Mechanical Properties of Poly(ethylene terephthalate) Fibers Imparted Hydrophilicity with Aminolysis

KAZUHIKO FUKATSU

Faculty of Living Science, Kumamoto Women's University, Kumamoto 862, Japan

SYNOPSIS

Poly(ethylene terephthalate) fibers were aminolyzed with hydradine hydrate and ethylenediamine. The moisture regain of aminated fibers increased with increasing weight loss. It was suggested that the aminolysis reaction took place mainly in the amorphous regions. This leads to an increase of the accessibility of moisture. The mechanical properties of the aminated fibers were reported as a function of the weight loss by the aminolysis reaction; tenacity, stiffness, and wrinkle recovery were considered and discussed with regard to fine structures. General trends of decreasing tenacity, stiffness, and wrinkle recovery with increasing weight loss were observed for fibers aminated by hydrazine hydrate and ethylenediamine. Within this trend, there is difficulty for application of aminolysis that will not provide superior performance in the polyester fiber property such as tensile strength, stiffness, and wrinkle recovery.

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers, commonly known as polyester fibers, are widely used, especially after blending with cotton, wool, viscose rayon, etc.[1] Polyester fibers have taken the major position in textile all over the world although they have many drawbacks, e.g., (a) low moisture regain (0.4%). Because of low moisture regain, polyester fabric is uncomfortable to wear in hot climates since the fabric is unable to absorb perspiration from the body of the wearer; and (b) the fiber has a tendency to accumulate static electricity, which creates a number of problems.

Numerous research papers are available and a considerable amount of research work is in progress on the chemical treatment of polyester fibers to overcome their disadvantages.[2] In particular, several studies have appeared on the imparting of the hydrophilicity to polyester fibers with a grafting technique[3] and aminolysis.[4,5] To impart the hydrophilicity, previous studies on the chemical degradation of the polyester fibers have been concerned with the chemical nature of the degradation and little consideration has been given to the changes of mechanical properties taking place.

In the present investigation, hydrazine hydrate and ethylenediamine were chosen because they reacted easily with PET. This leads to increase the accessibility of moisture, bringing about the increase of moisture regain.[6] The objective of this study was to provide comparison of the effects of this treatment on mechanical properties and to obtain a general perspective regarding to the spectrum of performances.

EXPERIMENTAL

Materials

The polyester fabric cloth used was in the form of filament woven fabric cloth made from filament yarns, i.e., warp yarn: 75 denier, 38 filaments, and zero twist; weft yarn: 100 denier, 50 filaments, and zero twist. It weighed about 80 g/m^2. All chemicals were of reagent grade and were used without further purification.

Reaction of PET with Amines

The sample fabrics (10 × 10 cm) were weighed and then treated for various times in aqueous solution containing 50% hydrazine hydrate or ethylenediamine at the desired temperature, the samples being

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shaken throughout the reaction at a liquor-to-sample ratio of 20 : 1. After the reaction, the sample fabrics were washed with distilled water and allowed to air-dry. The weight loss of the fabrics in the aminolysis was measured by drying to a constant weight in a vacuum oven at 50°C.

Determination of Density

The densities (d) of the sample fibers were measured in a density gradient tube established with carbon tetrachloride and n-heptane so as to give a working range of 1.45–1.30 g/cm^3. The tube was maintained at 30°C by means of a water jacket and calibrated using standard floats. The assumed densities of fully crystalline and fully amorphous regions are 1.445 and 1.335 g/cm^3, respectively. The crystallinity (x) is measured by the following equation:

$$\frac{1}{d} = \frac{x}{1.455} + \frac{1-x}{1.335}$$

Molecular Weight Measurement

The specific viscosity (ηsp) of 0.5% solution in phenol–tetrachloroethane (1 : 1) mixture solution was measured at 25°C using an Ostwald viscometer. The intrinsic viscosity ([η]) was calculated from the value of the Huggins viscosity slope constant using the specific viscosity (ηsp). The molecular weight (M_n) was calculated by the following equations[7]:

$$[\eta] = \{(1 + 1.4 \cdot \eta\,\mathrm{sp})^{1/2} - 1\}/0.35$$

$$[\eta] = 2.1 \times 10^{-4} \cdot \mathrm{M}_n^{0.82}$$

Differential Thermal Analysis

The differential thermal analysis (DTA) was measured using the Shimadzu DTA-40M differential thermal analyzer. The sample was heated at 10°/min from ambient temperature to 500°C in an air atmosphere. α-Al_2O_3 (calcined at 1500°C) was used as a standard material.

Determination of Moisture Regain

The moisture regain was performed at 95% RH. The sample fabrics were conditioned for a minimum of 48 h at 25°C over a saturated sodium sulfate aqueous solution in a closed container. The moisture regain was determined by vacuum desicator method[8] and calculated by the formula

$$R = 100\ w / W$$

where R = moisture regain, w = weight of the moisture, and W = dry weight of the sample.

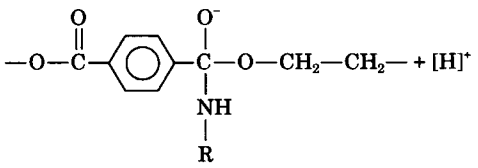
Mechanical Properties Measurements

The basic mechanical properties of the fibers and fabrics were carried out by the procedure standardized by the Japanease Industrial Standard Committee (JIS). Conditioning of fiber and fabric specimens for 24 h at 20°C and 65% RH was adopted as the standard condition. Standard test methods were used to evaluate tenacity and elongation of fibers (JIS L 1073), bending stiffness of fabrics (JIS L 1096), and conditioned and wet wrinkle-recovery angles (JIS L 1096: the Monsanto method). The wet wrinkle-recovery angle measurements were begun after immersion of the specimen in water for 10 min. Where appropriate, tests were conducted only in the warp direction. The tensile properties of the fibers were studied with the help of the Shimadzu DCS-100 autograph (with a full-scale load of 100 g, crosshead speed of 5 cm/min, gauge length of 5 cm, and chart speed of 5 cm/min).

RESULTS AND DISCUSSION

Aminolysis of PET with Amines

The polyester fiber undergoes aminolysis. There is a nucleophilic attack of the nitrogen on the carbonium center of the carbonyl ester. This would normally be a rapid reaction. The actual mechanism may involve the amine attack on the electron-deficient carbonyl carbon atom, forming a following reactive intermediate:



(R = —NH_2 or —CH_2—CH_2—NH_2)

Since the reaction to form this reactive intermediate is fast, the rate-determining step of the degradation is the reaction of the steady-state concentration of the conjugate amine/ester complex. It is assumed that the amine randomly attacks the carbonyl groups of the polymer molecular present on the surface of the fiber and removes them as short chains. Following the degradation, there was a considerable weight loss, as shown in Figure 1. Finally, the short chains are aminolyzed to dihydrazide terephthalate or diethylenediamino terephthalate. Fig-

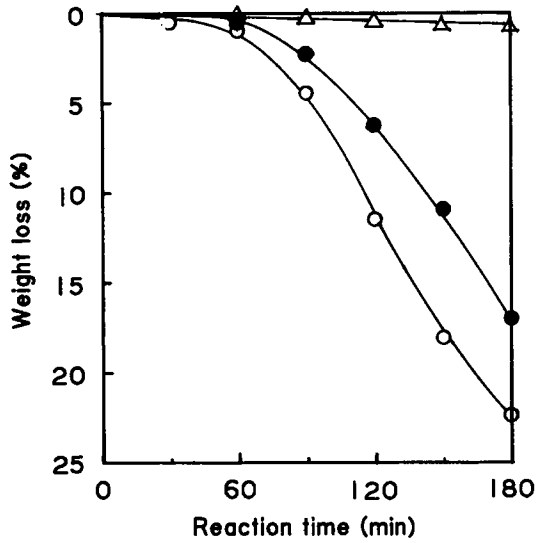


Figure 1 Plot of weight loss of polyester fibers vs. reaction time with hydrazine hydrate and ethylenediamine: (○) hydrazine hydrate at 30°C; (△) ethylenediamine at 30°C; (●) ethylenediamine at 70°C.

ure 1 shows the weight loss that was produced by immersing the fiber in 50% amine aqueous solution for various times. At 30°C in hydrazine hydrate, the weight loss easily takes place. On the other hand, in ethylenediamine, there is little weight loss, but at 70°C, the weight loss shows a significant decrease.

Molecular Weight and Crystallinity of Aminated PET

Examination of Figure 1 together with results in Figures 2 and 3 shows that initially some reduction in molecular weight occurs in the first stages of the reaction with little weight loss. This phenomenon appears to be larger in ethylenediamine than in hydradine hydrate. The molecular fragments resulting from initial cleavage of the ester bonds are too large to be extracted. This suggests that there is a rapid fall in the molecular weight due to attack in the amorphous regions, but little low molecular weight material is formed and, hence, the sample weight and crystallinity are almost unchanged. However, compared with results of two amines used in this study, the agreement is not good, although the same reaction occurs. These differences are due to an ability of the penetration of aminolyzing agents into polyester fiber. In the case of hydrazine hydrate, the aminolysis is highly selective so that an amorphous region in the vicinity of the surface of the polyester fiber is removed, rapidly leaving residues that are highly crystalline. Therefore, the reduction in the molecular weight is relatively smaller than that in ethylenediamine and the crystallinity becomes greater with increasing weight loss. Though this result suggests that the recrystallization of PET proceeds with the aminolysis, actually it seems reasonable to assume that this phenomenon is due to the degradation of amorphous regions. On the other hand, in the case of ethylenediamine, the penetration into the polyester fiber becomes progressively greater with a rise of temperature and the aminolysis also occurs at an internal amorphous region of the polyester fiber. This leads to the reduction in the molecular weight that is larger than that observed in hydrazine hydrate as in Figure 2.

Differential Thermal Analysis (DTA)

Figure 4 shows typical DTA traces. An endotherm caused by melting temperature (T_m) is observed in these samples. Varma et al.[9] reported that the endotherm peak (T_m) appears at higher temperature as crystallinity is raised. But in this study, as mentioned above, although the crystallinity increased with increasing the weight loss by aminolysis, the endotherm peak position showed a shift somewhat to the low-temperature side and its peak became progressively broader and smaller. This behavior could be attributed to the presence of short chains produced by the aminolysis in amorphous regions and the action as an impurity of the low molecular compound produced, which leads to melting point depression. It may be considered that the broading of the peak is based on the reduction in the molecular weight, the crystallization, and the melt of crystal

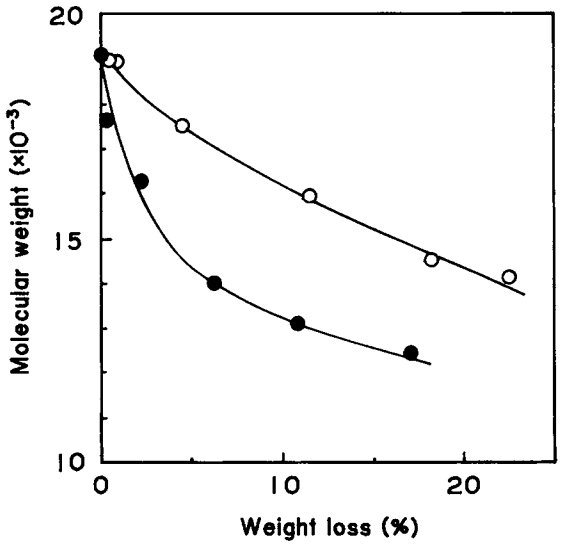


Figure 2 Relationship between molecular weight and weight loss by the treatment of the fiber: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

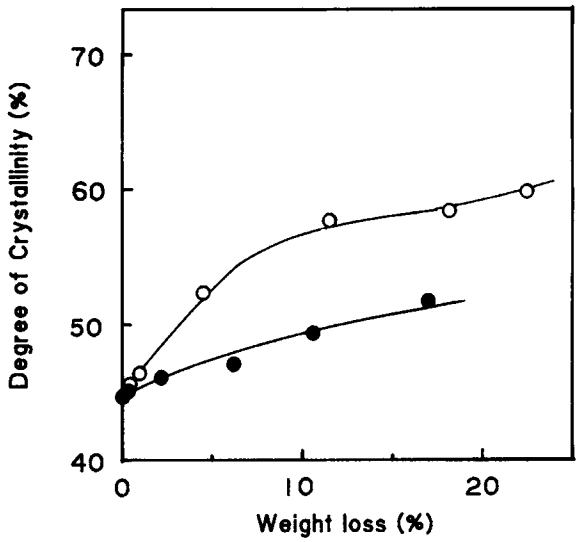


Figure 3 Changes of crystallinity by aminolysis as a function of weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

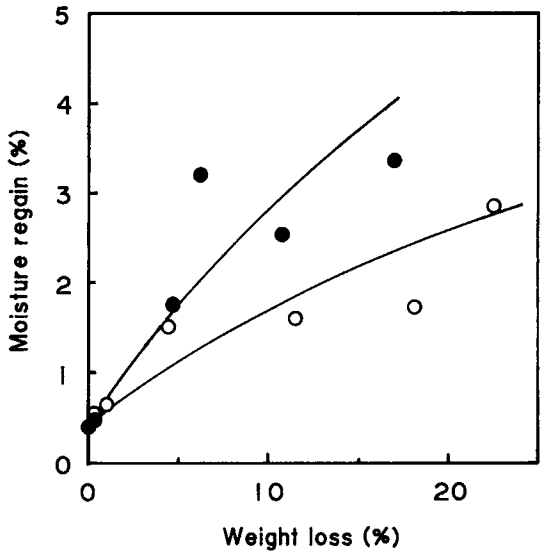


Figure 5 Changes of moisture regain of polyester fabrics as a function of weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

at a heating process. Also, the heat of fusion becomes progressively smaller as the aminolysis proceeds. Although this effect may suggest that crystal changes to amorphous in the neighborhood of crystalline regions, further details of this reaction are not clear.

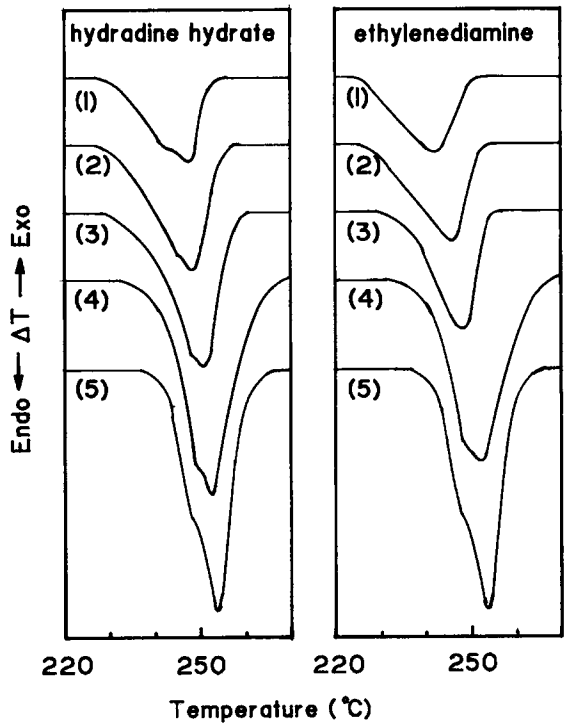


Figure 4 DTA curves of aminated polyester fabrics. Reaction time: (1) 180 min; (2) 150 min; (3) 120 min; (4) 90 min; (5) 0 min.

Moisture Regain

The moisture regain of aminated polyester fibers with various weight loss was measured under 95% RH and 25°C. The results are shown in Figure 5. From these results, it is evident that the moisture regain increases with increase in the weight loss level. In comparison of the two amines used in this investigation, it is seen that the moisture regain in ethylenediamine increases considerably as compared to that in hydrazine hydrate. This phenomenon may be explained as follows: The moisture regain is restricted by the degree of the destruction in the molecules that exists in an internal amorphous region of the polyester fiber. The internal amorphous region is as susceptible to aminolysis by ethylenediamine than it is by hydrazine hydrate.

Mechanical Properties

Tensile properties (tenacity, breaking elongation, and initial modulus) of polyester fiber, aminolyzed with amines, viz. hydrazine hydrate and ethylenediamine, to various weight loss levels have been investigated. The results of tenacity, breaking elongation, and initial modulus are shown in Figures 6, 7, and 8, respectively. It may be expected[9] that the mechanical properties of fiber are improved as they provide superior performance because the crystallinity increases with the proceeding of aminolysis, as mentioned above. However, a remarkable difference from the expected result in these properties occurs in aminated fibers when compared to un-

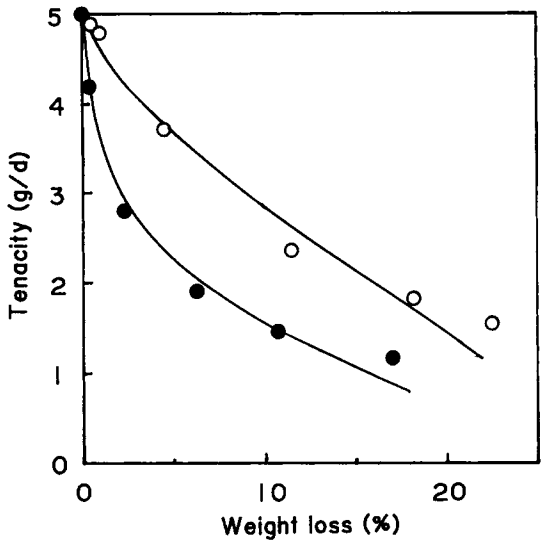


Figure 6 Relationship between tenacity and weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

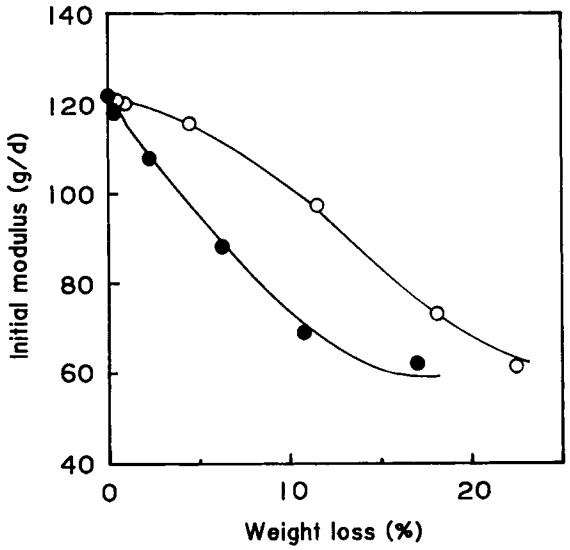


Figure 8 Relationship between initial modulus and weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

treated fibers. Tenacity and initial modulus of fiber are actually decreased by aminolysis. These phenomena may be attributed to the decay of crystal network structures caused by the degradation of amorphous regions. The behavior of elongation is the same as that of tenacity. These results indicate that the polyester fiber, which was aminolyzed, became generally brittle on the basis of the fine structure. In brief, the mechanical properties of the polyester fiber are not improved by aminolysis and, conversely, the aminated polyester fibers are much inferior to the polyester fiber in many respects.

The bending stiffness of fabrics as a function of the weight loss is shown in Figure 9. This property decreases with increasing of the weight loss, and an approximately linear relationship exists between the decrease in the stiffness and the weight loss. In general, an increase in density of fabric significantly improves bending stiffness.[10] But in this investigation, because the density of fabric does not vary with

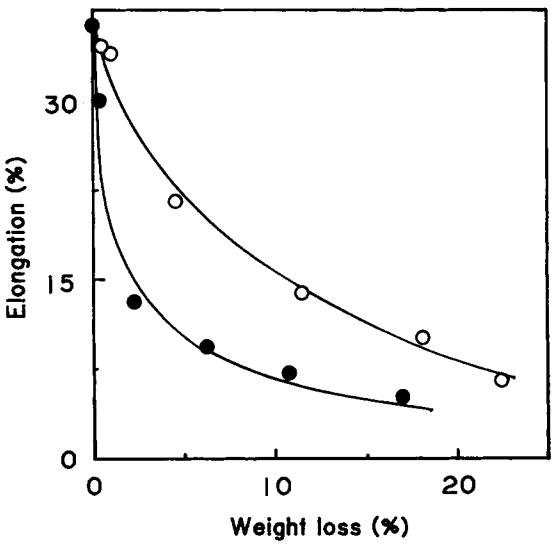


Figure 7 Relationship between elongation and weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

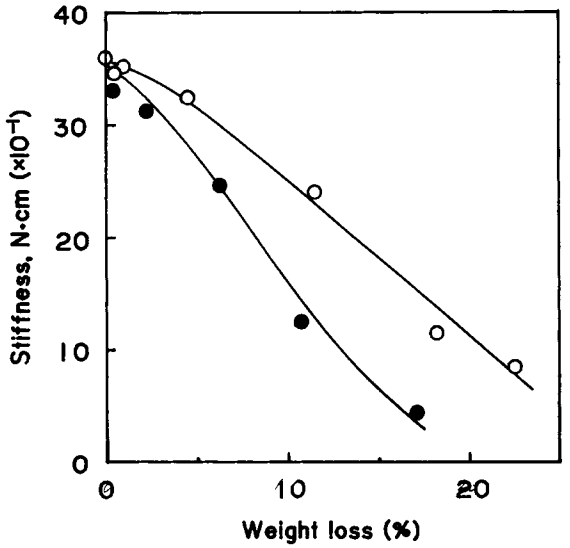


Figure 9 Relationship between stiffness and weight loss: (○) hydrazine hydrate at 30°C; (●) ethylenediamine at 70°C.

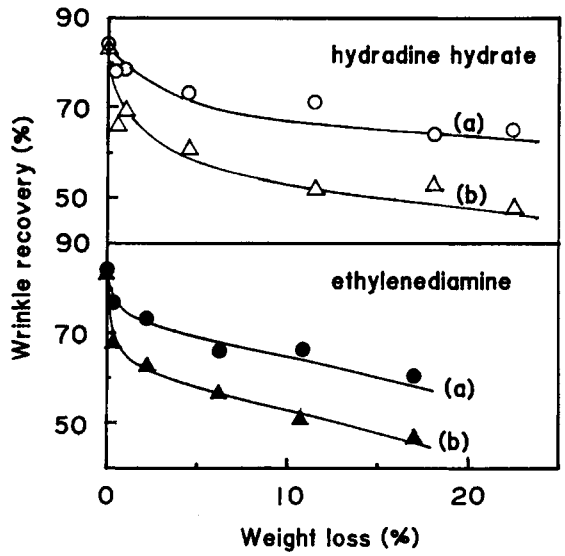


Figure 10 Relationship between wrinkle recovery and weight loss: (a) dry; (b) wet.

aminolysis, the lowering of bending stiffness is not due to a change of density of fabric but due to that of fiber properties caused on fine structure. The aminated polyester fabric has substantially reduced bending stiffness compared to the untreated polyester fabric, as a result of the destruction of amorphous regions. As mentioned above, the lowering of initial modulus may greatly affect the bending stiffness.

The wrinkle recovery of polyester fabrics having good performance under normal conditions is scarcely lowered under the action of water as to limit the utility of the fabric. In this investigation, conditioned and wet wrinkle-recovery angles were measured and values of those for fabrics as a function of the weight loss is shown in Figure 10. Both wrinkle-recovery angles decrease with increasing weight loss. The reason that these angles decrease with increasing weight loss is the same as that of the decrease in bending stiffness; i.e., it is due to the lowering of initial modulus in the aminated polyester fiber. Comparison of conditioned and wet wrinkle recovery indicates that a reduction in wrinkle recovery is greater in the wet fabric than in the conditioned one. This effect is believed to result from a change in the degree of water-plasticization of the wet fiber. As in the aminated polyester fabric having the hydrophilicity, the degree of swelling is increased (the weight loss is increased) and the wrinkle-recovery angle is reduced by the action of water as a plasticizer.

CONCLUSIONS

The various properties of polyester fibers imparted with hydrophilicity via aminolysis were investigated utilizing molecular weight, crystallinity, DTA, and mechanical properties measurements. As a result of the aminolysis, the crystallinity of the fiber increased and the melting temperature decreased with increasing weight loss. These results suggested that the degradation took place at the amorphous regions at the early stage of aminolysis. Also, tenacity, elongation at break, and initial modulus of the fiber, bending stiffness, and wrinkle recovery of fabrics decreased with increasing weight loss. It was considered that the change of those mechanical properties was attributed to the decay of crystal network structures caused on the degradation of amorphous regions. Comparison of conditioned and wet wrinkle recoveries of fabrics indicated that a reduction in wrinkle recovery was greater due to changes in the degree of water-plasticization of the wet fiber.

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