Technical Paper

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Dependence of Alkali Hydrolysis of Poly (ethylene terephthalate) Fibers on Temperature of Heat Setting in the Unstressed State**Shouhua Niu,*¹ Tomiji Wakida,*¹ Mitsuo Ueda,*¹ Shinji Ogasawara*², and Hitoshi Fujimatsu*²**

*¹ Department of Chemistry and Materials Technology, Kyoko Institute of Technology,
Matsugasaki, Sakyoku, Kyoto, 606 Japan

*² Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda, Nagano
386 Japan

Abstract : Two kinds of poly (ethylene terephthalate) fibers, regular and partially oriented yarns, were heat set at 100 °C–220 °C in the unstressed state and then alkali hydrolyzed with 10% aqueous NaOH solution at 90 °C. The rate of hydrolysis of the fibers with alkali was found to depend on heat setting temperature, *i. e.*, weight loss initially decreased with increasing heat setting temperature up to 140 °C and then increased at high temperatures. Shrinkage, disperse dyeing property, crystallinity and X-ray diffraction patterns were also measured with respect to the changes in the fine structure of fiber during heat treatment and alkali hydrolysis.

1. Introduction

Caustic treatment of polyester fibers has been extensively studied to improve their hydrophilicity and other comfort-related properties [1–4]. Recently new synthetic fibers, the so-called 'Shin Gosen', which usually consist of physically modified polyester fibers with different shrinkage, denier and varied cross section, have been of special interest in the preparation of the silk-like fabrics. Alkali treatment often plays an important role in the improvement of their ascetic properties. Reaction of polyester fibers with NaOH is evidently a heterogeneous reaction and thus greatly affected by the fine structure of a fiber such as crystallinity, crystallite size, the orientation of crystallite as well as amorphous region, but little attention has been paid to it [5]. We previously reported the effect of heat setting on hydrazine and alkali treatment of poly(ethylene terephthalate) fibers subjected to heat treatment in the fixed state. Although fiber crystallinity increased with increasing heat setting temperature, weight loss from these treatments initially decreased to minimum and subsequently increased again over certain temperatures [6–8]. The results are similar to the well-known disperse dyeing properties of heat-set polyester fibers [9–15].

In this paper, two kinds of polyester fibers, regular poly(ethylene terephthalate) and partially oriented poly(ethylene terephthalate) yarns were subjected to heat treatment in the unstressed state and then to alkali hydrolysis, and the effect of heat setting on alkali hydrolysis was investigated.

2. Experimental

2.1 Materials

Two kinds of polyester fibers, regular poly(ethylene terephthalate) fibers (PET) and partially oriented poly(ethylene terephthalate) yarns (POY) were used. PET fibers of 100 denier and 36 filaments were produced at a speed of 1400 m/min and then drawn 4 times at 175 °C, and POY fibers of 75 denier and 36 filaments were produced at a speed of 3500 m/min by Japan Ester Co. Ltd.

Sodium hydroxide (95%), acetone, toluene, carbon tetrachloride and chlorobenzene used were of guaranteed reagent grade. Miketon Fast Red Violet R (C.I. Disperse Violet 1) was used in the disperse dyeing.

2.2 Heat Treatment

The PET and POY fibers were lapped in an aramid net and heat set at 100 °C, 120 °C, 140 °C, 160 °C, 180 °C, 200 °C and 220 °C for 10 minutes in the unstressed

state using a pin stenter. Changes in fiber length before and after heat setting were measured 10 times for each sample and the average was calculated as shrinkage. After heat treatment the heat-set and the unset fibers were cleaned with toluene, acetone and distilled water, and dried in an oven and then kept in a desiccator over P_2O_5 for a week.

2.3 Alkali Hydrolysis

Alkali hydrolysis was done with 10% aqueous NaOH solutions at 90 °C with a liquor ratio of 1 : 150 for 60 min with mild mechanical agitation. After the treatment the fibers were rinsed with distilled water and dried. Weight loss was calculated from the change in fiber weight before and after the hydrolysis.

2.4 Disperse Dyeing

Disperse dyeing was carried out with 0.6 g/L aqueous C.I. Disperse Violet 1 solution at 110 °C with a liquor ratio of 1 : 250 for 12 hours using a MINI-COLOUR 12-E dyeing machine. After dyeing the fibers were washed with distilled water and dried. The adsorbed dyes on the fibers were extracted with chlorobenzene and determined spectrophotometrically as described before [6,7].

2.5 Crystallinity

Crystallinity was calculated from fiber density measured at 25 °C using a density gradient column containing a mixture of toluene and carbon tetrachloride in the same manner as described previously [6,7].

2.6 Wide Angle X-ray Diffraction

Wide angle X-ray diffraction patterns were measured using a PHILIPS PW-1730 X-ray generator at a power of 45 kV and an electric current of 55 mA. The camera was set at a distance of 4.0 cm and the exposure time was 60 minutes.

2.7 Scanning Electron Microscopy

The heat-set and the hydrolyzed fibers were observed using a HITACHI S-800 scanning electron microscope (SEM) at a magnification of 3000. The fiber diameters were measured from SEM photograph and changes in cross sectional area with alkali hydrolysis were calculated from the change in fiber diameter before and after alkali hydrolysis.

3. Results and Discussion

3.1 Shrinkage

Shrinkage dependence of PET and POY fibers on heat-setting temperature is shown in Fig. 1. Shrinkages

Fig. 1 Changes in shrinkage and diameter with heat setting temperature for PET (■, ◆) and POY (□, ◇) fibers.

increased for both fibers gradually with increasing heat setting temperature due to heat-induced bond rotation as discussed in detail by Bosley [16]. Shrinkages of POY fibers were much greater than those of PET fibers by more than 40% over the whole range of heat setting temperature from 100 °C to 220 °C. In fact, a macroscopic length change is an evidence of a corresponding change in the fine structure of fibers, especially in molecular chain orientation. Therefore dye uptake with disperse dyes and the rate of hydrolysis with alkali for POY fibers are expected to be affected significantly as discussed below.

On the other hand, shrinkage during heat treatment was always accompanied by fiber expansion. Fiber diameters of the heat-set PET and POY fibers were measured through SEM observation and the typical results are also shown in Fig. 1. In comparison with PET fibers, increase in fiber diameter was large for heat-set POY fibers because of their high shrinkage, but no great changes in diameter were found with increasing heat setting temperature for both fibers. The diameter of POY control was smaller than that of PET control, however, diameters of all heat set POY fibers were larger than those of PET fibers heat set at the same temperature. It can thus be concluded that high rate of hydrolysis for POY fibers as discussed below may not derive from the variation in surface area of fibers, which is often considered to be a critical factor affecting the rate of hydrolysis of polyester fibers with alkali [17].

Fig. 2 Effect of heat setting temperature on weight loss from alkali hydrolysis for PET (●) and POY (○) fibers.

3.2 Weight Loss

It is well-known that alkali progressively degrades polyester by saponification of its ester linkages and results in a loss in weight of the fibers. Dependence of weight loss on heat setting temperature for PET and POY fibers is shown in Fig. 2. Weight losses from alkali hydrolysis for both fibers initially decreased with increasing heat setting temperature up to 140 °C and then increased at high temperatures. Weight loss of POY fibers was higher than that of PET fibers over the whole range of heat setting temperature. The cause of low weight loss for PET control, however, cannot be explained yet.

Compared with that of PET fibers, no significant change in weight loss for POY fibers was found with increasing heat setting temperature up to 160 °C. A similar tendency was also found in the disperse dyeing of the heat set POY fibers as reported in the following discussion.

3.3 Dye Uptake

Saturation dye uptakes of PET and POY fibers with C.I. Disperse Violet 1 are given in Fig. 3. The dependence of dye uptake on heat setting temperature for the heat-set fibers observed here was similar to that first reported by Marvin [9] and then studied extensively [10-15] on the basis of the changes in crystallite size, amorphous volume around the crystallite, lateral order distribution etc., but the real mechanism is not clear because of the complexity of amorphous structure of the

Fig. 3 Effect of heat setting temperature on dye uptake of C. I. Disperse Violet 1 for heat-set PET (■) and POY (□) fibers, and alkali-hydrolyzed PET (●) and POY (○) fibers.

fiber. In the dyeing of PET and POY fibers, dye uptake decreased with increasing heat setting temperature, reached a minimum at around 180 °C and then increased again at high temperatures.

Dye uptake for POY fibers was much higher than that for PET fibers over the whole range of heat setting temperature, indicating that POY fibers are more accessible to disperse dyes. However no significant difference in dye uptake was observed for POY fibers with increasing heat setting temperature as also observed in the alkali hydrolysis of POY fibers. High shrinkage of POY fibers over the whole range of heat setting temperature is considered to lead to a great decrease in orientation of crystallites and amorphous regions, which has a levelling effect on the diffusion of dyes into fibers, even though fiber crystallinity increased progressively with increasing heat setting temperature. Consequently the dye uptake curve of POY fibers tended to be leveled off. Nevertheless, an unmarked but discernible minimum was observed at a heat setting temperature of about 180 °C.

On the other hand, dye uptake increased slightly with alkali hydrolysis for PET and POY fibers. Since alkali hydrolysis occurs at the surface of the fibers and the hydrolyzed parts fall away, the inner part of a fiber will least change. This increase in dye uptake, thus, can only be explained by assuming that the inner part of a fibers is somewhat different from the fiber as a whole. Changes in cooling rate in the diametrical direction of a

fiber during melt spinning and subsequent heat treatment of polyester fibers have been considered to contribute to the formation of skin layer [18] and result in an increase in dye uptake after hydrolysis.

3.4 Crystallinity

The dependence of crystallinity on heat setting temperature is shown in Fig. 4. The crystallinity increased with increasing heat setting temperature and there was

Fig. 4 Effect of heat setting temperature on crystallinity of heat-set PET (■) and POY (□) fibers, and alkali-hydrolyzed PET (●) and POY (○) fibers.

little difference in crystallinity between PET and POY fibers. Nevertheless, a differences in weight loss as well as in dye uptake were remarkable between them as shown above. The fact suggests the great differences in the crystallite size and its orientation as well as the structure in amorphous regions between the two fibers.

Almost no increase in crystallinity was found with alkali hydrolysis for both the heat-set PET and POY fibers except for the unset fibers. For the unset fibers, great increase in crystallinity with hydrolysis was considered to be due not to alkali hydrolysis, but to the heat treatment in the alkali solution at 90 °C.

3.5 X-ray Diffraction

To elucidate the changes in the crystallite structure of PET and POY fibers with heat treatment and subsequent alkali hydrolysis, we subjected them to wide angle X-ray diffraction measurement. X-ray diffraction photographs for the heat-set and hydrolyzed PET and POY fibers are shown in Figs. 5 and 6, respectively. The reflections of the (010), ($\bar{1}10$) and (100) planes for the heat-set PET fibers became evident and increased in intensity, suggesting the growth of crystallites and increase in crystallinity, but no significant decrease in crystallite orientation was observed with increasing heat setting temperature. These reflections for POY fibers gradually separated and

Heat set PET fibers

Heat set and alkali hydrolyzed PET fibers

Fig. 5 Wide angle X-ray diffraction patterns for heat-set and alkali-hydrolyzed PET fibers.

Heat set POY fibers

Heat set and alkali hydrolyzed POY fibers

Fig. 6 Wide angle X-ray diffraction patterns for heat-set and alkali-hydrolyzed POY fibers.

Fig. 7 SEM photographs ($\times 3000$) of alkali-hydrolyzed PET fibers.

became sharper with increasing heat setting temperature, also indicating the increase in crystallite size. Since the length along the arcs became longer with the increase of heat setting temperature, crystallite orientation was greatly decreased. The difference in the diffraction pat-

terns among the heat set POY fibers was clearly less than that among the PET fibers, which also reflected that the fine structure in the heat-set POY was, to some extent, leveled off.

These diffractions for PET fibers became even sharper

Fig. 8 SEM photographs ($\times 3000$) of alkali-hydrolyzed POY fibers.

Fig. 9 Changes in cross sectional area ($\Delta A/A_0$) with alkali hydrolysis for PET (●) and POY (○) fibers.

with alkali hydrolysis, also suggesting that there is a difference in crystallite size and orientation for the fibers before and after alkali hydrolysis. For POY fibers, however, little changes in the X-ray diffraction pattern were found.

3.6 SEM Photographs

SEM photographs of the hydrolyzed PET and POY fibers are shown in Figs. 7 and 8, respectively. Alkali hydrolysis of polyester fibers takes place predominantly

at the surface. The formation of craters on the fiber surface is one of the characteristics of alkali hydrolysis of polyester fibers. Craters formed on the surface of POY fibers were much larger than those on PET fibers, indicating that the heat-set POY fibers are more easily attacked by alkali. Degree of etching by alkali well reflected changes in weight loss for both PET and POY fibers with the fibers heat set at 140 °C least attacked. Cracks perpendicular to fiber axis, however, formed on the surface only for POY fibers heat set at 100 °C and 120 °C. The cause of the formation of these cracks is not clear yet.

Decrease in cross sectional area with alkali hydrolysis was calculated from the change in fiber diameter before and after hydrolysis. The results for PET and POY fibers are shown in Fig. 9 and correspond to weight loss with a minimum at a heat setting temperature of 140 °C.

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