constant value of tenacity up to a weight loss of 7% further supports the finding that alkali ablates the polymer from the surface almost uniformly and the observed decrease in breaking strength is mainly due to decrease in denier. The decrease in tenacity at higher weight losses may be due to the formation of pits on the surface which probably act as weak points when fiber is elongated under stress. The initial modulus of filaments obtained from the slope of the initial linear portion of stress-strain curves remains practically unchanged. Results on breaking strength, tenacity, and initial modulus of treated and control samples, compared in Table IV, are similar to those reported earlier.^{9,10,26,27}

Flexural Rigidity

Data on flexural rigidity of fabrics recorded in Table IV show a decreasing trend with increasing concentration and time of treatment. This indicates a softer feel for hydrolyzed polyester fabrics, with increasing weight loss in the treatment. Rate of lowering of flexural rigidity relatively fast in the beginning becomes progressively slower with increasing weight loss in the treatment. A weight loss of the order of 7% decreases flexural rigidity to half of its original value.

Flex Abrasion Resistance

Data on abrasion resistance of control and treated polyester fabrics are given in Table V. It can be seen from the table that the flex abrasion life of fabrics increases with weight loss, reaches a maximum at nearly 8-9% weight loss, and then shows a steep decrease with further increase in weight loss. It appears that at lower levels of weight loss, alkaline hydrolysis removes the outer skin of the fiber/filaments uniformly without much of a pitting, exposes

TABLE IV
Properties of Control and Hydrolyzed Fabrics

Sr. no.	Conc. of NaOH (moles)	Physical properties				Mechanical properties					Physicochemical properties				
		% Weight loss	Air permeability ($\text{cm}^3/\text{cm}^2/\text{s}$)	Openness ($\times 10^6 \text{ cm}^2$)	Denier	% Strength loss	Flexural rigidity ($\text{mg} \cdot \text{cm}$)	Tenacity (g/den)	Initial modulus (g/den)	Crease recovery angle (deg)	CDT (s)	% Moisture regain	Contact angle (deg)	\bar{M}_n	Soil release (%)
1.	0	—	74	0.60	89.4	0.0	35	3.67	22.0	298	234	0.40	82	20,856	73
2.	1	2.3	85	0.69	89.2	3.8	24	3.67	22.0	304	—	0.38	80	20,771	92
3.	2.5	7.0	88	0.82	85.0	6.4	17	3.61	22.0	296	200	0.40	79	20,639	92
4.	4	14.7	100	0.94	81.6	13.3	15	3.48	22.1	304	189	0.39	76	20,551	92
5.	5	24.0	99	—	76.8	24.4	12	3.23	22.3	300	125	0.39	72	20,318	94

Properties of fabrics hydrolyzed with different concentrations of sodium hydroxide at 100°C for 5 minutes.

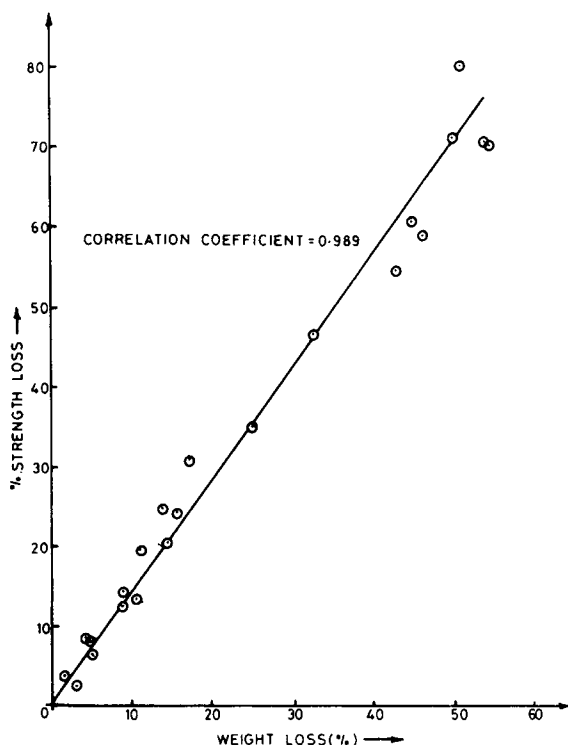


Fig. 6. Correlation between strength loss and weight loss for hydrolyzed spun/filament fabric.

inner relatively more plastic layer at the surface, and thereby increases abrasion resistance of fiber/filaments. The decreasing trend of abrasion resistance at higher weight losses may be due to increased pitting of the fiber surface and the pits so formed serve as centres for crack formation.²⁴

Crease Recovery Angle

Dry crease recovery angle of treated polyester fabrics was found to be almost the same as that of the control fabric (Table IV).

Results on mechanical properties of treated polyester fabrics discussed above are in accordance with the hypothesis that alkaline hydrolysis of polyester up to a weight loss of 7–8% is a surface phenomenon and core of the fiber/filament remains practically unaffected.

TABLE V
Flex Abrasion Life of Polyester Fabrics Treated at 100°C for 5 minutes

Sr. no.	Concentration of NaOH (moles)	Weight loss %	Abrasion resistance number of cycles
1.	0	0.0	7,013
2.	1	1.6	7,562
3.	2.5	2.9	8,221
4.	4	8.5	8,516
5.	5	19.8	3,165

Critical Dissolution Time

Data on critical dissolution time (CDT) included in Table IV show that CDT decreases with increasing severity of the hydrolytic degradation. The dissolution of polyester is caused by the gradual destruction of the fiber structure and weakening of the intermolecular forces on penetration of phenol between molecular chains. Alkaline hydrolysis of polyester removes the outer skin of fibers/filaments, making them thinner, and in addition, creates pits on the surface, which probably act as active sites for the diffusion of phenol into the fiber structure. As a result, CDT shows a decreasing trend with increasing weight loss in the treatment.

Thermal Analysis

Both control and treated samples exhibited first-order melting endotherm at the same temperature. Normalized area under the melting endotherm, a measure of the degree of crystallinity of the polymer remains almost unchanged in the process of hydrolysis. This indicates that alkaline hydrolysis of polyester is topochemical and does not preferentially occur in either regions of low order or of high order.

Moisture Regain

Bulk hydrophilicity, measured as moisture regain, of modified polyester remains almost the same as that of the untreated fabric (Table IV) in conformity with the observations of Sanders and Zeronian.¹² It supports the finding that alkaline hydrolysis is a surface phenomenon generating hydrophilic groups mainly on the fiber surface. Effect of the generated hydrophilic groups on moisture regain is highly diluted by the presence of a large volume of the core of the fiber which remains practically unaffected in the process of hydrolysis.

Molecular Weight

Data on molecular weight recorded in Table IV show that there is an insignificant decrease in molecular weight of the treated samples with increasing concentration of alkali. As discussed earlier, in the process of alkaline hydrolysis, outer skin of the polyester fiber/filament is removed. Molecular chains already cleaved at the fiber surface are further attacked preferentially by alkali and ultimately go into solution. The polymer chains present in the core of the fiber appear to remain practically unaffected. As a result, the observed slight but not very significant decrease in molecular weight is not unexpected.

Vertical Wicking Height

Vertical wicking height increases exponentially with the wicking time. Rate of wicking, relatively fast in the beginning, becomes progressively slower with increasing time and finally reaches a constant value. A representative set of results are shown in Figure 7.

The wicking of water in a vertically hung fabric strip occurs under the combined action of surface tension, viscous, and gravitational forces. In the

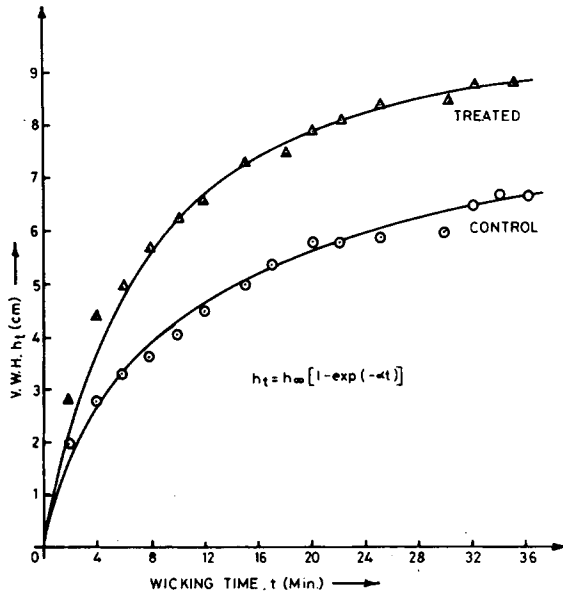


Fig. 7. A representative set of results showing the dependence of vertical wicking height on wicking time. The fabric was treated with 5 M NaOH at 100°C.

initial stages of wicking, gravitational force is negligible and water advancement occurs relatively fast under the influence of the former two factors. With time, as height of water in the strip increases, gravitational pull becomes increasingly important, progressively slowing the rate of advancement of water front, and finally ceases when gravitational pull equals that of driving force due to surface tension, and wicking height reaches a limiting value, as observed. An empirical relationship,

$$h_t = h_{\infty} [1 - \exp(-\alpha t)] \tag{5}$$

where, α is a constant, h_t is the vertical wicking height at time t , and h is the limiting value of vertical wicking height, satisfactorily describes the wicking data. Applicability of Eq. (5) is checked in Figure 8, wherein $\log(h_{\infty} - h_t/H_{\infty})$ values have been plotted against t . All plots are straight lines as required by Eq. (5). Values of the exponent, α , estimated from the slope of the straight lines are included in Table VI. It can be seen from the table that values of α increase with increasing treatment time, indicating a similar trend for the rate of attainment of the limiting vertical wicking height (VWH).

It is found that at all concentrations, VWH increases with treatment time, reaches a maximum, and then shows a decreasing trend with further increase in time. The treatment time corresponding to maximum decreases with increasing concentration of alkali. Data on vertical wicking height of treated samples are plotted against treatment time in Figure 9. The correlation between VWH and loss in weight of the fabric is shown in Figure 10. It can be inferred from the figure that maximum VWH in the treatment is obtained at 4–8% loss in weight of the fabric.

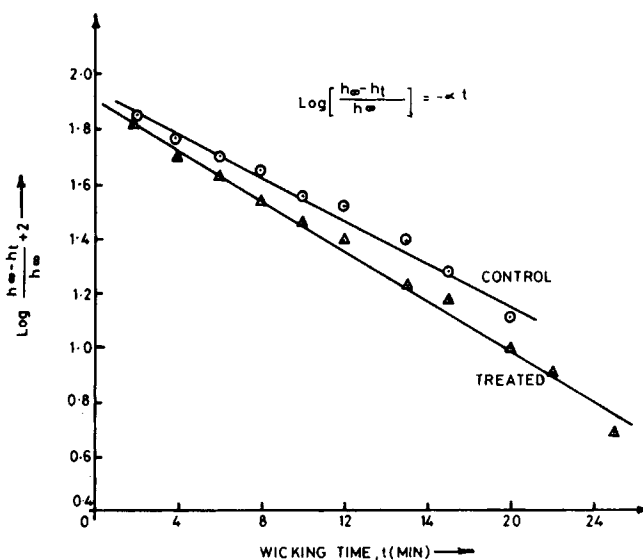


Fig. 8. Test of validity of Eq (5) for the description of wicking data, given in Figure 7.

As discussed in the preceding section, in the initial stages of reaction, at lower weight loss levels, random scission of polymer chains generates hydrophilic groups at the fiber surface, and thereby increases vertical wicking height under influence of increasing surface tension forces. At higher levels of weight loss, reaction predominantly proceeds through the "unzipping" mechanism, causing dissolution of the polymer without significant increase in the number of hydrophilic groups at the surface, and consequently, VWH is expected to reach a limiting value. It seems that at higher weight loss levels, the increasing number and depth of pits formed on the fiber surface with increasing weight loss in the treatment, act as reservoirs for storage of water, depleting its supply for advancement during the course of wicking. As a result, the observed decreasing trend of VWH measured after a constant time interval of 5 min, with increasing weight loss at moderate levels of hydrolysis is not unexpected.

Contact Angle

Contact angle, a measure of surface hydrophilicity, shows significant improvement after alkaline hydrolysis (Table IV). Fiber or film/water/air

TABLE VI
Exponent α for Fabrics Treated with Alkali Solution at 100°C

Sr. no.	Treatment time (min)	$\alpha \times 10$
1.	0	0.88
2.	1	1.08
3.	3	1.13
4.	5	1.27

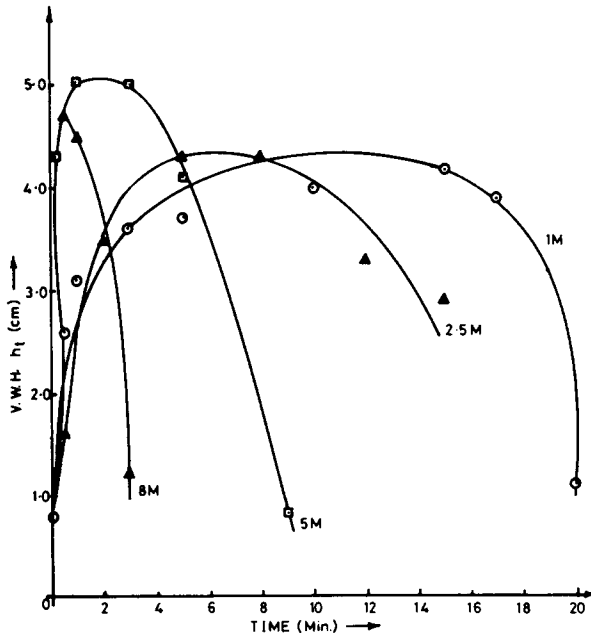


Fig. 9. Dependence of vertical wicking height on treatment time for the hydrolyzed spun/filament polyester fabrics at 100°C with sodium hydroxide solutions of different concentrations.

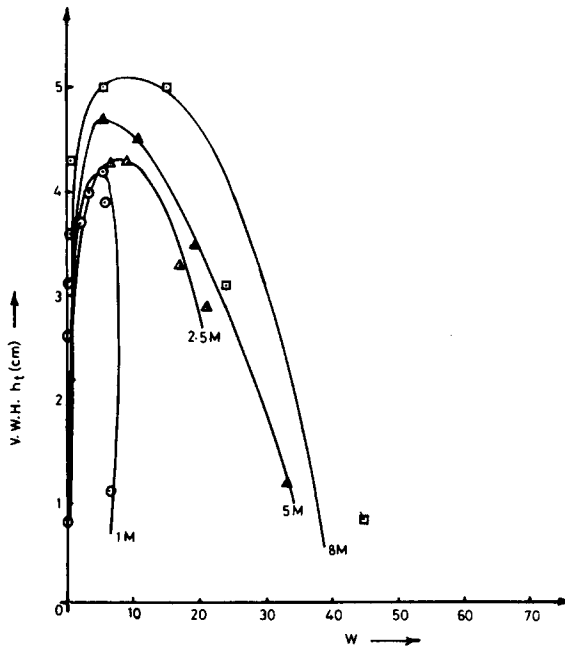
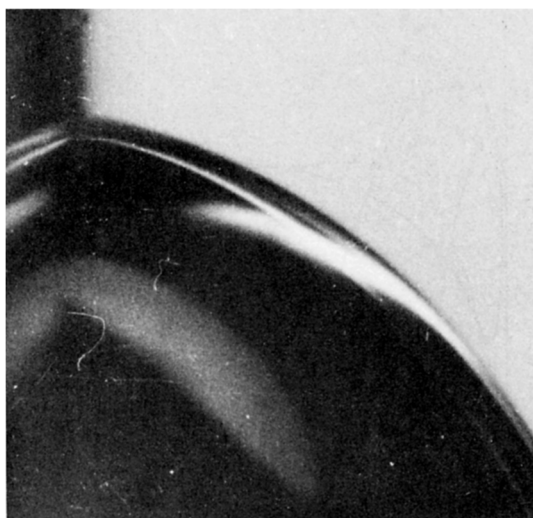
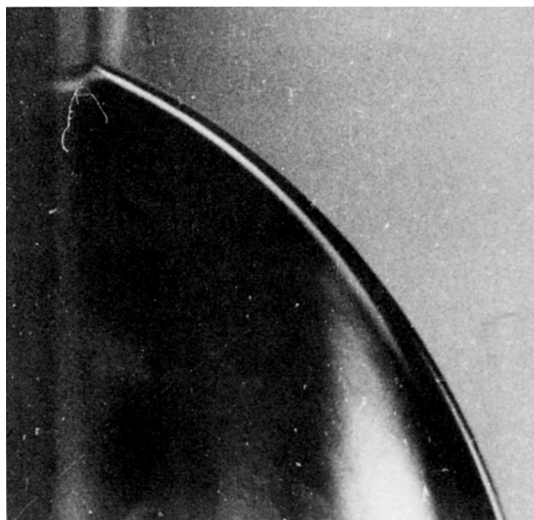


Fig. 10. Correlation between vertical wicking height and weight loss for spun/filament polyester fabrics treated under different concentrations.



(a)



(b)

Fig. 11. Photographs of water drop on control (a) $\theta = 78^\circ$; and hydrolyzed (0.5% weight loss) polyester films (b) $\theta = 65^\circ$.

contact angle decreases with increasing concentration of alkali. Effect is more pronounced with polyester film. Photographs showing the appearance of water drop on control and treated polyester films are compared in Figure 11. The observed decrease in contact angle may partly be due to the increase in the number of hydrophilic groups on the surface after hydrolysis and partly due to the increased roughness of the surface of the fiber/filament/film on account of pitting.¹²

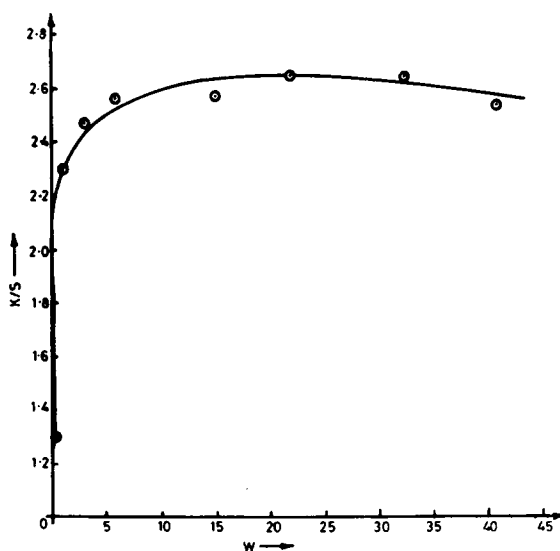


Fig. 12. Dependence of basic dye uptake on weight loss for spun/filament polyester fabrics.

Soil Release

Alkaline hydrolysis of polyester increases surface hydrophilicity of the fabric making the removal of oily soil from the hydrolyzed fabric easier as compared to the untreated fabric. Data on oily soil release of treated and control polyester fabrics, given in Table IV, are in accordance with the expectations on the basis of increased surface hydrophilicity of the fabrics. It may be noted that a similar observation has been made earlier by other investigators.²⁸

Basic Dye Uptake

With a view to assessing the extent of generation of carboxylic acid groups in the process of hydrolysis, dyeing behavior of control and treated polyester fabrics with a cationic dye was studied. Results plotted in Figure 12 show that the dye uptake is relatively fast in the beginning (up to a weight loss of nearly 5%), becomes progressively slower with increasing weight loss in the treatment, indicating a similar trend for the generation of $-\text{COOH}$ group at the surface in accordance with the requirements of the mechanism proposed earlier.

Disperse Dye Uptake and Rate of Dyeing

Results on the dyeing behavior of polyester fabrics with disperse dye (Dispersol Red-B-2B) are given in Figure 13. Dye uptake decreases with weight loss, reaches a minimum at around 6% weight loss, and then increases with further increase in weight loss in the treatment. Disperse dyeing of polyester occurs under the influence of hydrophobic interaction. Any improvement in hydrophilic character of either of the two is therefore expected to have an adverse effect. Decrease in disperse dye uptake at lower levels of

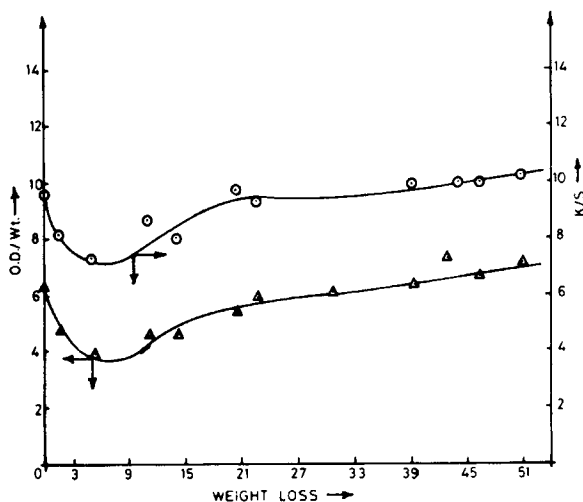


Fig. 13. Dependence of disperse dye uptake of spun/filament fabric on weight loss in the treatment.

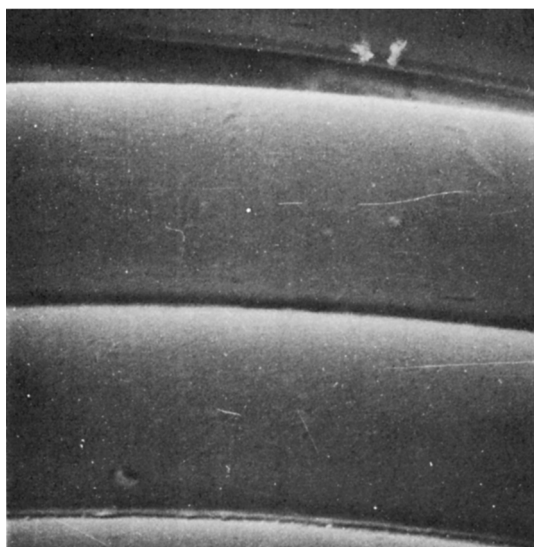
weight loss seems to be due to the increase in surface hydrophilicity by the generation of hydrophilic groups on the fiber surface. As increase in weight loss at relatively higher levels does not result in a corresponding increase in the number of hydrophilic groups on the fiber surface, and on the other hand, increases progressively the surface area due to pitting favoring dye uptake, the curves showing the dependence of dye uptake on weight loss are expected to pass through a minimum with increasing weight loss in the treatment, as observed experimentally. The discrepancy in the findings of earlier investigators^{8, 15, 16} on dyeing behavior of hydrolyzed polyester fabrics may, therefore, be due to the difference in the levels of weight loss in the treatments. Rate of dyeing of the treated fabrics was found to be almost the same as that of the untreated fabric.

SEM Studies

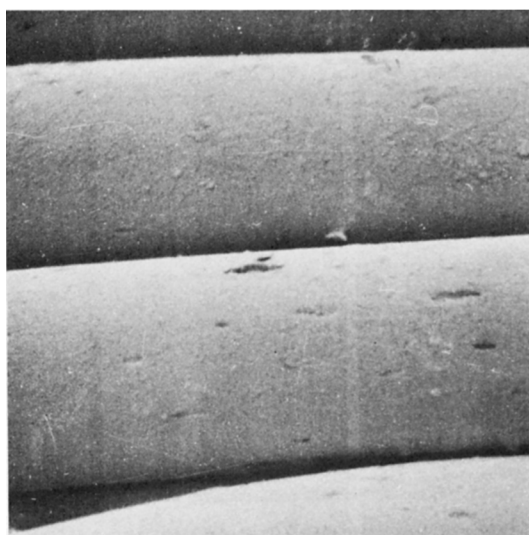
In order to ascertain the extent of damage on the fiber surface in the treatment, samples were viewed under a scanning electron microscope. The scanning electron photomicrographs of the hydrolyzed and control fabric samples, compared in Figure 14, are similar to those presented elsewhere.^{12, 16, 26, 27} The control fiber/filament has a fairly smooth surface. In the case of treated samples, it appears that alkali attacks almost the entire surface of the fiber and causes its erosion. With progress of the reaction, erosion propagates inside the fiber resulting in the formation of elongated pits or cavities on the surface. Both the depth and the frequency of occurrence of pits increase with increasing weight loss in the treatment.

CONCLUSION

Alkaline hydrolysis of polyester fabrics is essentially a surface phenomenon and does not occur preferentially in crystalline or amorphous regions of the fiber/filament. In the initial stages of reaction, polymer chains are randomly



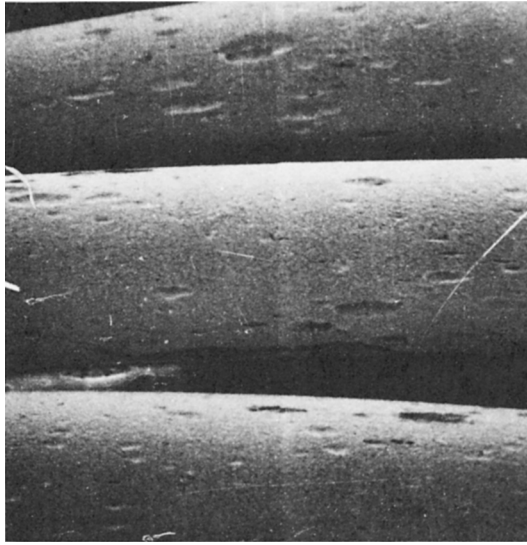
(a)



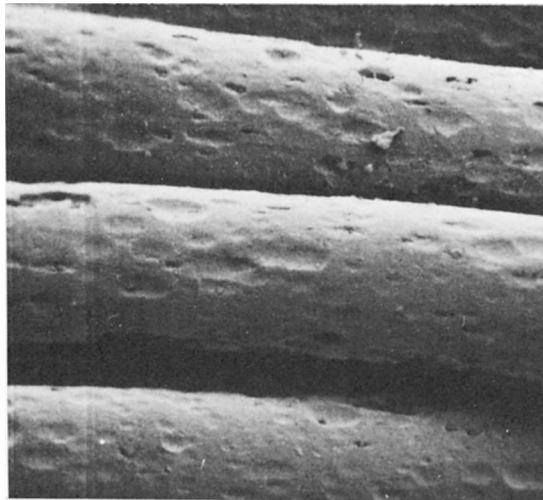
(b)

Fig. 14. SEM photomicrographs of control and hydrolyzed polyester fabrics. Control (a); 5% weight loss (b); 20% weight loss (c); 50% weight loss (d).

cleaved at the surface leading to the generation of hydrophilic groups on the surface of the fiber, but later reaction proceeds mainly through the “unzipping” mechanism, causing dissolution of the polymer without further significant increase in the number of hydrophilic groups on the surface. At lower levels of weight loss, surface properties of polyester are considerably modified, whereas those dependent on bulk of the polymer remain almost unchanged.



(c)



(d)

Fig. 14. (Continued from the previous page.)

The deterioration in properties of polyester at higher levels of weight loss is mainly due to the pitting of the fiber surface in the process of hydrolysis.

The authors thank the Director, ATIRA, for permission to publish this paper. Thanks are also due to Shri R. B. Patel and Shri P. J. Bose for their help in studies on mechanical properties and SEM, respectively. One of us (JKD) is thankful to CSIR (New Delhi) for the award of a junior research fellowship.

References

1. S. M. Suchecki, *Textile Industries*, **74**, 141 (1977).
2. R. Kumar, J. Dave, and H. C. Srivastava, in *Polyester Textiles*, M. L. Gulrajani, Ed. Proc. 37th All India Text. Conf., 1980, p. 279.
3. Anon, *Man-made Textiles*, **34**, 61 (1957).
4. A. J. Hall, *Textile World*, **113**, 108 (1963).
5. De Maria, *Am. Dyestuff Rep.*, **68**, 10 (1979).
6. A. M. Gorrafa, *Textile Chem. Color.*, **12**, 83/33 (1980).
7. Anon, *Japan Textile News*, **312**, 11 (1980).
8. M. R. Padhye and R. S. Singhi, *Cobourage*, **28**, 13 (1981).
9. V. A. Shenai and N. K. Nayak, *Textile Asia*, **13**, 59 (1982).
10. K. D. Houser, *Textile Chem. Color.*, **15**, 70/37 (1983).
11. C. G. G. Namboori, *Textile Chem. Color.*, **1**, 50 (1969).
12. E. M. Sanders and S. H. Zeronian, *J. Appl. Polym. Sci.*, **27**, 4477 (1982).
13. B. M. Latta, *Textile Res. J.*, **54**, 766 (1984).
14. H. Pfeifer, *Man-made Textiles*, **41**, 12 (1964).
15. E. Waters, *J. Soc. Dyers Color.*, **66**, 609 (1950).
16. S. Mackawa, *Japan Textile News*, **294**, 87 (1979).
17. ASTM Standard Test Method, D-1910-64, Part 24 (1972).
18. ASTM Standard Test Method, D-1777-64.
19. ASTM Standard Test Method, D-1388-64, Part 32 (1975).
20. ASTM Standard Test Method, D-1175, Part 32 (1976).
21. ASTM Standard Test Method, D-1295-67, Part 32 (1976).
22. ASTM Standard Test Method, D-2495, Part 33 (1979).
23. T. H. Grindstaff, *Textile Res. J.*, **39**, 958 (1969).
24. D. A. S. Ravens and I. M. Ward, *Trans. Faraday Soc.*, **57**, 150 (1961).
25. A. Todd, *Nature* (London), **174**, 4405 (1954).
26. M. S. Ellison, L. D. Fisher, K. W. Alger, and S. H. Zeronian, *J. Appl. Polymer Sci.*, **27**, 247 (1982).
27. S. H. Zeronian, M. J. Collins, D. L. Fisher, and S. L. Hawk, *J. Indus. Fabrics*, **3**, 19 (1984).
28. N. T. Lijemark and H. Ashnes, *Textile Res. J.*, **41**, 732 (1971).

Received April 11, 1986

Accepted May 2, 1986