Ammonia-Gas and Liquid Ammonia Treatments of Silk Fabric

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ABSTRACT: Silk fabric, Habutae, was treated with 100% ammonia-gas under atmospheric pressure and at pressures of 2, 4, and 6 kgf/cm^2, and with liquid ammonia at −33°C. The effects of the treatment were investigated on the basis of the X-ray diffraction, DSC thermogram, moisture regain, water absorption, dyeing property, and mechanical property of the fabric. Crystallinity and equilibrium dye uptake were increased apparently by the liquid ammonia treatment, whereas effect of the ammonia-gas treatment was less than the liquid ammonia treatment. KES (Kawabata Evaluation System) shearing, bending, and tensile parameters were obtained. The modulus *G*, *B*, and hysteresis widths 2HG, 2HG5, and 2HB were decreased with the ammonia-gas treatment. On the contrary, the liquid ammonia treatment increased the parameters considerably. Therefore, it seemed that the ammonia-gas treatment is effective in enhancing the soft hand of the silk fabric. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3487–3492, 2006

Key words: liquid ammonia; ammonia-gas; silk; mechanical property; dyeing property

INTRODUCTION

Liquid ammonia treatment has been practically done in textile finishing since 20 years ago, and is been carried out as a pretreatment of the shape stability and for improving the soft hand of cotton fabric. The liquid ammonia treatment of cottons caused a decrease of the apparent dyeing rate comparing with the mercerization despite a considerable decrease in the crystallinity.[1–3] The liquid ammonia treatment is not always effective in increasing the dyeing rate not only for the cellulosic fiber,[2,4,5] but also for the nylon 6 fiber. The liquid ammonia treatment brought about a partial transition of the crystallite structure of nylon 6 fiber from the γ- to the α-form, and improved the soft hand and dyeing properties of the nylon 6 fabric.[6] Recently, we researched on the ammonia-gas processing of the textile fiber. Wool fabric increased the dyeing rate and equilibrium dye uptake considerably by the treatment.[7] Also regenerated cellulosic fabrics such as viscose rayon, lyocell, cupro, and polynosic were treated with ammonia-gas. The treatment is especially effective to improve the soft hand of the regenerated cellulosic fabrics.[8,9]

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In this study, silk fabric, Habutae, was treated with ammonia-gas using an experimental equipment of Iwatani, Japan, and also the liquid ammonia with a practical range of Nisshinbo, Japan. Effect of the treated fabrics was investigated on the basis of the X-ray diffraction and DSC analysis, water absorption, dyeing behavior with two acid dyes, and Kawabata Evaluation System (KES) mechanical property.

EXPERIMENTAL

Materials

Silk fabric, Habutae (58 g/m^2) was treated with a 100% ammonia-gas under atmospheric pressure (0.098 MPa, AP) and at pressures of 2, 4, and 6 kgf/cm^2 corresponding to 0.196, 0.392, and 0.588 MPa for 60 min at 50°C. The equipment for the treatment (Iwatanai, Japan) was used according to the previous procedure.[5] The liquid ammonia treatment was carried out at −33.4°C using an equipment available at Nisshinbo, Japan.[10]

Physical property

X-ray diffraction profile of the fiber was obtained by means of equatorial scan with Cu Kα monochromatic X-rays using a Rigaku X-ray diffractometer, model III-DMAX. DSC measurement was carried out with a

TA DSC 2910 at a constant heating rate of 10°C/min for a specimen of about 3 mg in a dry nitrogen atmosphere. Dry and wet crease angle was measured with a Monsanto Crease Angle tester in both warp and filling directions each ten time to get an average.

Moisture regain and water absorption were measured according to the following procedure. The treated fabric was impregnated in water for 24 h and then centrifuged for 20 min at 3000 rpm (W_1). Subsequently, the fabric was kept for 48 h at 65% RH (W_2), and finally dried for 3 h at 105°C (W_0). Moisture regain and water absorption were calculated by the following equations:[10,11]

$$\text{Moisture regain (\%)} = \frac{W_2 - W_0}{W_0} \times 100$$

and

$$\text{Water absorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

As a measure of the textile hand by the treatments, shearing, bending, and tensile properties were measured with a KES (Kawabata Evaluation System F-7) apparatus (Kato Tech, Japan). From the chart, shearing modulus G, shearing hysteresis widths 2HG and 2HG5, bending modulus B, bending hysteresis width 2HB, linearity of tensile LT, work of tensile WT, recovery of tensile RT, elongation maximum of tensile EMT parameters were obtained.

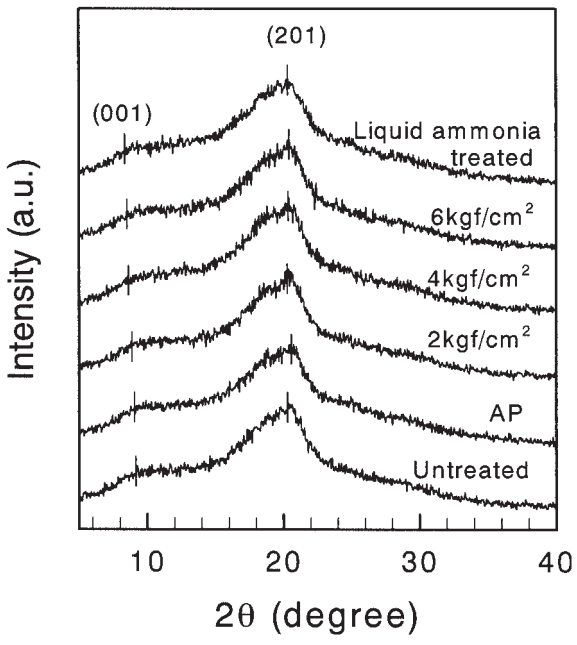

Figure 1 X-ray diffraction patterns of ammonia-gas and liquid ammonia-treated silk fibers.

TABLE I
Crystallinity of Silk Fibers Treated with Ammonia-Gas and Liquid Ammonia

Treatment	Crystallinity (%)
Untreated	36.1
Ammonia-gas treated	
AP	36.0
2 kgf/cm^2	36.1
4 kgf/cm^2	36.0
6 kgf/cm^2	35.7
Liquid ammonia treated	39.9

Dyeing

The treated silk fabrics were dyed with two acid dyes, leveling type C.I. Acid Red 13 and milling type C.I. Acid Blue 83. Dyebath was adjusted to pH 4.5 for Acid Red 13 and pH 5.5 for Acid Blue 83 with potassium dihydrogen phosphate and disodium hydrogen phosphate buffers (1 : 1). Initial dye concentration in dyeing rate and equilibrium dye uptake was prepared to 2×10^{-4} mol/L for Acid Red 13 and 4×10^{-4} mol/L for Acid Blue 83. Dyeing was carried out at 60 and 80°C, at a liquor ratio of 500 : 1.

RESULTS AND DISCUSSION

X-ray diffraction

It is well known that the polypeptide chains of fibroin are of considerable length, and may occur in any of the two conformations.[12] In the soluble form of fibroin (the gland fibroin), the molecules occur in α-form (Silk I) with intramolecularly hydrogen bonded helical structure, which is less stable. The structure reverts to a more stable β-form (Silk II), in which the molecular chains are in their fully extended conformation by application of mechanical stresses or changes in solvent condition. In the thread-like macrostructure of the fibrous fibroin, the molecules in their β-conformation are closely packed in three dimensional structures.

Figure 1 shows X-ray diffraction profiles of the ammonia-gas and liquid ammonia treated silk fibers in equatorial direction. Generally, the silk fiber has a β-form crystal, and the peaks of (001) and (201) reflection. The intensity of (201) reflection peak increased a little by the liquid ammonia treatment. (201) reflection peak is typical of silk fibroin with oriented β-sheet crystalline structure.[13] The crystallinity of the silk fibers treated with ammonia-gas and liquid ammonia was shown in Table I. The crystallinty was unchanged by the ammonia-gas treatment, whereas it increased apparently a little by the liquid ammonia treatment. From the results, it seems that change of the internal

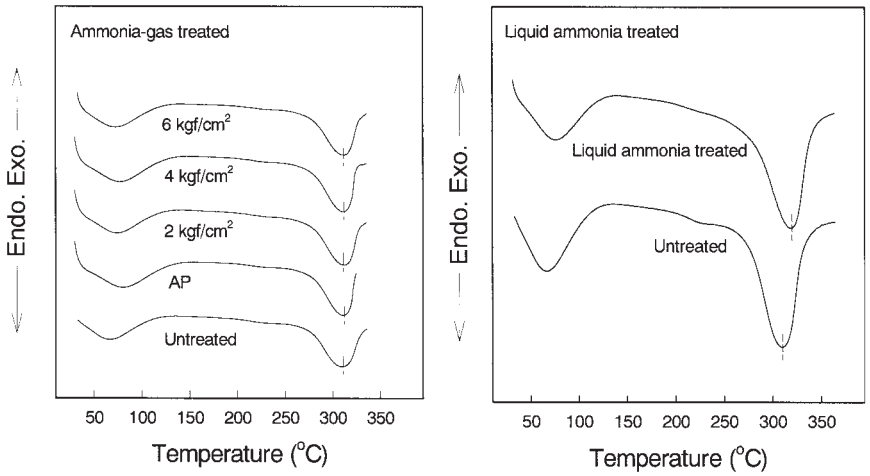

Figure 2 DSC thermograms of ammonia-gas and liquid ammonia-treated silk fibers.

structure of the fiber influences the dyeing, mechanical property, and the fabric hand.

DSC analysis

Figure 2 shows the DSC thermogram of the silk fibers treated with ammonia-gas and liquid ammonia. Peak of the untreated fiber was at 309.2°C, while that of the liquid ammonia was at 319.6°C (Table II). It is true that higher the crystallinity, higher the decomposition temperature of the silk fibroin. Peak temperature of the untreated and well-crystallized silk fibroin by the treatment was estimated to be between 309 and 320°C by the treatments. It is well known that crystallinity and molecular orientation play an important role in relation to the dyeing and mechanical property.[13] As is evident from an increase of the decomposition of the liquid ammonia treatment and an increase in the molecular orientation and crystallinity of the silk fiber. From this result, the water adsorption was decreased a little by liquid ammonia. On the other hand, the peak of the ammonia-gas treated fibers was almost unchanged compared with the untreated silk fiber regardless of the gas pressure.

Moisture regain and water absorption

Moisture regain and water absorption are one of the important parameter of the amorphous region of the textile fiber. In a previous study,[14] we reported on the ozone-gas treatment of the silk fabric. Moisture regain increased only a little by the ozone-gas treatment, on the contrary water absorption decreased considerably. Nevertheless, equilibrium dye uptake with milling type Acid Blue 83 increased apparently, although there was no change with leveling type Acid Red 13 as shown later.

Table III shows the moisture regain and water absorption of the silk fabrics treated with ammonia-gas and liquid ammonia. Moisture regain decreased a little with the ammonia-gas, whereas it increased apparently with the liquid ammonia. On the other hand, although water absorption of the fabric was almost unchanged by the ammonia-gas treatment, water ab-

TABLE II
Decomposition Temperature of Ammonia-Gas and Liquid Ammonia-Treated Silk Fabrics

Treatment	Decomposition temperature (°C)
Untreated	309.2
Ammonia-gas treated	
AP	310.4
2 kgf/cm^2	311.4
4 kgf/cm^2	311.4
6 kgf/cm^2	311.4
Liquid ammonia treated	319.6

TABLE III
Effect of Ammonia-Gas and Liquid Ammonia Treatments on Moisture Regain and Water Absorption of Silk Fabrics

Treatment	Moisture regain (%)	Water absorption (%)
Untreated	9.37	41.1
Ammonia-gas treated		
AP	9.39	42.6
2 kgf/cm^2	9.31	44.2
4 kgf/cm^2	9.28	42.6
6 kgf/cm^2	9.23	40.6
Liquid ammonia treated	9.45	37.6

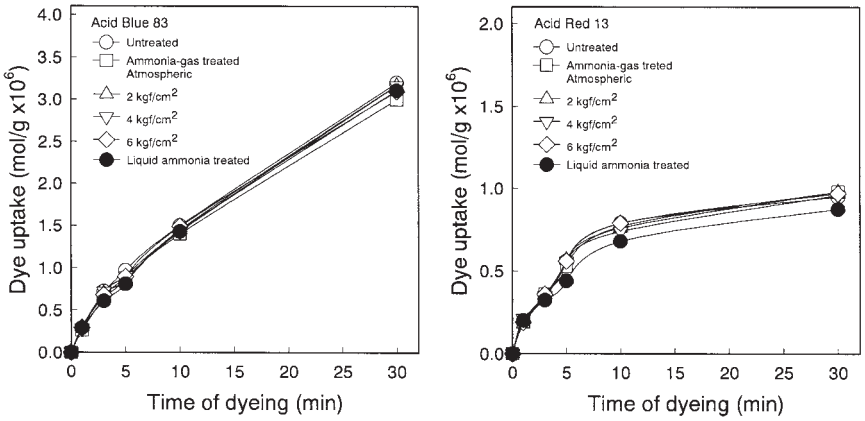

Figure 3 Dyeing rate of acid dyes on ammonia-gas and liquid ammonia-treated silk fabrics.

sorption was controlled apparently by the liquid ammonia treatment. Nevertheless, equilibrium dye uptake of the acid dyes for the liquid ammonia-treated fabric increased considerably as described later.

As is evident from the ozone-gas treatment,[14] it is clear that a decrease in the water absorption and crystallinity is not always corresponded to a change of the equilibrium dye uptake. Therefore, it seems that the change of the amorphous structure by the treatments plays a great role for the water absorption and dyeing property.

Dyeing properties

Apparent dyeing rates of the ammonia-gas and liquid ammonia-treated silk fabrics with Acid Red 13 and Acid Blue 83 are shown in Figure 3. The apparent dyeing rates of the fabric with both acid dyes, milling type Acid Blue 83 and leveling type Acid Red 13, were almost unchanged by the ammonia-gas and liquid ammonia treatments. The equilibrium dye uptake and time of half-dyeing of the treated fabrics are shown in Tables IV and V, respectively. The equilibrium dye uptake increased apparently with the treatments, especially with the liquid ammonia treatment. We expected that an increase of the equilibrium dye uptake of the silk fabric with the acid dyes would correspond to an increase in the active amino group of the silk fabric available for dyeing because of the relaxation of the amorphous region by the treatments. In a previous study,[2,10,11] we reported that liquid ammonia treatment of the cottons induced a considerable decreases in crystallinity, nevertheless the apparent dyeing rate with Direct Blue 1 was controlled a little compared with that of the untreated fabric. However, the equilibrium dye uptake of the liquid ammonia treated cottons increased more than the untreated. Therefore, it seems that the compact amorphous region induced by the liquid ammonia treatment is much more available for dye exhaustion in a long dyeing time.

As evident from the results of the liquid ammonia treatment of the silk fabric, although the treatment of the silk fabric causes an increase of the crystallinity, it is clear that the equilibrium dye uptake increased considerably regardless of a decrease of the dyeing rate.

TABLE IV
Equilibrium Dye Uptake of Acid Dyes on Ammonia-Gas and Liquid Ammonia-Treated Silk Fabrics

Treatment	Equilibrium dye uptake (10^5 mol/g)	
	Acid Red 13	Acid Blue 83
Untreated	1.37	16.58
Ammonia-gas treated		
AP	1.41	16.68
2 kgf/cm^2	1.42	17.44
4 kgf/cm^2	1.40	17.61
6 kgf/cm^2	1.42	18.16
Liquid ammonia treated	1.71	21.56

TABLE V
Time of Half-Dyeing of Acid Dyes on Ammonia-Gas and Liquid Ammonia-Treated Silk Fabrics

Treatment	Time of half-dyeing (min)	
	Acid Red 13	Acid Blue 83
Untreated	12	179
Ammonia-gas treated		
AP	12	203
2 kgf/cm^2	12	199
4 kgf/cm^2	12	205
6 kgf/cm^2	12	225
Liquid ammonia treated	12	306

TABLE VI
Effect of Ammonia-Gas and Liquid Ammonia Treatments on Crease Recovery of Silk Fabric

Treatment	Crease recovery (%)			
	Dry		Wet	
	Warp	Filling	Warp	Filling
Untreated	88.1	83.3	55.6	53.0
Ammonia-gas treated				
AP	90.7	85.4	58.6	54.0
2 kgf/cm^2	90.7	86.9	58.5	54.3
4 kgf/cm^2	90.3	85.7	58.5	54.4
6 kgf/cm^2	90.6	85.7	57.8	55.0
Liquid ammonia treated	48.9	39.1	50.6	53.9

TABLE VIII
Bending Property of Silk Fabric Treated with Ammonia-Gas and Liquid Ammonia

Treatment	Bending modulus B (gf cm^2/cm)	Bending hysteresis width 2HB (gf cm/cm)
Untreated	0.0261	0.0120
Ammonia-gas treated		
AP	0.0288	0.0129
2 kgf/cm^2	0.0287	0.0123
4 kgf/cm^2	0.0278	0.0112
6 kgf/cm^2	0.0271	0.0120
Liquid ammonia treated	0.1127	0.0348

Mechanical property

Table VI shows crease recovery with regard to the mechanical property. Dry and wet crease recoveries were improved apparently a little by the ammonia-gas treatment, whereas it decreased considerably with the liquid ammonia treatment. It was clear that change of the internal structure of the fiber influenced to a decrease of the crease recoveries. Tables VII and VIII show the KES shearing and bending parameters. G, 2HG, and 2HG5 increased considerably with the liquid ammonia treatment, while the parameters of the ammonia-gas-treated fabrics decreased apparently compared with the untreated. Furthermore, B and 2HB increased remarkably by the liquid ammonia treatment, while those of the ammonia-gas-treated fabrics were almost the same as that of the untreated.

Therefore, we expected that liquid ammonia treatment of the silk fabric would cause a crisp hand reflecting an increase of the crystallinity. On the contrary, it is clear that the ammonia-gas treatment is apparently effective to increase the soft hand of the silk fabric despite of a small effect on the internal structure and dyeing property.

Table IX shows tensile parameters of the treated fabrics. It is well known that LT corresponds to the stiffness of the fabric. Reversely, the softness increases with a decrease of the value than one. The value of the liquid ammonia-treated fabric increased clearly compared with the untreated, whereas it decreased by the ammonia-gas treatment. Therefore, it is clear that the ammonia-gas treatment is effective to improve the soft hand. Also, WT of the fabric corresponds to the extensibility of the fabric. It increased by the ammonia-gas and liquid ammonia treatments, especially by the later. RT decreased a little by both treatments. Therefore, liquid ammonia treated silk fabric with a higher degree of molecular orientation displayed better tensile performance.

CONCLUSIONS

Silk fabric, Habutae, was treated with ammonia-gas and liquid ammonia to investigate the effect on the internal structure of the fiber, dyeing behavior, and mechanical properties. The ammonia-gas treatment caused almost no change in dyeing behavior, while the liquid ammonia treatment increased considerably. On the other hand, the ammonia-gas treatment de-

TABLE VII
Shearing Property of Silk Fabrics Treated with Ammonia-Gas and Liquid Ammonia

Treatment	Shearing modulus G (gf/cm degree)	Shearing hysteresis width	
		2HG (gf/cm)	2HG5 (gf/cm)
Untreated	0.23	0.06	0.45
Ammonia-gas treated			
AP	0.23	0.04	0.29
2 kgf/cm^2	0.21	0.02	0.25
4 kgf/cm^2	0.22	0.01	0.24
6 kgf/cm^2	0.22	0.04	0.28
Liquid ammonia treated	0.63	0.51	2.72

TABLE IX
Tensile Property of Silk Fabrics Treated with Ammonia-Gas and Liquid Ammonia

Treatment	LT	WT (gf cm/cm^2)	RT (%)	EMT (%)
Untreated	0.611	4.89	74.55	3.16
Ammonia-gas treated				
AP	0.595	6.47	68.80	4.51
2 kgf/cm^2	0.594	6.51	69.23	4.39
4 kgf/cm^2	0.580	6.61	67.20	4.45
6 kgf/cm^2	0.597	6.54	68.85	4.55
Liquid ammonia treated	0.685	7.43	72.25	4.43

LT, linearity of tensile (dimensionless); WT, work of tensile (gf cm/cm^2); RT, recovery of tensile (%); and EMT, elongation maximum of tensile (%).

creased KES shearing and bending parameters, *G*, *B*, 2*HG*, 2*HG*5, and 2*HB* compared to the untreated, whereas those of the liquid ammonia treatment increased considerably. Therefore, the ammonia-gas treatment is effective to increase the soft hand of the silk fabric. The liquid ammonia treatment changed to crisp hand.

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