Changes Induced in Silk-Like Polyester Properties by Alkoxides Treatment

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ABSTRACT: The action of alkali treatment in both aqueous and alcoholic media is investigated to attain silk-like polyester fabric. The use of alkoxide solutions is more effective on polyester fabric. Rapid loss in weight up to 15–20% occurs at ambient conditions. Immersion and padding techniques are applied. The effect of treatment on some properties of polyester fabric are given through measurements of tensile strength, drapability, permeability, density gradient, crystallinity, thermogravimetric analysis, and scanning electron microscopy. Optimization of the treatment conditions is also suggested. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1829–1837, 2005

Key words: alkoxide; modification; polyester

INTRODUCTION

It is well established that the alkaline hydrolysis of polyester fibers using aqueous sodium hydroxide is confined to the polymer surface.[1] When using methanolic sodium hydroxide, the attack is found to be more severe and weight loss occurs more rapidly.[2]

Namboori and Haith[3] have investigated the hydrolysis of polyester fiber using various bases in nonaqueous media as well as the hydrolysis using aqueous sodium hydroxide. The differences in reactivity of the bases as determined by the weight loss were investigated. Sodium methoxide forms methyl ester end groups during the ester interchange reaction with polyester, resulting in a more rapid loss in weight than using aqueous sodium hydroxide. Analysis of polyester via hydrolysis with methanolic sodium hydroxide as compared to that with aqueous sodium hydroxide, specifically in terms of the location of attack and tensile and thermal properties, was carried out by Holms and colleagues.[2] Wool treatment with sodium methoxide or sodium hydroxide at low concentration in 2-propanol medium for a substantial shrinkage reduction in fabric dimensions was also carried out.[4] Leeder and Rippon[5] have investigated the wool treatments under anhydrous (nonswelling) conditions with potassium *tert*-butoxide dissolved in *tert*-butanol, with the aim of confining the reaction to the outer surface of the fibers.

The present work is to investigate the action of sodium hydroxide in alcoholic media, such as methanol, ethanol, propanol, and butanol, on polyester fabric. Evaluation of the treated polyester fabrics is given through measuring the loss in weight, the tensile strength, density, crystallinity, and thermal characteristics. Changes in surface features of the polyester fibers are scanned by electron microscopy.

EXPERIMENTAL

Material

Polyester fabric (78 dtex, 34 filament) was provided by Misr Rayon Co., Kafr El-Dawar, Egypt. The fabric was soaped at 40°C for 30 min, thoroughly washed, and air dried at room temperature. All chemicals used were of reagent grade.

Treatments

Immersion technique

Polyester samples of known weights were treated in 2.5*M* aqueous sodium hydroxide solution using liq. ratio 1 : 50 at 60°C for 1h. Other samples of known weight were treated in 0.25*M* sodium hydroxide in alcoholic media at the same conditions. A control sample was prepared by treating the fabric in alcohol at the same conditions. All samples were treated at different temperatures (25°–60°C) for various time intervals up to 24 h.

Padding technique

The padding technique was performed by soaking the fabric in alcoholic sodium hydroxide solutions

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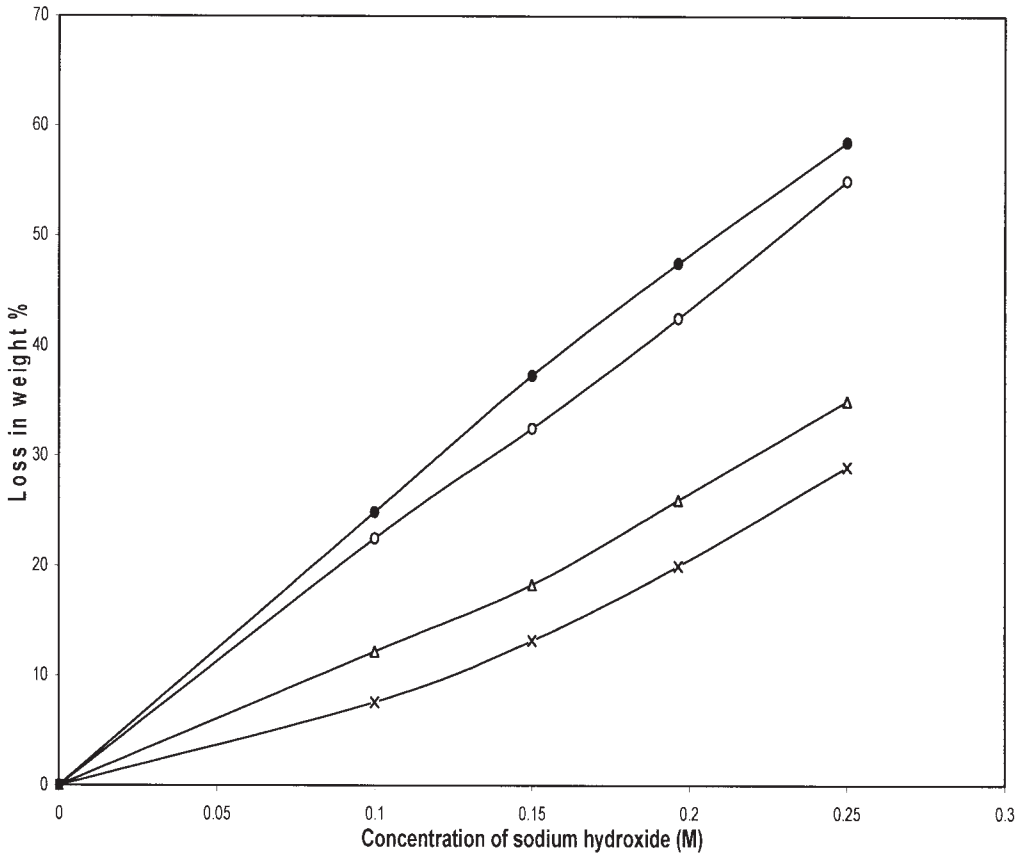

Figure 1 Effect of concentration of sodium alkoxide on the loss in weight of treated polyester fabric. Conditions: 60°C, 1h, liq. ratio 1 : 50, x-x in methanol, O-O in ethanol, ●-● in propanol, Δ-Δ in butanol for 30 min.

at 25°C, followed by squeezing under pressing rollers to 100% pick up. Some samples were stored in polyethylene bags overnight at room temperature, and the other samples were directly subjected to thermal treatment in an oven at temperatures 50° and 80°C for different time intervals up to 30 min. The samples were then rinsed thoroughly, dried, and allowed to attain constant weight.

Characterization

The untreated and treated polyester fabrics were characterized through measurements of the loss in weight, tensile strength, air permeability, drapability, density, crystallinity, thermogravimetric analysis, and electron scanning microscopy.

The **loss in weight** of the treated polyester fabric was calculated according to the equation:

$$\%\text{loss in weight} = \frac{(W_O - W)}{W_O} \times 100$$

where W_O is the original dry weight of the sample, and W is the dry weight of the sample after treatment.

Density measurements were carried out at 21°C (±2°C) in a density gradient column prepared with carbon tetrachloride and *n*-heptane. The apparent degree of crystallinity X_d, expressed as a volume fraction, was calculated from density measurements using the relation[6]:

$$X_d = (\rho - \rho_a)/(\rho_c - \rho_a)$$

where ρ represents the density of the semicrystalline sample, ρ_c is the density of a perfect polymer crystal (= 1.455 g/cm^3), and ρ_a is the density of an amorphous polyester (= 1.335 g/cm^3).[6]

Thermogravimetric analysis was carried out using the thermal analyzer 7 series (Perkin–Elmer, Boston, MA) with attached TG unit. The movable thermostatically controlled electric furnace was used to heat the sample at the desired rate. The sample was heated at a rate of 10°C/min, and the loss in weight of the samples was recorded versus temperature from 50°to 1100°C.[7,8]

Drapability of the untreated and the treated polyester fabric was carried out by Draptester (Toyo Seiki,

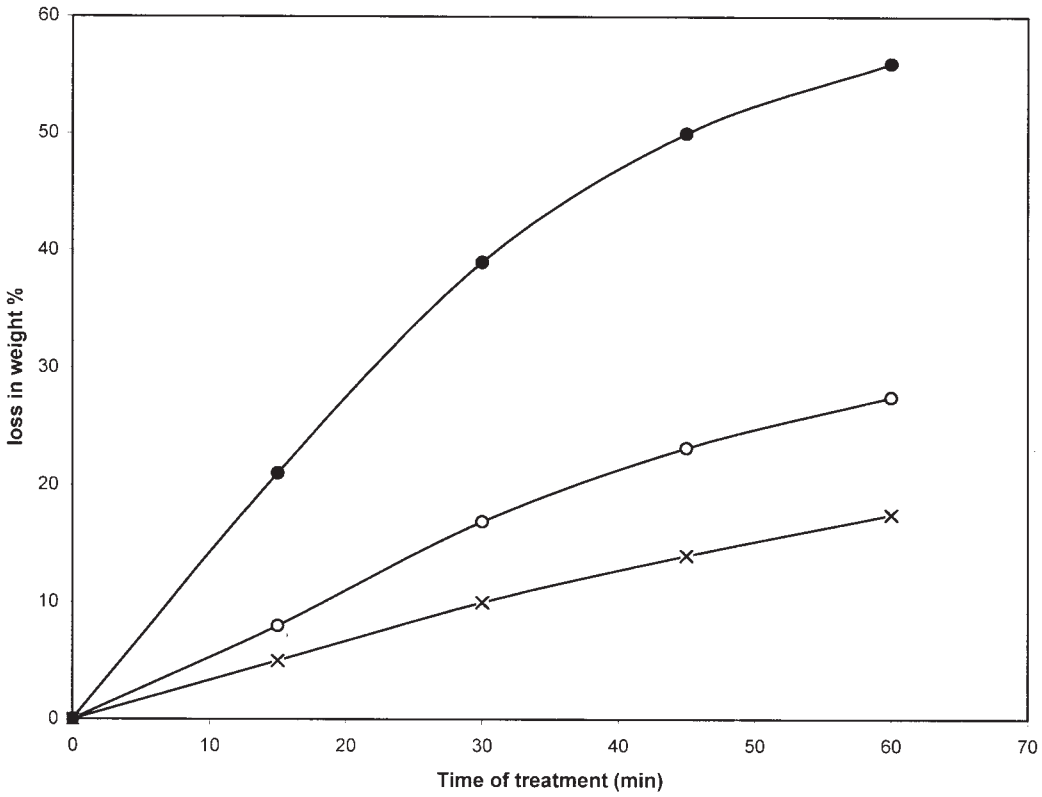

Figure 2 Effect of time of treatment on the loss in weight of treated polyester fabric at different temperatures. Conditions: 0.25*M* sodium propoxide solution, x-x 40°C, O-O 50°C, ●-● 60°C.

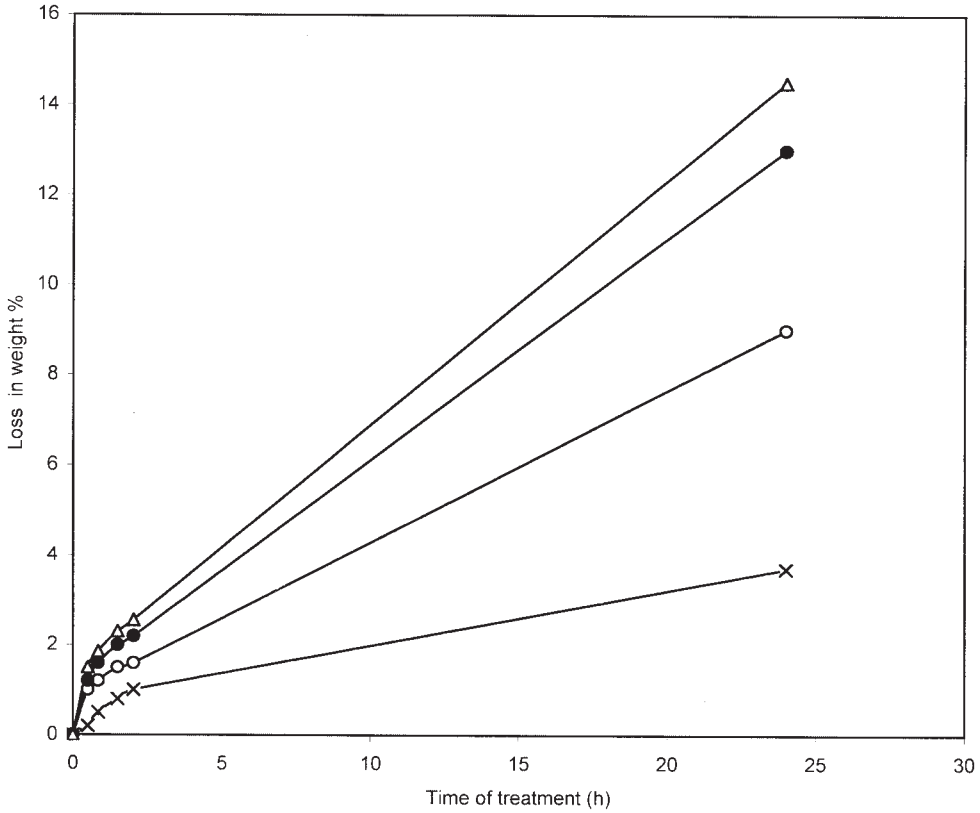

Figure 3 Effect of time of treatment on the loss in weight of treated polyester fabric. Conditions: 0.25*M* sodium alkoxide, room temperature (~ 25°C), liq. ratio 1 : 50, x-x in methanol, o-o in ethanol,●-●in propanol, Δ-Δ in butanol.

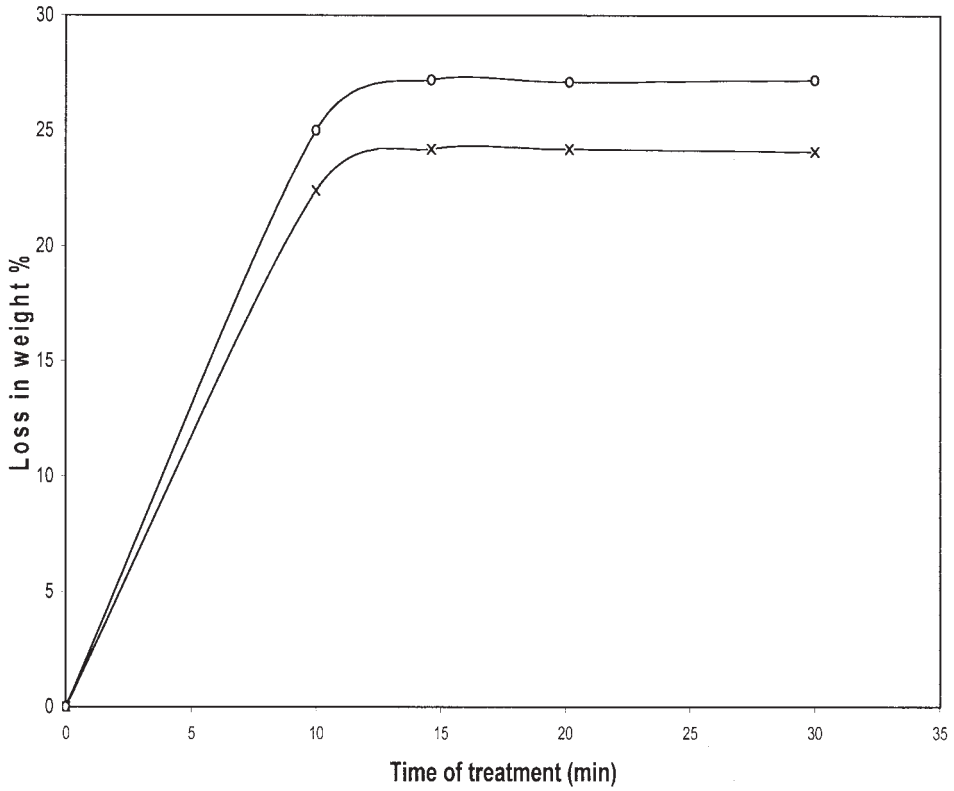

Figure 4 Effect of time of treatment on the loss in weight of treated polyester fabric by padding technique at different temperatures. Conditions: 1*M* sodium propoxide, padding technique, pick up 100%, x-x 50°C, o-o 80°C.

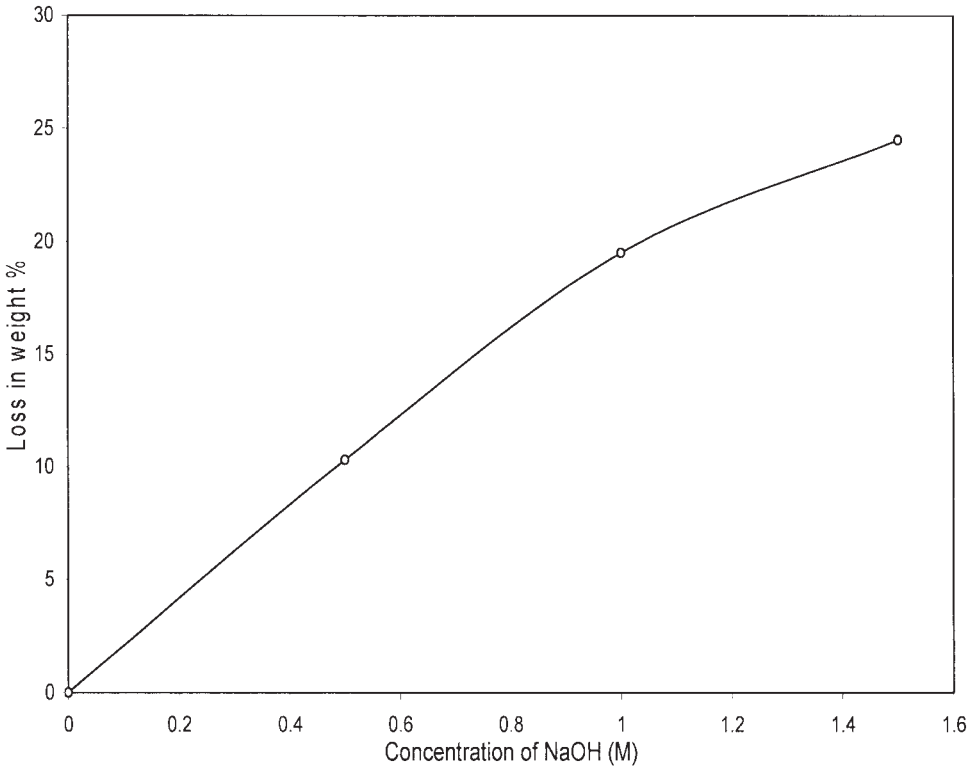

Figure 5 Effect of concentration of sodium propoxide on the loss in weight of polyester fabric. Conditions: padding technique, pick up 100%, room temperature (~ 25°C), 24h.

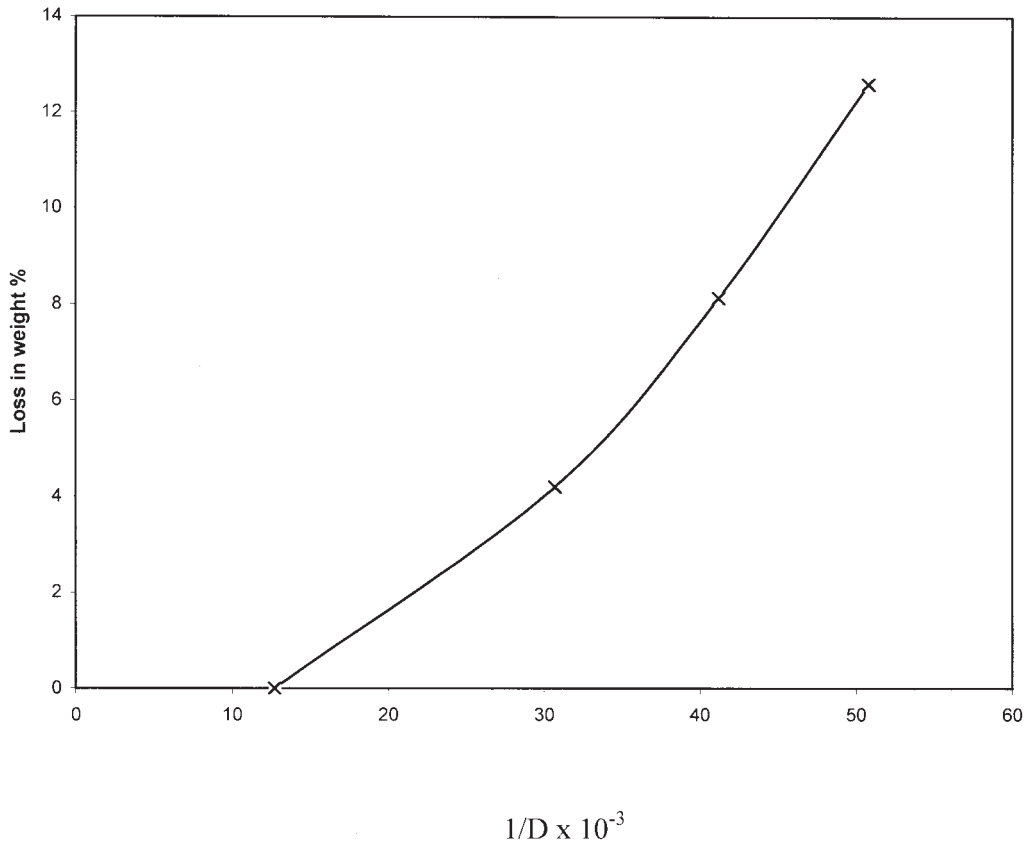

Figure 6 Effect of dielectric constant of the treatment medium on the loss in weight of treated polyester fabric. Conditions: 0.25*M* NaOH, immersion technique, room temperature (~ 25°C), 24h, liq. ratio 1 : 50. 1/D values: water, 12.7×10^{-3}; methanol, 30.7×10^{-3}; ethanol, 41.2×10^{-3}; propanol, 50.8×10^{-3}.

Japan), and the draping coefficient is evaluated from the following equation:

$$\text{Drape coefficient} = (A_S - A_O)/(A_I - A_O)$$

where A_S = project area of the sample (cm^2), A_1 = big disk area (cm^2), and A_O = small disk area (cm^2).

RESULTS AND DISCUSSION

Loss in weight

Immersion technique

The weight of the polyester samples was determined accurately before and after treatment. The loss in weight was calculated. The weight loss due to treatment of the polyester fabric using 2.5*M* aqueous sodium hydroxide solution at 60°C for 1 h by the immersion technique of treatment with liq. ratio 1 : 50 was found to be 5%.

The weight loss of polyester fabric due to the attack of sodium alkoxide in relation to the concentration of sodium hydroxide at the same previous conditions is presented in Figure 1. It can be seen that the produced loss in weight was found to be concentration dependent and proceeded more rapidly as compared to the case of using aqueous sodium hydroxide, despite the lower concentration of the used alkoxide. It was also noticed that the resultant loss in weight increased in

TABLE I
Permeability, Draping Coefficient, and Tensile Strength of Untreated and Treated Polyester Fabric

Sample	Permeability $cm^3/cm^2.sec$	Draping coefficient	Elongation at break %	Tensile strength (Kg)	% decrease in tensile
Untreated	10.6	0.91	29	107	0
Treated with ethoxide	19	0.63	32.5	84	21.5
Treated with propoxide	35	0.48	20	70	34.5

Conditions: 1 M sodium alkoxide, padding technique, pick up 100%, room temperature (≈ 25°C), 24 h.

TABLE II
Density and Crystallinity of Untreated and Treated Polyester Fabric

Sample	Density (g/cm^3)	Crystallinity %
Untreated	1.3835	40.4
Treated with ethoxide	1.3968	51.5
Treated with propoxide	1.4056	58.8

Conditions: 1M sodium alkoxide, padding technique, pick up 100%, room temperature (≈ 25°C), 24 h.

the order propanol > ethanol > methanol when used as the reaction medium. The effect of time of treatment with sodium propoxide at different temperatures on the loss in weight of the polyester fabric is given in Figure 2. The results showed that the temperature is an effective parameter on the hydrolysis of polyester fabric, resulting in a loss in weight of about 55% at 60°C.

To attain a mild loss in weight, the treatment was intended to be carried out at room temperature. The effect of time of treatment with the aforementioned alkoxides at room temperature for 24 h using the immersion technique on the loss in weight of the polyester fabric is shown in Figure 3. The resultant loss in weight was found to depend on the time of treatment, where a maximum loss in weight of 15% was obtained upon using sodium butoxide.

Padding technique

Polyester fabric was immersed in sodium propoxide (1*M*), padded under pressing rollers to pick up of 100%, then bagged in polyethylene directly heat treated in an oven for 15–30 min at either 50° or 80°C. The effect of time of treatment of the polyester with propoxide solution on the loss in weight is given in Figure 4. It can be seen that the loss in weight was found to be approximately the same after 15 min of treatment at either 50° or 80°C.

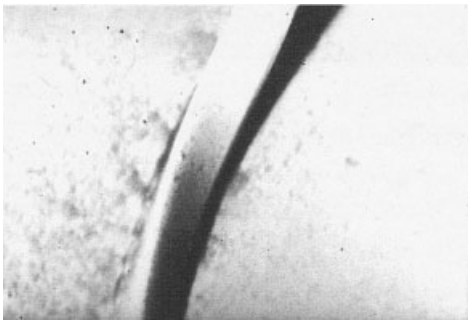

Figure 7 Scanning electron micrograph of untreated polyester fabric.

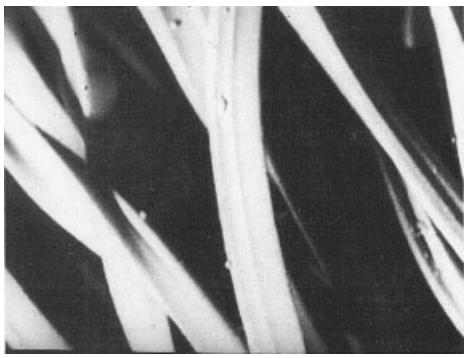

Figure 8 Scanning electron micrograph of treated polyester fabric with sodium ethoxide solution. Conditions: 1*M* sodium ethoxide, padding technique, pick up 100%, 25°C, 24 h.

The treatment of the polyester fabric using the padding technique was tried at room temperature. The padded fabric was stored in polyethylene bags for 24 h. The effect of concentration of sodium propoxide on the loss in weight of the polyester fabric is shown in Figure 5. The loss in weight was found to be concentration dependent. A concentration of 1*M* sodium hydroxide in alcoholic media was chosen as the optimum concentration that gives an acceptable loss in weight (≤20%).

Dielectric constant

Dielectric constant is defined by the relative permittivity of the matter. Physically, the dielectric effect is due to polarization of the matter in the medium.[9] Figure 6 shows the relation between the dielectric constant (D) of the used alcoholic media of treatment and the corresponding loss in weight of the polyester fabric. It is clear that as 1/D increases, the resultant loss in weight increases. It was reported that the alkoxide group is more reactive than the hydroxyl group. The reactivity increases by increasing the side chain of the used alcohol.[10]

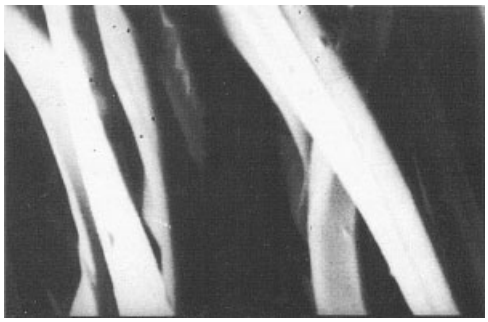

Figure 9 Scanning electron micrograph of treated polyester fabric with sodium propoxide solution. Conditions: 1*M* sodium propoxide, padding technique, pick up 100%, 25°C, 24 h.

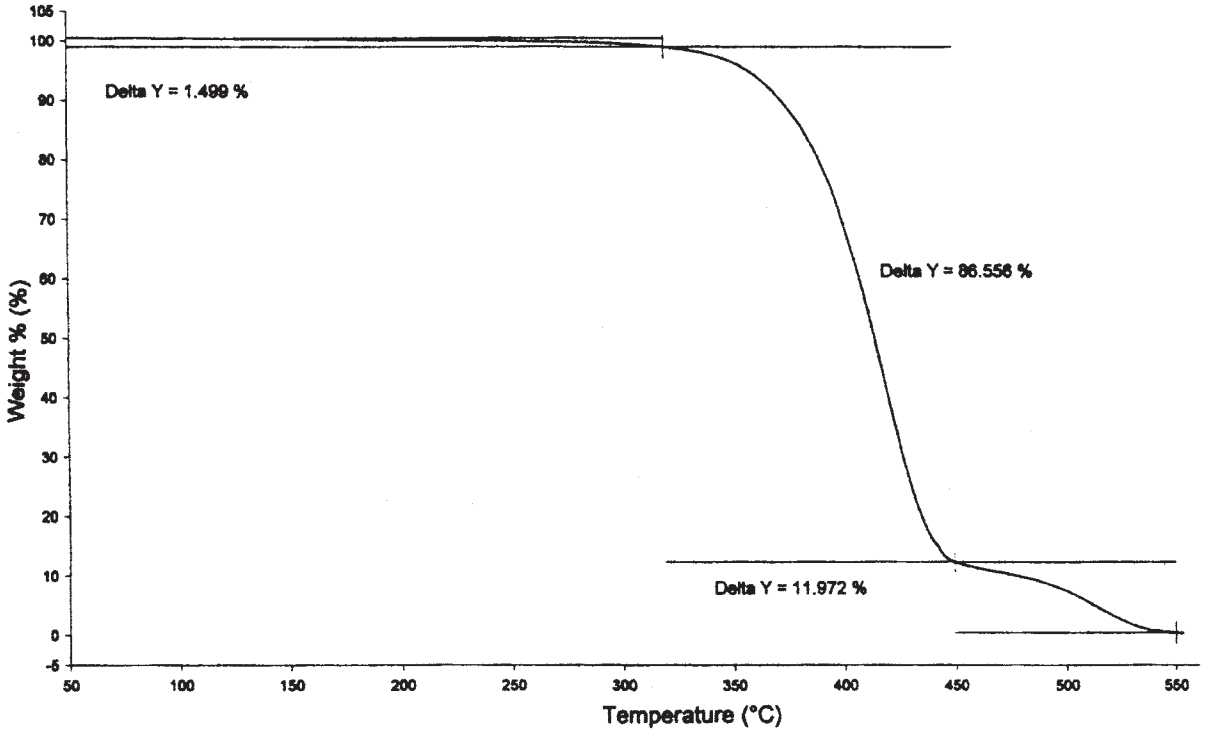

Figure 10 Thermogravimetric analysis of untreated polyester fabric.

Mechanical properties

The tensile strength, elongation at break, permeability in air, and draping coefficient of the untreated and treated polyester fabric with ethoxide and propoxide solutions are given in Table I. It can be observed that the tensile strength of the treated polyester fabric with both ethoxide and propoxide solutions decreased by 21.5% and 34.5%, respectively. It was also shown that the permeability in air of the treated polyester fabric was increased. This may be due to the attained loss in weight in the treated polyester fabric. The draping coefficient of the treated polyester fabric decreased. This means that the drapability and the handle of the treated polyester fabric was improved by the aforementioned treatment.

Density and crystallinity

Table II shows that the density of the polyester fabric was found to increase by the alkoxide treatments. Accordingly, the corresponding crystallinity was also increased. However, as reported elsewhere,[2] the reaction with sodium methoxide solution occurs at the periphery, rendering it less porous and therefore more dense. This may be due to the relatively large methyl ester groups occupying former voids.[2] This holds true with our findings with respect to ethoxide and propoxide treatments.

The obtained tensile data (moderate loss in tensile strength) and the previous intrinsic viscosity results (no change in intrinsic viscosity) from literature[2] indicate that the alkoxide solution does not penetrate the fiber to a significant extent. The noticeable increase in density is most likely due to the more dense surface of the treated polyester.

Scanning electron microscopy

Changes in surface properties without accompanying whole-fiber damage were previously obtained by treatment with sodium and potassium *tert*-butoxides and isopropoxide.[11] Similarly, nearly the same results were obtained by treating the polyester fabric with both ethoxide and propoxide solutions (Figs. 7–9). It can be noticed from the scanning electron micrographs of the untreated (Fig. 7) and treated polyester fabric with sodium ethoxide (Fig. 8) and propoxide (Fig. 9) that there is a change on the surface of the polyester fabric without whole-fiber damage. This may be due to the use of alkoxide solutions causing a reduction in the whole-fiber swelling and thus imparting beneficial effects on the fiber surface.[11]

Thermogravimetric analysis

Thermogravimetric analysis curves of both untreated and treated polyester fabric with ethoxide and

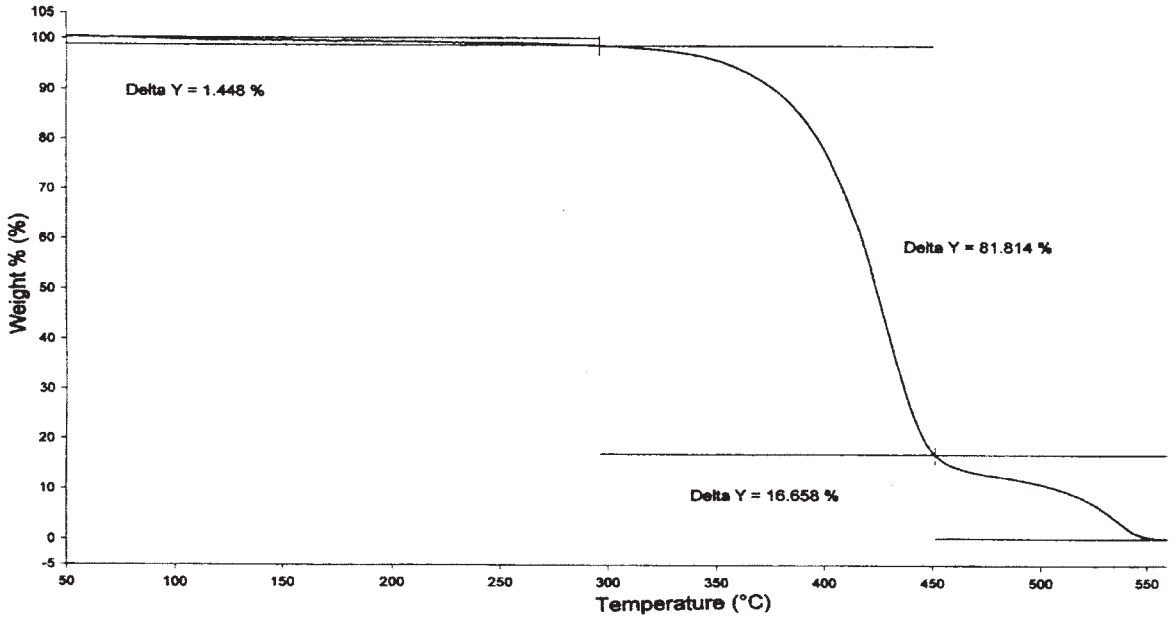

Figure 11 Thermogravimetric analysis of treated polyester fabric with sodium ethoxide solution. Conditions: 1*M* sodium ethoxide, padding technique, pick up 100%, 25°C, 24 h.

propoxide solutions are shown in Figures 10–12. Thermogravimetric analysis can be classified into three steps, as suggested by Chatterjee.[12] The initial reaction may be the breaking of bonds and conversion of the polyester macro-molecule into lower molecular weight species. The fragmental molecules undergo further decomposition until the molecular chains come to an end, that is, tend to carbonization.[12,13]

It can be seen from Table III that the temperature of starting degradation was found to decrease by treatment of the polyester fabric with the aforementioned reagents. This may mean that the thermal stability of the fiber decreased slightly by the action of treatment, and it relates to the breaking down of the bonds of the fibers by the action of alcohol. The end of the temperature of degradation and the corresponding loss in

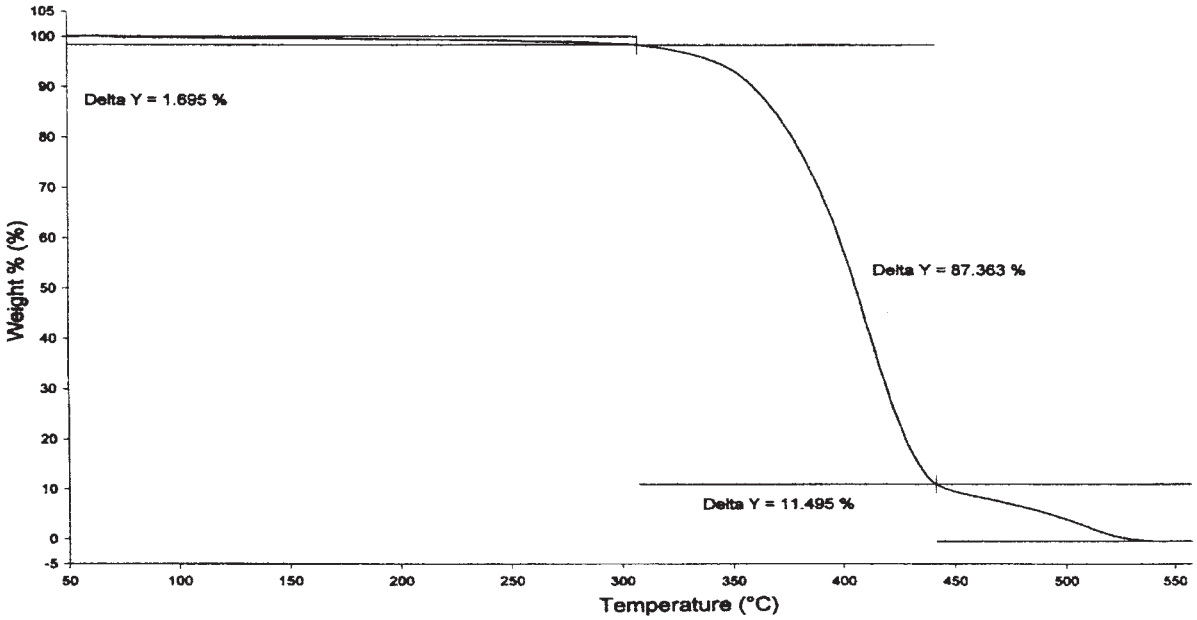

Figure 12 Thermogravimetric analysis of treated polyester fabric with sodium propoxide solution. Conditions: 1*M* sodium propoxide, padding technique, pick up 100%, 25°C, 24h.

TABLE III
Thermogravimetric Analysis of Untreated and Treated Polyester Fabric

Sample	Starting degradation temperature (°C)	End of degradation temperature (°C)	% loss in weight
Untreated	319.1	449.3	86.5
Treated with ethoxide	296.6	451.2	81.8
Treated with propoxide	307.4	441.4	87.4

Conditions: 1M sodium alkoxide, padding technique, pick up 100%, room temperature (≈ 25°C), 24 h.

weight did not show a noticeable change. This means that no degradation had occurred by the treatment and, therefore, the effect of treatment may be restricted to the surface, which holds true with other findings.[2,11]

CONCLUSIONS

Hydrolysis of polyester fabric by using aqueous sodium hydroxide differs from that by using sodium alkoxide solutions (non aqueous medium) with respect to the resultant loss in weight. Rapid loss in weight up to 15–20% occurred at ambient conditions of treatment by both immersion and padding techniques. The treatment conditions were optimized to give a mild loss in weight. This can be summarized by treating the polyester fabric with 0.25*M* and 1*M* sodium alkoxide solutions at room temperature for 24 h by immersion or by padding technique. Applying the latter may save materials and energy consumption to achieve a cleaner technique. Characterization of the treated polyester fabric via density, crytallinity, mechanical properties, scanning electron microscopy, and thermogravimetric analysis of the fiber was given. The treatment resulted in a more dense fiber and higher crystalline ability. The drapability, handle, and permeability in air of the treated polyester fabrics were improved. The relative decrease in the tensile strength ranged between 21 and 34%. The thermal stability was slightly decreased, but it seems that no degradation occurred and the action is confined to the surface of the fiber.

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