

Physical Properties of Wool Keratin Yarn Modified with Dibasic Acid Anhydrides

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Synopsis

The structure and physical properties of wool keratin yarns modified with dibasic acid anhydrides, namely, succinic and glutaric anhydride are analysed by thermomechanical analysis (TMA), differential scanning calorimetry (DSC), thermogravimetry (TG), and on the basis of measurements of the tensile properties. The optimum temperature for the reaction with dibasic acid anhydride can be achieved at 65°C. The weight gain of wool yarn treated with glutaric anhydride was 3% larger compared with that of the sample treated with succinic anhydride for the reaction time of 4 h. However, the acyl contents of the wool yarn treated with succinic and glutaric anhydride was the same. The moisture regain values of the wool yarn treated with glutaric anhydride were much lower by about 2% compared with those for the wool yarn treated with succinic anhydride. The original properties in mechanic of the wool yarn are not damaged even after the modification with dibasic acid anhydride. Taking into account the dyeability and thermal properties of the chemically modified wool keratin yarns, it would seem that the ester crosslinks are easily formed in keratin much more by the glutarylation than by succinylation.

INTRODUCTION

The physical and thermal properties of wool keratin yarn have been studied extensively by various researchers.¹⁻³ Based on a detailed study of the setting behavior and set stability of benzoylated wool fabric,¹ it was concluded that the chemical introduction of bulky acyl groups markedly enhanced these properties. Few studies have been reported, however, on the properties of wool yarn modified with dibasic acid anhydrides. The thermal properties of wool keratin yarn have been analyzed in relation to the structural characteristics.^{8,9} Sakabe et al.,² who investigated the thermal behavior of component proteins separated from wool keratin, attributed the endothermic peak at 220°C and at 250–270°C to the melting of the α -helix structure and of the β structure of the microfibrils, respectively. Regarding the thermal properties of the α -helix of wool keratin, it was shown that the three peaks in the dynamic loss modulus-temperature curves at about 210, 60, and -50°C could be assigned to the disordering of the α -crystallites in keratin, the micro brownian motion of the keratin back bone chains, and the side chain motion, respectively.³

One of the authors analysed the thermal properties, crystalline structure, and the morphological features of silk fiber grafted with various kinds of vinyl monomers, methylmethacrylate,⁴ 2-hydroxyethylmethacrylate/methacrylamide

mixture system⁵ and methacrylonitrile.⁶ It seemed interesting, from the point of view of chemical modification of natural fibers, to compare the structural and physical properties of wool keratin yarn chemically modified with grafted silk fiber.

In a previous paper,⁷ we studied the physicochemical properties of the silk fiber treated with dibasic acid anhydrides and demonstrated that the crease recovery values of the silk fabric increased by glutarylation rather than by succinylation and that glutarylation prevented the silk yellowing caused by UV irradiation.

The present study was undertaken to analyze the chemical and structural changes of wool keratin yarn associated with the treatment with dibasic acid anhydrides, such as succinic and glutaric anhydride by differential scanning calorimetry (DSC), thermogravimetry (TG), thermomechanical analysis (TMA), and on the basis of measurements of the tensile properties.

MATERIALS AND METHODS

Wool keratin yarn (2/49s) was cleaned by acetone/ethanol mixture system in a Soxhlet extractor for 12 h to remove the wax, then rinsed in distilled water, dried to constant weight, and conditioned in air at room temperature before use. Succinic and glutaric anhydride were of laboratory reagent grade purchased from the Wako Pure Chemical Industries. Dimethylformamide (DMF) was distilled under reduced pressure before use. The sample yarn (ca. 1 g) was treated with 10% (w/v) succinic or glutaric anhydride in DMF at different temperatures for 2 h to determine the optimum temperature for the reaction, and at 65°C for different periods of time (1, 2, and 4 h) in another experiment; this was attached to a reflux condenser and held in a thermostatically controlled bath. At the end of the reaction, the samples were washed with acetone at 55°C for 1 h to remove the unreacted dibasic acid anhydride, and then successively with tap water.

The weight gain was calculated from the increase in weight of the original yarn after chemical reaction as follows:

$$\text{Add-on (\%)} = (W_2 - W_1) / W_1 \times 100$$

where W_1 and W_2 denote the weight of the original keratin yarn and the chemically modified yarn dried at 105°C to constant weight, respectively. Control sample was obtained by treatment with the DMF alone.

The wool keratin yarns treated with dibasic acid anhydrides rested for 1 week in a conditioned room where the temperature was 20°C and RH 65% were dried in a forced draft oven at 105°C to achieve a constant weight and weighted, thus the moisture absorption was obtained

$$\text{Moisture absorption (\%)} = (W_3 - W_2) / (W_1) \times 100$$

where W_3 denotes the weight of the sample after moisturing.

The differential scanning calorimetry (DSC) measurement and the thermomechanical analysis (TMA) were carried out as described in a previous paper.⁷

Dyeability characteristics using acidic (Kayanol Blue-N2G) and cationic dyes (Astrazon Red BL) were examined. The former dyeing was carried out at 85°C for 60 min in the neutral bath and the latter at 85°C for 30 min in the acidic one, keeping a material-to-liquor ratio of 1 : 100. The dye concentration was kept at 2.5% (owf) for the Kayanol Blue N2G containing 0.5% anion active agent (Noigen HC, Daichi Kogyo) and at 2% for the Astrazon Red BL containing 0.2% acetic acid and 0.5 g/L sodium acetate. The dye uptake values were measured with a Hitachi Color analyzer 607 and expressed in terms of K/S values.

Strength and elongation at break were measured on a wool keratin yarn with an automatic Tensilon tensile tester (Toyo Baldwin Co., UTM-II) at 20°C and 65% RH at a strain rate of 10%/min. Each value is the average of 25 results.

The surface of the treated wool sample was examined, after gold coating, with a JEOL JAX-333S scanning electron microscope.

RESULTS AND DISCUSSION

Effect of Temperature

In order to research the optimum temperature for chemical modification, the wool keratin yarns were treated at different temperatures for 2 h with 10% (w/v) dibasic acid anhydrides in DMF. The effect of the temperature on weight gain is shown in Table I. It was observed that the weight gain increased with the rise of temperature above 50°C. The reaction between wool and dibasic acid anhydrides proceeded rapidly with further increase of the temperature above 65°C. Thus, under the present reaction conditions, the optimum temperature for the reaction was 65°C. It is interesting to note that the optimum temperature (65°C) of the modified keratin yarn reacting with dibasic acid anhydride is about 10°C lower than that of the silk fiber.⁷ These findings suggest a difference in the chemical reactivity of side chains mainly of the lysine residues of wool and the tyrosine residues of the silk fibroin. That is to say, *N*-acyl groups are introduced mainly by the action of dibasic acid anhydride onto the wool fiber containing a large amount of basic amino acid residues such as lysine and histidine. On the other hand, *O*-acyl groups are mainly introduced in the

TABLE I
Weight Gain and Acyl Content of the Wool Keratin Yarn (2/49s) Treated with Succinic and Glutaric Anhydride in Dimethylformamide for 2 h at Different Temperatures

	Reaction temperature (°C)				
	40	50	65	70	80
Succinylation					
Weight gain (%)	1.3	1.8	14.9	16.9	18.9
Acyl content (mol/10 ⁵ g)	11.2	17.5	127.4	144.4	161.5
Glutarylation					
Weight gain (%)	1.5	1.9	16.9	20.0	23.0
Acyl content (mol/10 ⁵ g)	11.3	14.8	129.0	152.7	175.6

silk fiber containing a relatively large amount of tyrosine residues compared with the amounts of lysine and histidine.

Acyl Content and Moisture Regain

The weight gain of the wool keratin yarn were determined to analyse the structural changes in the course of the treatment with dibasic acid anhydrides (Fig. 1). The intensity of the reaction with the succinic and glutaric anhydrides increased within a 2 h period and was maximum at ca. 4 h. Although the values of weight gain associated with the treatment with succinic and glutaric anhydrides increased in a similar manner within 2 h, the weight gain of wool treated with glutaric anhydride was 3% larger compared with that of the sample treated with succinic anhydride for a reaction time of 4 h. However, it was noteworthy that the acyl contents of the wool treated with succinic and glutaric anhydride in DMF at 65°C for 4 h were 150 and 155 mol/10⁵ g. These results were essentially the same regardless of whether the wool keratin yarns were treated with succinic or glutaric acid anhydrides.

Figure 2 that shows the moisture regain reflects the structural changes induced by the chemical modification onto wool yarn. The changes in the moisture regain of the specimen were measured in relation to the weight gain. The slope of the linear curve of the wool yarn treated with succinic anhydride decreased with the increase in weight gain. The moisture regain values of the wool treated with glutaric anhydride were much lower by about 2% compared with those for the wool treated with succinic anhydride at the weight gain of ca. 15% at which the moisture regain decreased to reach the equilibrium level. These results may have been affected by the changes in the physical properties induced by the chemical modification due to the differences in the reactivity of wool yarn to succinic and glutaric anhydrides.

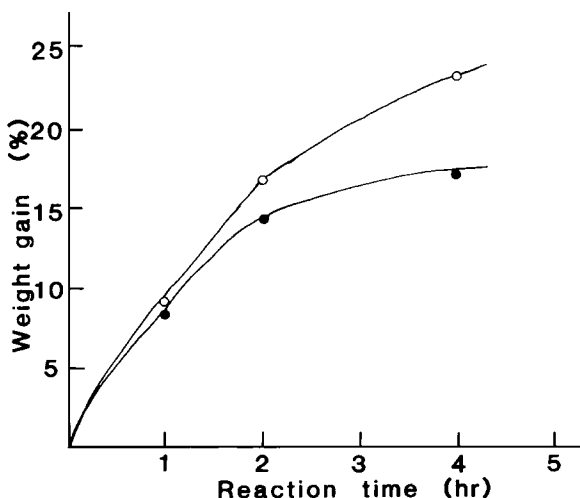


Fig. 1. Weight gains of the wool keratin yarns (2/49s) treated in dimethylformamide containing 10% (w/v) succinic (●) or glutaric (○) anhydride at 65°C for different periods of time. The material-to-liquor ratio of 1 : 100 remained.

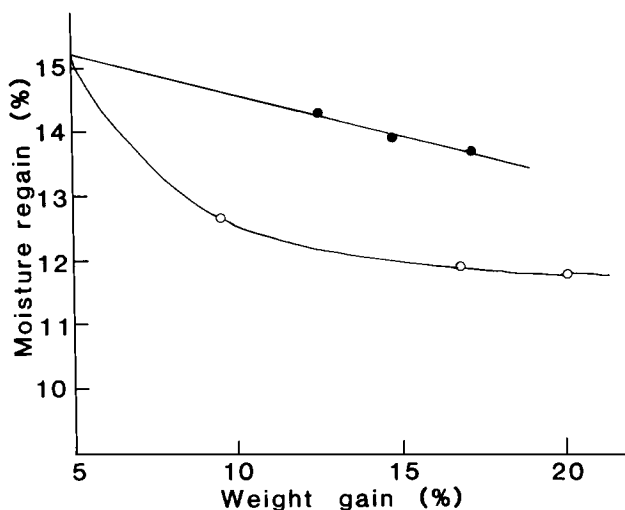


Fig. 2. Moisture regain of the wool keratin yarns treated in dimethylformamide containing 10% (w/v) succinic (●) or glutaric (○) anhydride at 65°C for different periods of time in relation to the weight gains.

Thermal Properties of the Modified Wool Keratin Yarn

In order to analyse the thermomechanical properties of the wool keratin yarn including the contraction and extension in the heating process, TMA curves for the modified wool keratin fibers were obtained (Figs. 3 and 4). Control wool specimen showed a very slight contraction of about 0.1% in the temperature range between 25–100°C; thereafter the length of the specimen remained unchanged up to 200°C. The control specimen showed an abrupt extension in length above a temperature of 229°C. As shown in Fig. 3, the temperature in the TMA curves of the wool treated with succinic anhydride during the shift toward the contraction decreased to 70°C for the wool treated with succinic anhydride with a weight gain of 18.9%. The temperature at which two approximately straight lines intersected above 200°C decreased from 210°C for the wool fiber treated with succinic anhydride for 1 h to 150–160°C for the wool treated for 4 h.

Figures 5 and 6 show the DSC curves of the modified wool keratin yarn. The control wool yarn showed a broad endothermic peak in the temperature range between 230–270°C. The endothermic peak at 220°C and at 250–270°C are attributed to the melting of the α -helix structure, and of the β -structure of the micro fibrils and matrix protein.² Wool yarn treated with succinic anhydride in DMF exhibited an endothermic peak at 219 and 230°C (Fig. 5). It should be emphasized that the control wool does not show any trace of endothermic peak at about 220°C, suggesting the greater thermal stability of the α -helix fraction in the contraction. On the other hand, the wool treated with glutaric anhydride in DMF for more than 2 h exhibited a sharp endothermic peak at 213°C in addition to the broad and apparent endothermic peak in the temperature range from 236–243°C, in contrast to the reaction of the succinylated wool and control wool. These differences in the thermal properties of wool keratin caused by the dibasic acid anhydride treatment needs further clarification.

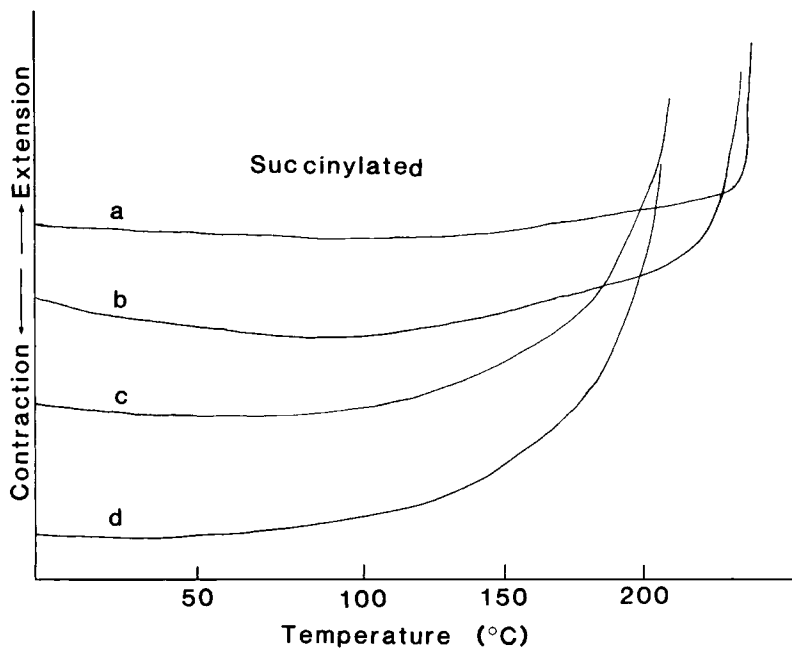


Fig. 3. Thermomechanical analysis curves of single wool keratin fibers treated with succinic anhydride in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2; (d) 4.

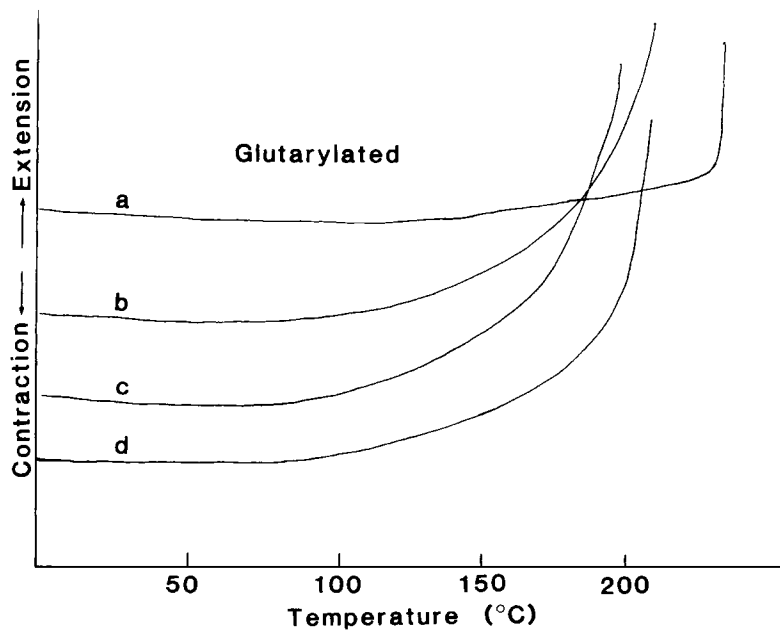


Fig. 4. Thermomechanical analysis curves of single wool keratin fibers treated with glutaric anhydride in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2.

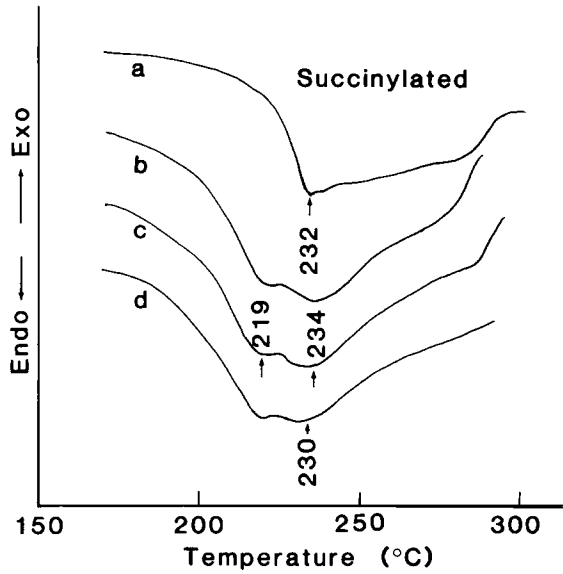


Fig. 5. DSC curves of succinylated wool keratin yarns in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2; (d) 4.

The weight loss residues of the wool yarn in the course of the heating process was determined by TG thermogravimetry (TG) (Figs. 7 and 8). The wool treated with succinic anhydride showed a weight loss (first weight loss) in the

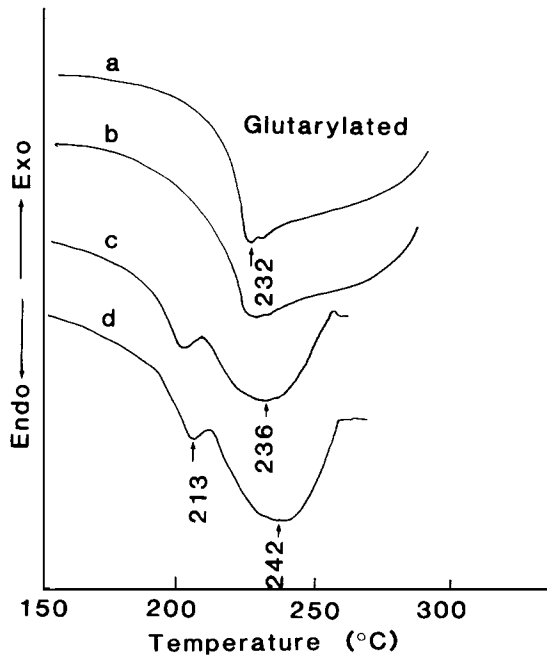


Fig. 6. DSC curves of glutarylated wool keratin yarns in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2; (d) 4.

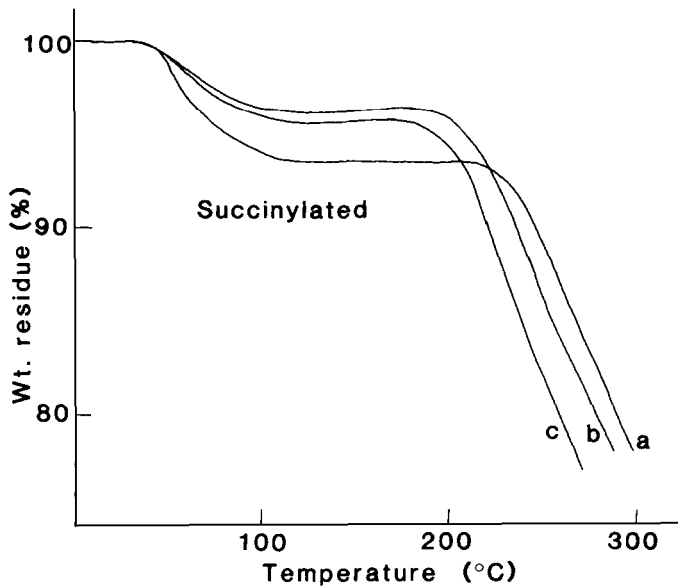


Fig. 7. Thermogravimetric curves of succinylated wool keratin yarns in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2; (d) 4.

temperature range between 30–130°C which was attributed to the evaporation of the humidity absorbed in the specimen. The second weight loss at above 180°C was due to the thermal decomposition. These results showed that the position of the temperature coincides with that of the endothermic peak which appeared on the DSC curves. The value of the weight loss of the wool yarn

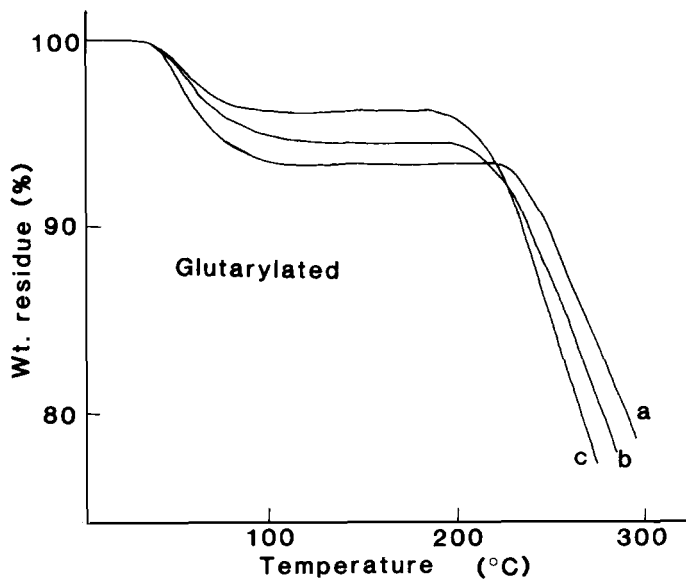


Fig. 8. Thermogravimetric curves of glutarylated wool keratin yarns in dimethylformamide at 65°C for different periods of time. Time (h): (a) 0; (b) 1; (c) 2; (d) 4.

TABLE II
The *K/S* Values of the Succinylated and Glutarylated Wool Keratin Yarns (2/49s)
Dyed with Astrazon Red BL and Kayanol Blue N2G

Sample	Astrazon Red BL		Kayanol Blue N2G	
	<i>R</i> ^a (%)	<i>K/S</i> ^b	<i>R</i> (%)	<i>K/S</i>
Control	17.99	1.87	1.83	26.33
S 17.6 ^c	1.73	27.91	8.69	4.80
S 13.5	1.86	25.89	7.91	5.36
G 20.3	1.95	24.65	6.03	6.97

^{a,b} *R*, *K*, and *S* are the reflectance of monochromatic light, the absorption coefficient, and the scattering coefficient, respectively.

^c S 17.6, S 13.5, and G 20.3 are the wool keratin yarns treated with succinic anhydride with weight gains of 17.6% and 13.5% and treated with glutaric anhydride with weight gain of 20.3%, respectively.

treated with glutaric anhydride was slightly smaller than that of the yarn treated with succinic anhydride within the entire temperature range.

Dyeability

The dyeing behavior of the wool keratin yarn treated with dibasic acid anhydrides was evaluated for the dyeability characteristics using 2 kinds of dye stuffs so as to clarify the change in the reactivity of the keratin yarn (Table II). A significant increase in the dye (Astrazon Red BL) uptake by the succinylated wool yarn was observed, compared with that of glutarylated wool. The succinylated wool dyed with Kayanol Blue N2G showed a slightly smaller decrease in the dye uptake than the glutarylated. These results demonstrating the difference in dye uptake appear to have made a considerable distribution to the increased interaction between the dye molecules and free carboxyl groups

TABLE III
Mechanical Properties of Wool Keratin Yarns (2/49s) Treated with Dibasic Acid Anhydrides

Sample	Strength (g)	Elongation (%)	Initial tensile resistance (kg × 100%)
Control	358	36.1	4.9
Succinylated ^a			
S-1	396	35.2	5.9
S-2	400	36.5	6.0
S-3	375	37.3	5.5
Glutarylated ^b			
G-1	371	36.5	4.9
G-2	379	37.9	5.5
G-3	371	37.9	5.0

^a S-1, S-2, and S-3 are the wool keratin yarns treated with succinic anhydride in DMF at 65°C for 1, 2, and 4 h, respectively.

^b G-1, G-2, and G-3 are the wool keratin yarns treated with glutaric anhydride in DMF at 65°C for 1, 2, and 4 h, respectively.

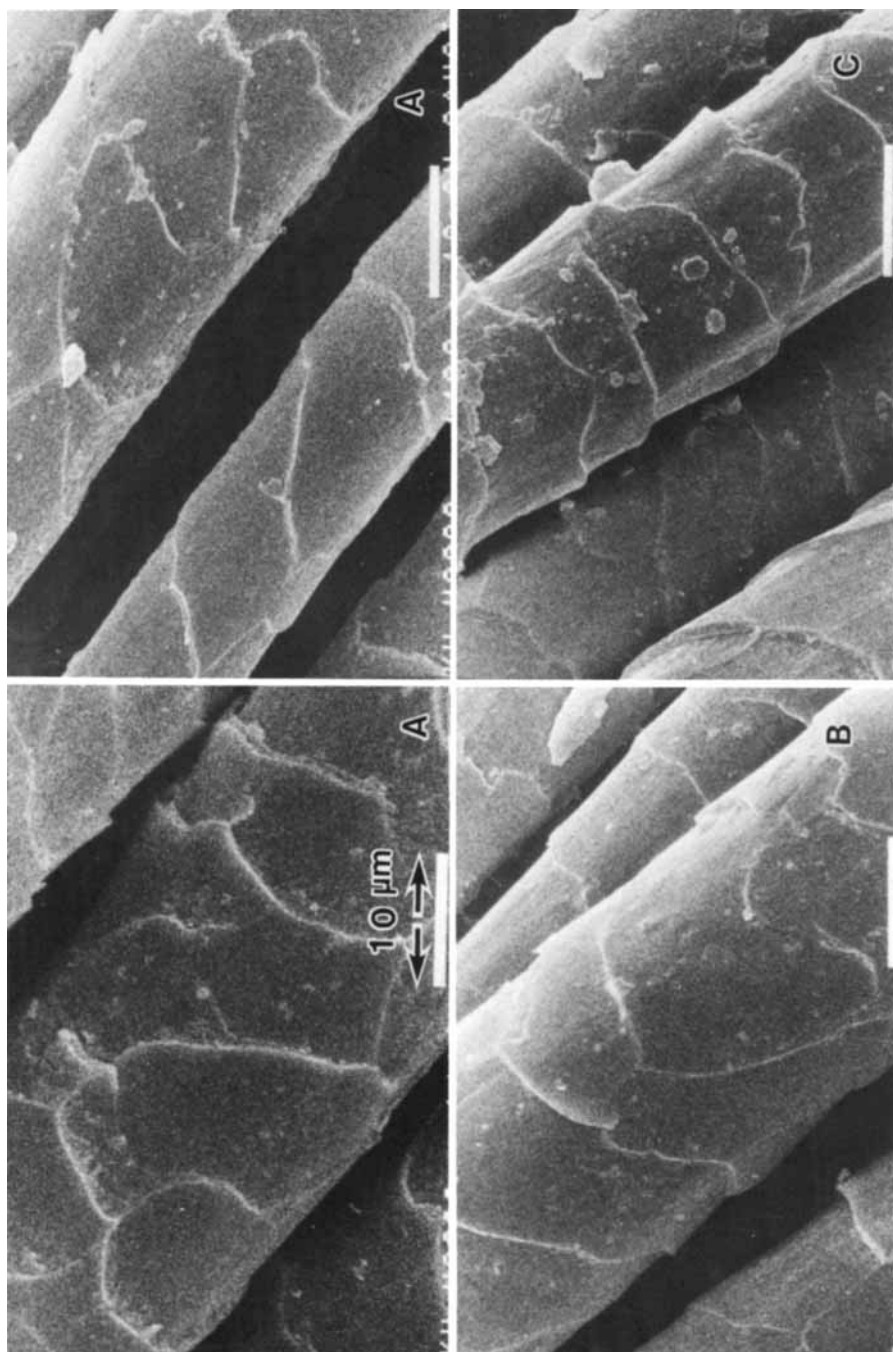


Fig. 9. Scanning electron microscopic observation of the control sample (A) and the wool keratin yarn treated with succinic (B) and glutaric (C) acid anhydride in dimethylformamide at 65°C for 2 h.

present in the modified chains. As might be expected, it would seem that the ester crosslinks are easily formed in keratin much more by the glutarylation than by the succinylation.

Tensile Property

The mechanical properties of wool keratin yarn are tabulated in Table III. It is found that both modifications by succinylation and glutarylation do not have any significant influence on the strength and elongation at break of the wool keratin yarn. It is also seen that the value of initial tensile resistance corresponding to the Young's modulus of the keratin fiber remained unchanged, compared with that of the original property in mechanic of the wool not damaged even after the modification with dibasic acid anhydrides. These findings are also consistent with the previous results of succinylated or glutarylated silk fibers.⁷

We have elucidated in a previous paper that the optimum temperature for the chemical modification onto silk fiber with dibasic acid anhydrides is 75°C, shifting 10°C higher than that of the wool keratin yarn. These findings suggest that the greater reactivity of the active site of the wool yarn containing a relatively large amount of basic acid side chains compared with silk fibroin.

Yarn Morphology

Figure 9 shows the surface of the wool keratin yarn modified with succinic and glutaric anhydride. The surface of the wool yarn treated with different kinds of dibasic acid anhydride appeared to be as smooth as that of the control wool yarn.

References

1. B. Milligan and L. J. Wolfran, *J. Text. Inst.*, **63**, 515 (1972).
2. H. Sakabe, T. Miyamoto, and H. Inagaki, *Sen-i Gakkaishi*, **38**, 517 (1982).
3. K. Arai and M. Ishikawara, *Sen-i Gakkaishi*, **39**, 14 (1983).
4. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
5. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 2133 (1988).
6. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **39**, 1289 (1990).
7. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
8. A. Konda, M. Tsukada, and S. Kuroda, *Polym. Lett. Ed.*, **11**, 247 (1973).
9. W. D. Felix, M. A. McDowall, and H. Eyring, *Tex. Res. J.*, **33**, 465 (1963).

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