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Effect of the Calcium Nitrate Solution Treatment on the Tensile, Bending, and Shear Properties of Silk Fabric

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Abstract

Interests in creating three-dimensionally designed fabric materials are growing rapidly in the sectors of the fashionable textiles with the creativity, new functions, and aesthetics. A number of finishing methods have been developed and proposed to add or create new functions and designs for silk fabrics. Due to the strong hydrogen bonds between the molecules of silk fibroins, the thermal treatment methods used in thermoplastic fiber processing, which can easily deform the synthetic filament fabrics to endow three-dimensional appearance to the fabrics, are not applicable to the silk fabric treatment. In order to modify the fine structure of silk fiber, neutral salt solution treatment methods have been suggested.

In this study, the effect of the calcium nitrate solution on the physical and mechanical properties of silk fabrics was investigated by using the KES(Kawabata Evaluation System) equipment. Based on these findings, relationships between parameters, for example, the thickness and the compressional energy, the thickness and the compressional linearity, and the air permeability and the pore area statistical analysis were investigated. The relationships between the process parameters such as treatment temperature/time and the resulting fabric property parameters were also analyzed by using several SAS procedures.

Key Words : Silk, Calcium Nitrate, Bending, Thickness, Air permeability

I. Introduction

Increasingly prevalent in the past decade, textile products with added value and textile finishing methods that enhance the aesthetics and the sensibility of the products have emerged as the major textile materials and methods in the fashion trends. There has also been a burgeoning

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interest in creating three-dimensionally designed fabric materials for the diversity of the fashionable textiles. At the same time, there has been growing public recognition that the textile materials have to be manufactured, distributed, consumed, and recycled considering the human health factors, and the environment-friendliness.

Even though the majority of the current textile filament production is centered on the synthetic polymer textiles, the origin of the technology of the man-made fiber development lies in the observations and researches on the silk worm's cocoons made up of raw silk excreted through the salivary glands. This silk fiber has been known for its aesthetics, luster, and comfort for many years. A number of finishing methods have been developed and proposed to add or create new functions and designs for silk fabrics. Due to the strong hydrogen bonds between the molecules of silk fibroins, the thermal treatment methods used in thermoplastic fiber processing, which can easily deform the synthetic filament fabrics to endow three-dimensional appearance to the fabrics, are not applicable to the silk fabric treatment[1]. In order to modify the fine structure of silk fiber, neutral salt solution treatment methods have been suggested.

The neutral salt treatment of silk fiber breaks hydrogen bonds in between the fiber molecules through permeation of silk's fine structure. When this occurs, the fiber swells up and contracts. Both the concentration of neutral salt and the experimental conditions affect the structure of silk fiber.[2~5]

Fabric hand attributes may be obtained by subjective evaluations or objective measurements. Subjective evaluations involve the methods of describing fabric hands using adjective descriptors such as "smooth, soft, harsh, stiff, cool, bulky, etc." Sensory evaluations, however, often lead to inconsistent grading outcomes. Analysis techniques based on objective measurement principles have been developed to measure delicate fabric characteristics at low levels of deformation. With these measured objective parameters, it becomes possible to accurately predict fabric hand based on the translational equations.

In this study, the effect that the calcium nitrate solution has on the physical and mechanical properties of silk fabrics was investigated. Based on the findings, relationships between parameters, for example, the thickness and the compressional energy, the thickness and the compressional linearity, and the air permeability and the pore area statistical analysis were investigated. The relationship between the process parameters such as treatment temperature/time and the resulting fabric property parameters were also analyzed by using several SAS procedures[6~9].

II. Experimentals

1. Fabric specimens and chemicals

1) Fabric specimens

The fabric specimen used for the study was white silk fabric. The fabric weight per unit area was 52gf/m^2.

2) Reagent

$Ca(NO_3)_2 \cdot 4H_2O$(Samchun Pure Chemical Co., Ltd.) was used for the neutral salt solution treatment. The reagent was dissolved in de-ionized water at the specified concentration levels.

2. Experimental Methods

1) Neutral salt treatment

The silk fabric specimens were treated at the following treatment conditions.[10] The calcium nitrate aqueous solutions were used 41.7%(w/w) and 43.3%(w/w). Temperatures were 70, 80, and 90℃. Intervals of the treatment time were 2, 4, 6, 8, 10, 20, and 30 minutes. The silk fabric specimens were thoroughly rinsed in a water bath. <Table 1>

2) Measurement of the physical/mechanical properties using KES

The Kawabata Evaluation System(Kato Tech Co., Ltd., Japan) was used to make objective measurements related to the tactility in the treated silk fabrics. The KES was developed to measure the small deformations of textiles during hand manipulation. The system comprises a set of four newly automated instruments that measure tensile, shearing, bending, compression, and surface properties.

<Table 1> Treatment conditions of the silk fabric using Calcium nitrate solution

Treatment code	Concentration(%)	Temperature(℃)	Time(min)
A90-3	41.7	90	6
A90-4	41.7	90	8
A90-5	41.7	90	10
A90-6	41.7	90	20
A90-7	41.7	90	30
C70-1	43.3	70	2
C70-2	43.3	70	4
C70-3	43.3	70	6
C70-4	43.3	70	8
C70-5	43.3	70	10
C70-6	43.3	70	20
C70-7	43.3	70	30
C80-1	43.3	80	2
C80-2	43.3	80	4
C80-3	43.3	80	6
C80-4	43.3	80	8
C80-5	43.3	80	10
C80-6	43.3	80	20
C80-7	43.3	80	30
C90-1	43.3	90	2
C90-2	43.3	90	4
C90-3	43.3	90	6
C90-4	43.3	90	8
C90-5	43.3	90	10
C90-6	43.3	90	20
C90-7	43.3	90	30

(1) Bending

Bending properties of the fabric specimens were measured using the KES-FB2-Auto Pure Bending Tester. The range of bending deformation of the fabric is K= ±2.5 (cm^{-1}). B value, obtained from the slope of the M-K curve, represents the bending rigidity per unit fabric width in gf·cm^2/cm. Higher value of B indicates the fabric resists more during the bending deformation. 2HB value, calculated in the unit of gf·cm/cm, represents the hysteresis of bending momentum.

(2) Shearing

Parallel forces in opposing directions are applied to the fabric specimen until a maximum offset angle of 8° is reached. The KES-FB1-Auto Tensile and Shear Tester was employed for the testing. In order to achieve pure shearing deformation, specimen buckling should be avoid as much as possible.

(3) Compression

Compressional properties of the fabric specimens were measured using the KES-FB3-Compression Tester. This measuring instrument is designed to measure the compressional deformation of specimens with high accuracy and sensitivity. The sample is positioned on a platform equipped with a force transducer. A plunger driven by a motor descends at a rate of 0.02mm/sec, and compresses the fabric specimen. Measured parameters are as follows:

To - Fabric thickness(mm) at a very low compressive load of 0.5gf/cm2,

WC- Work done during compressional deformation, gf·cm/cm^2,

RC- Comressive resilience, the ratio of work recovered to the work done, %,

LC- Linearity of the compression curve, (LC=1 for the completely linearly compressive material).

(4) Tensile

Tensile properties were measured using the KES-FB1-Auto Tensile and Shear Tester.
It continuously measures the stress and strain parameters until the maximum force is reached. 5.0cm of a sample can be used effectively for the tensile deformation test.

LT represents the linearity of the extension load, ranging from 0 to 1.

WT represents tensile energy in gf/cm/cm^2.

RT represents tensile resilience in percent.

3) Air permeability test

Air permeability of the fabric specimen was measured using an air permeability tester(Textest FX3300, Switzerland) under the test pressure of 125Pa according to the specifications of ASTM D737.

4) Statistical analysis

The effect of treatment temperature and time on the physical or mechanical parameters, for example, bending rigidity(B), or shear hysteresis (2HG5) of the treated silk fabric specimens is analyzed using a few statistical methods, including the G3GRID procedure and the G3D procedure. The G3GRID procedure processes a data set to generate a new data set that the G3D procedure can use to create a three-dimensional surface plot. By using the G3GRID procedure, it is possible to create a rectangular grid of interpolated values from an original data set which might be irregularly spaced. The output data set may also be smoothed by selecting an appropriate number for the data smoothing option.

5) Pore area analysis

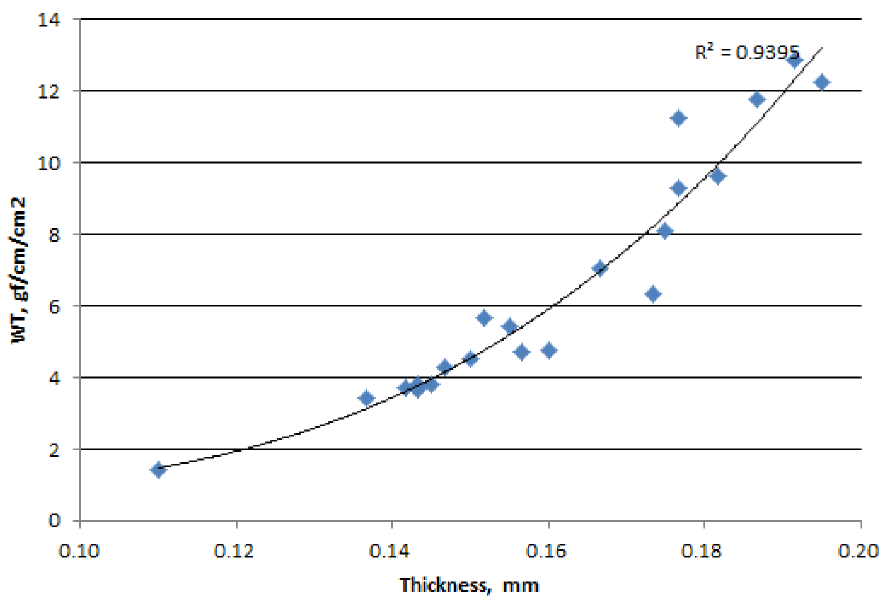
The pore size of the specimen was analyzed using an image analysis system comprising an optical microscope, a digital camera and the ImageJ software (National Institute of Health, U.S.A.). Transmitted light was used to take photographs of the fabric specimens under the optical microscope. The acquired color image was converted to a gray scale image, with subsequent binary image conversion based on the specified threshold value. The Analyze_ Particles function of the image analysis software was applied to the binary image. A number of pore objects with contour lines were created and corresponding area values in pixel units were also calculated. The area of the pore objects in the fabric specimen image were summed.

III. Results and Discussion

1. Tensile properties and thickness

In the tensile test, the fabric specimen is extended up to a specified maximum force. WT(tensile energy) represents the maximum amount of work or energy generated by the specimen's work during the tensile deformation. The larger the WT, the more work is generated by the specimen.<Fig. 1>

As the degree of contraction increases with the increase of treatment temperature and treatment time, the fabric crimp develops further, and the fiber diameter of the silk fabric specimen increases, leading to the increase of the WT value of the silk fabric specimen.

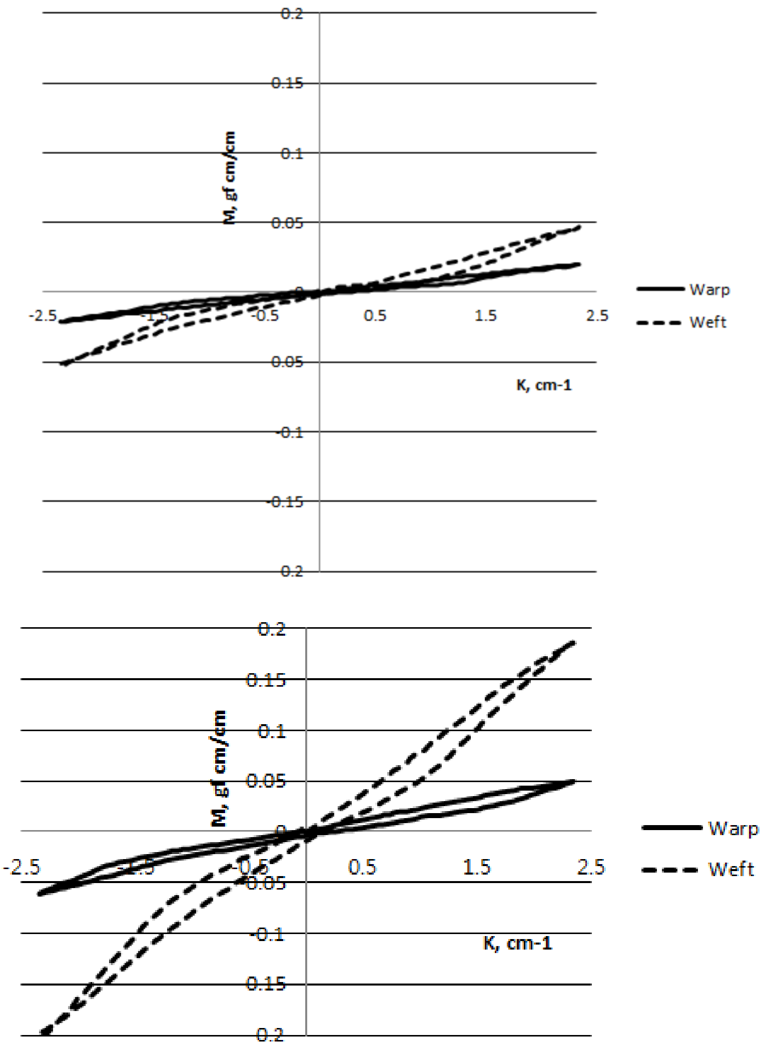


<Fig. 1> Relationship between the WT(Tensile Energy) and the thickness.

2. Bending properties and treatment parameters

<Fig. 2> shows the differences of the bending charts of the control specimen and C90-7. The slope of the bending moment curve of the control specimen is much lower than that of the C90-7. As the contraction of the silk fiber due to the neutral salt solution treatment proceeds, the diameter of the silk fiber increases along with the lengthwise shrinkage. This, in turn, increases the bending moment of the treated fabrics. Warp direction bending rigidity is lower than the weft direction bending rigidity.

From a point of view of the fiber itself, the flexural rigidity of a fiber can be defined as the



<Fig. 2> Bending chart of control specimen(upper) and C90-7(lower).

couple to bend the fiber to the unit radius of curvature[11].

$$\text{Flexural Rigidity} = \frac{1}{4\pi}\frac{\eta E T^2}{\rho} \times 10^{-5} gf\,cm^2$$

where ρ = density in g/cm,
T = count of filament in tex,
E = modulus in gf/tex,
η = shape factor of fiber cross-section.

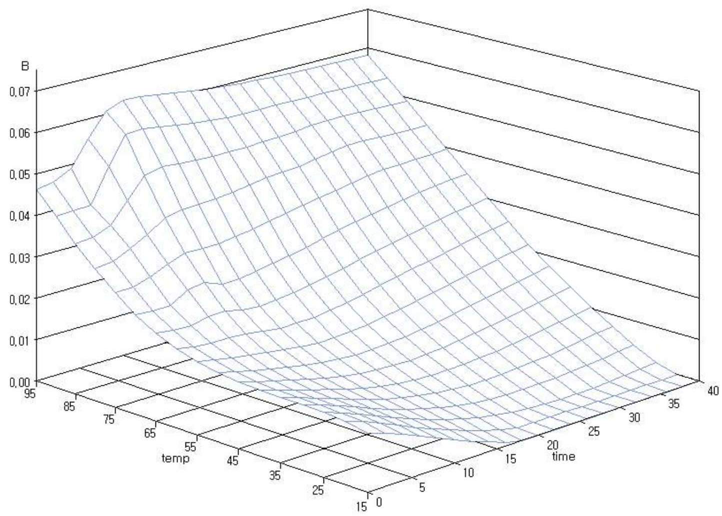
It becomes apparent that the flexibility of a fiber depends on its thickness, its shape, its tensile modulus, and its density. Due to the neutral salt solution treatment, the fiber shrinks in length, and the fiber diameter increases. The increase of fiber diameter increased the yarn diameter and fabric thickness, which leads to the increase of bending moment.

<Fig. 3> shows a 3-dimensional plot of the effect of the treatment temperature and time on the B(Bending Rigidity) of the silk fabric specimens. As the treatment temperature increases, the B value of the specimen increases. As the treatment time increase, the B value of the specimen shows the general trend of increase. However, at higher temperature around 80 or 90℃, there is a maximum point at 10 or 15 minutes. Prolonged neutral salt solution treatment would lower the B values at 80 or 90℃ afterwards.

3. Shearing properties and treatment parameters

In a standard shearing test procedure, the maximum shear deformation angle is set to 8 degrees. Shear rigidity (G) is calculated between ±0.5 degrees and ±5.0 degrees of shear deformation. 2HG5 represents the hysteresis of shearing during shear deformation measured at ±5.0 degrees.

<Fig. 4> shows the effect of treatment temperature and time on the shear hysteresis (2HG5). The 2HG5 of control specimen is 0.265, which is the highest of all specimens. It is probably due to the fact that the flat shape of filament yarn, warp and filling, of the control specimen provides higher contact area, generating



<Fig. 3> Effect of treatment temperature and time on B.

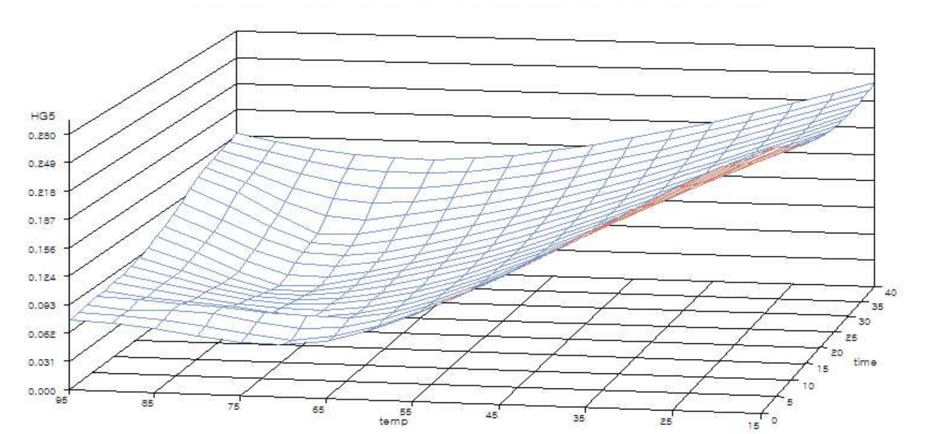
higher friction force, than the less flat shape of the others. As the shape of the filament yarn cross-section becomes less flat, the friction force becomes lower than that of the control specimen. After the minimum point around the temperature of 80 and time of 10 or 15 minutes, the 2HG5 value increases afterwards, probably due to the jamming of the fabric structure.

4. Compression

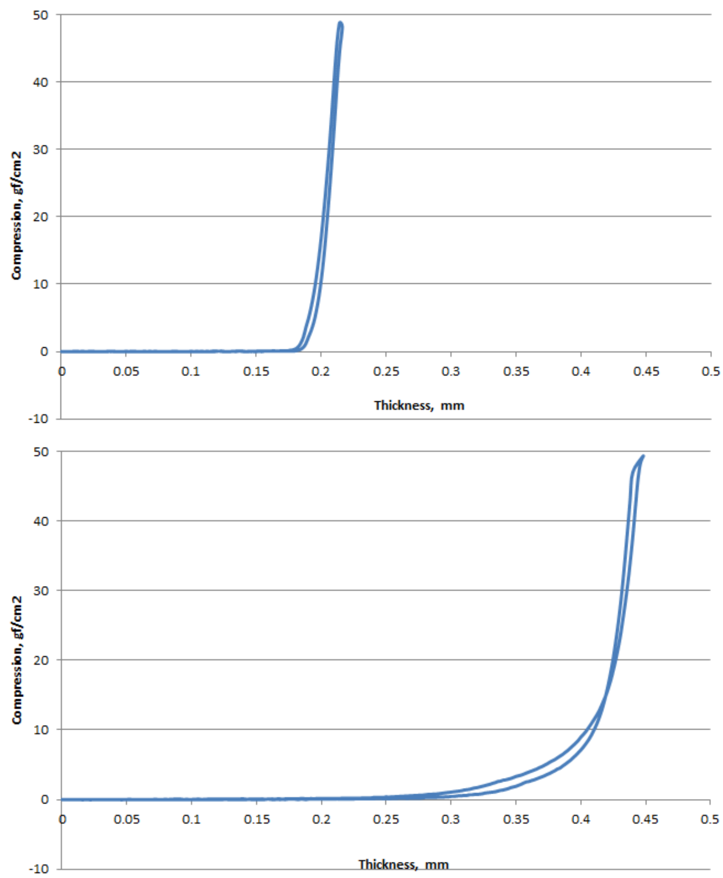
As shown in <Fig.5>, the compression charts of the control specimen and C90-7 are compared. There is a sharp contrast between the compression curves of the two specimens. The initial thickness measured at the pressure of 0.5gf/cm^2, To, of the control specimen (0.142mm) is much lower than that of C90-7(0.361).

The compressional energy, WC, proportional to the area under the compression curve, of the contol specimen(0.032) is also much lower than that of C90-7(0.089). The stiff increase of the compression curve of the control specimen is highly contrasted to the slow increase of that of specimen C90-7. The compressional linearity, LC, of the control specimen is 0.512, while that of C90-7 is 0.236.

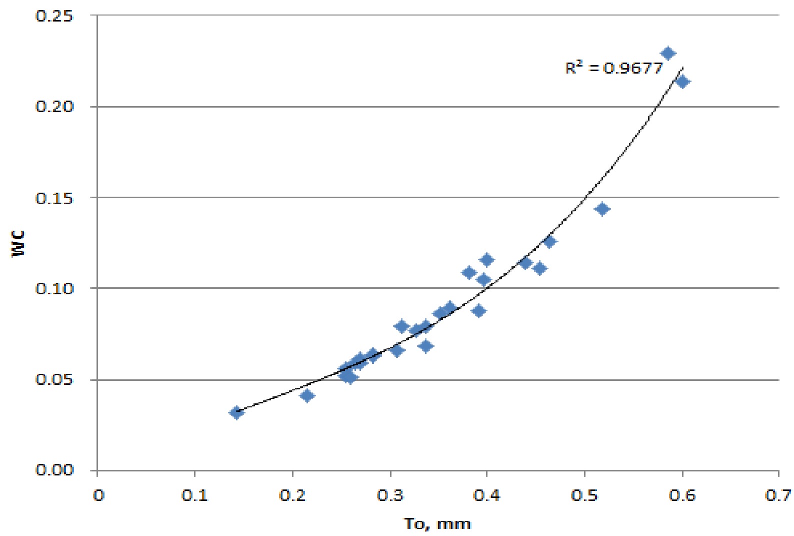
As the initial thickness of the silk fabric specimen increases, the compressional energy, WC, or compressional work done during the compression deformation also increases.<Fig.6> The coefficient of determination(R^2) is almost 0.97. From this relationship between the To and WC values of silk fabrics, it is possible to interpret that the contraction by the neutral salt solution treatment increased the bulkiness of the treated silk fabric specimens. The relationship between the LC and the initial thickness is shown in <Fig.7>. As the intial thickness increases, the compressional linearity, LC, decreases. The results from the compressional properties and the observations from the photomicrographs serve to indicate that the increase of the fiber diameter, and the configurational changes of the silk filaments, including less flat cross-section shape and the increase of fabric crimp percent due to the contraction, together play an important role for the increase of the fabric bulkiness.



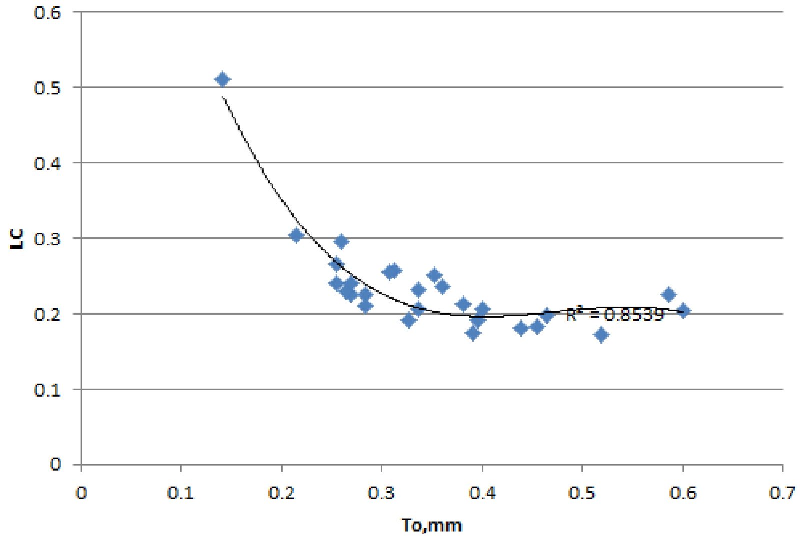
<Fig. 4> Effect of treatment temperature and time on 2HG5.



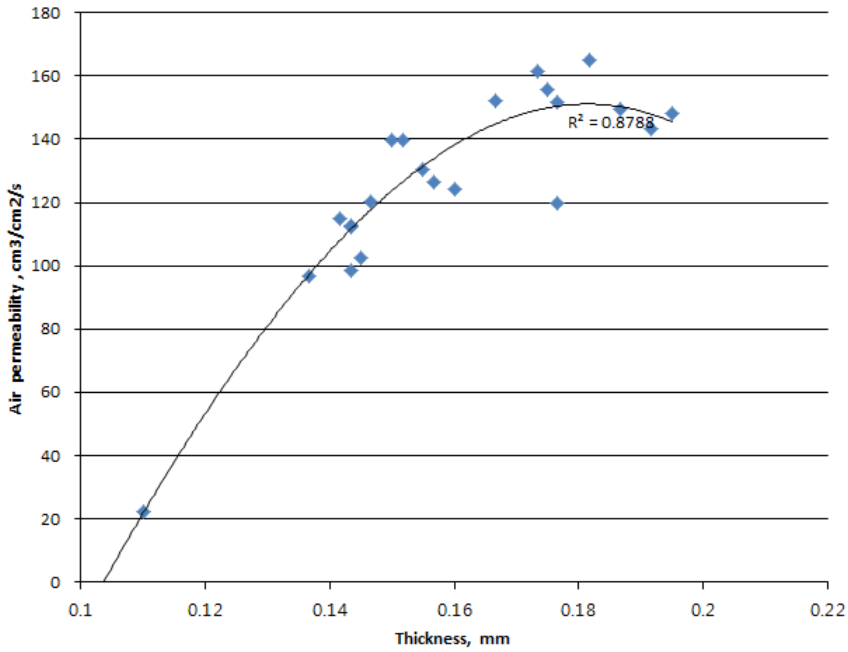
<Fig. 5> Comparison of compression charts (Upper: control, Lower: C90-7).



<Fig. 6> Relationship between WC and To.



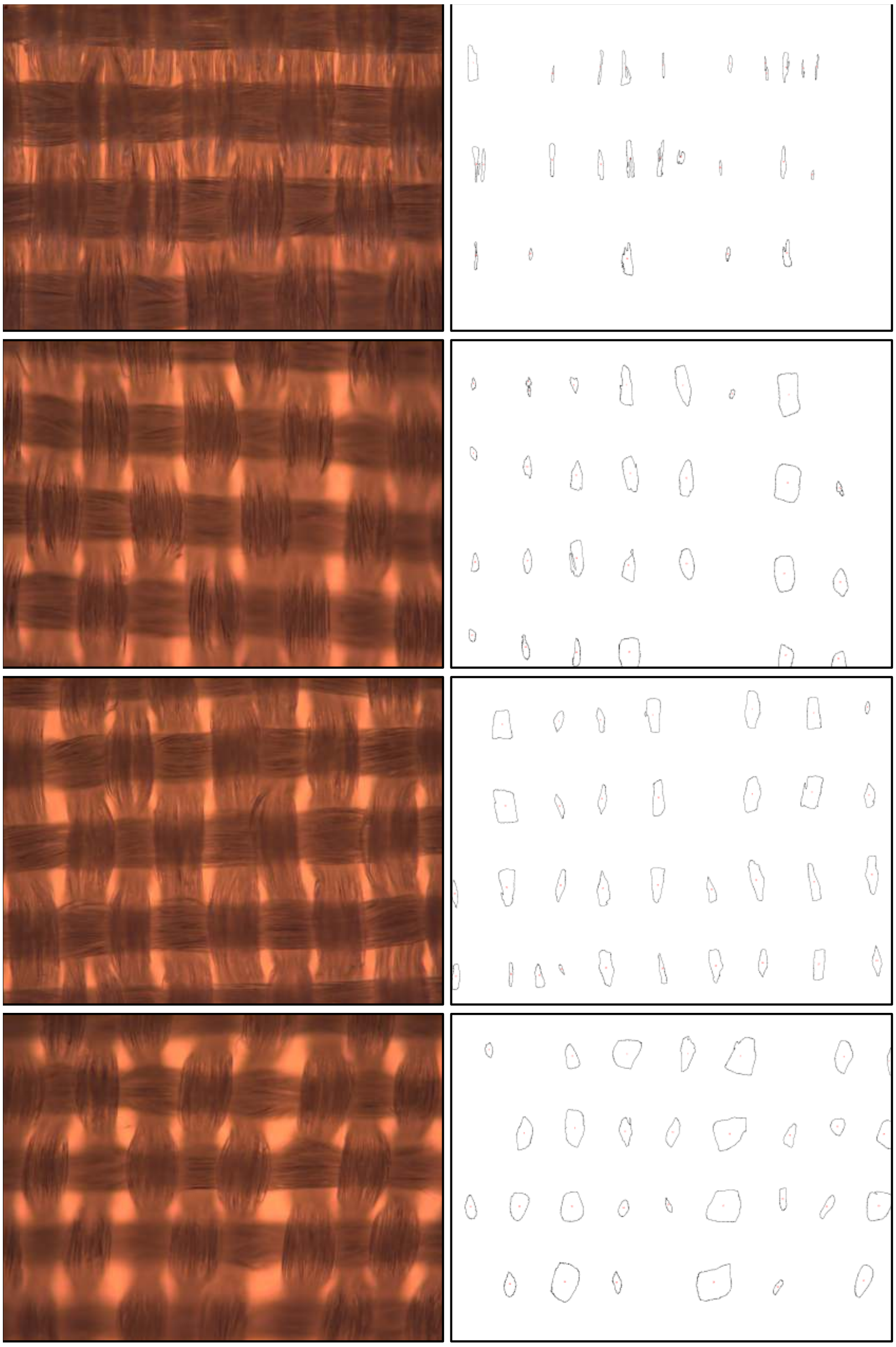
<Fig. 7> Relationship between WC and To.



<Fig. 8> Relationship between air permeability and thickness.

6. Thickness and air permeability

As the diameter of the contracted fiber increases, the thickness of the silk fabric increases. The contraction of the silk fabric also increases the fabric crimp. As shown in the photomicrographs, the width of the warp and filling yarns decreased along with the contraction, which in



a) control

b) C70-1

c) C80-1

d) C90-1

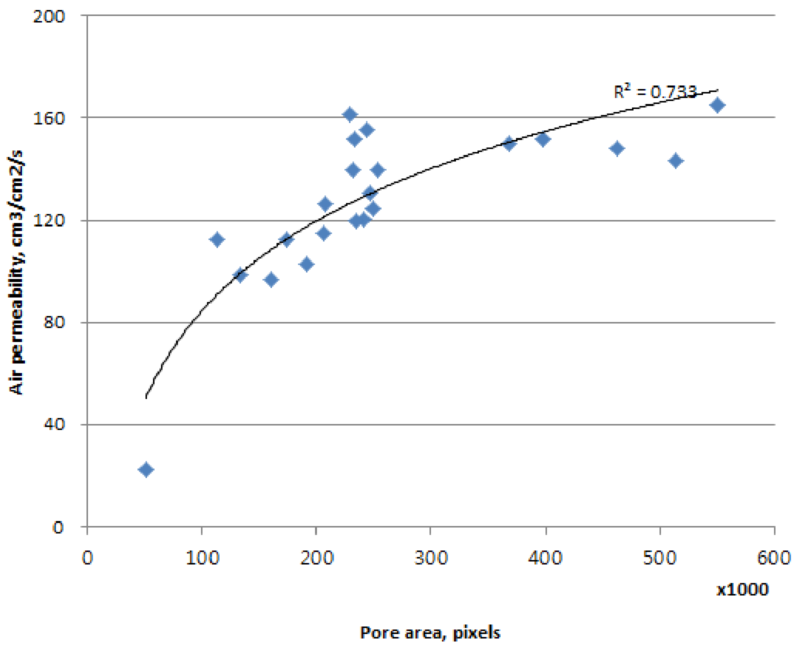
<Fig. 9> Photomicrographs of fabric specimens and contour images of fabric pores.

turn increased the pore area. At the same time, the vertical space between the warp and filling yarns at the yarn crossing point increased as evidenced by the decrease of the G or 2HG5 values. Therefore, in this specific study, the increase of thickness accompanied the increase of air permeability up to the thickness of 0.18mm.<Fig. 8> After that point, however, there is a decreasing tendency of air permeability probably due to the excessive jamming of the yarns. Therefore, after this optimum point, the fabric may have been excessively treated in the salt solution.

A general 'rule of thumb' assumption is that as the fabric thickness increases, the air permeability of the fabric decreases. In this series of treatments of silk fabric specimens, however, the air permeability of the treated fabric increased as the thickness increased up to some optimum treatment condition(0.18mm) with the maximum air permeability of ca. 165 $cm^3/cm^2/s$.

7. Air permeability and pore area analysis

In <Fig. 9>, a series of photomicrographs of the silk fabric specimens and the corresponding images of pore objects are shown. The warp and filling yarns of the control fabric specimen(a) are tightly woven with much smaller pores, while the yarns of the others(b,c, and d) are less tightly woven with larger and irregular pores. The filaments comprising the yarns of the control specimen look flat and parallel to the yarn axis. Those of the other specimens become less flat as the contraction treatment proceeded. The photomicrograph of C90-1 has a distinctive look of distorted filaments, which seems to be



<Fig.10> Relationship between the air permeability and the pore area measured using an optical image analysis system.

an indication that the fabric crimp increased due to the fabric contraction. <Fig. 10> shows the relationship between the air permeability and the pore area measured using an optical image analysis system. Due to the various structural changes during the neutral salt contraction treatment, the air permeability readings of the fabric specimens increased compared to the control specimen within the scope of this study.

Ⅳ. Conclusions

In this study, the effect that the calcium nitrate solution has on the physical and mechanical properties of silk fabrics was investigated. Based on the findings, relationships between parameters, for example, the thickness and the compressional energy, the thickness and the compressional linearity, and the air permeability and the pore area statistical analysis were investigated. The relationship between the process parameters such as treatment temperature/time and the resulting fabric property parameters were also analyzed by using several SAS procedures.

1. As the degree of contraction increases with the increase of treatment temperature and treatment time, the fabric crimp develops further, and the fiber diameter of the silk fabric specimen increases, leading to the increase of the WT value of the silk fabric specimen. The increase in WT can be attributed to the fact that fiber swells up and contracts. Changes in the fine structures of silk fiber, resulting from 1) the breakage of hydrogen bonds between fiber molecules and 2) the increase of amorphous regions of the fibroins, are highly related to the swelling and contracting.

2. The flexibility of a fiber depends on its thickness, its shape, its tensile modulus, and its density. Due to the neutral salt solution treatment, the fiber shrinks in length, and the fiber diameter increases. The increase of fiber diameter increased the yarn diameter and fabric thickness, which leads to the increase of bending moment.

3. The 2HG5 of control specimen is 0.265, which is the highest of all specimens. It is probably due to the fact that the flat shape of filament yarn, warp and filling, of the control specimen provides higher contact area, generating higher friction force, than the less flat shape of the others. As the shape of the filament yarn cross-section becomes less flat, the friction force becomes lower than that of the control specimen. After the minimum point around the temperature of 80 and time of 10 or 15 minutes, the 2HG5 value increases afterwards, probably due to the jamming of the fabric structure.

4. From the relationship between the To and WC values of silk fabrics, it is possible to interpret that the contraction by the neutral salt solution treatment increased the bulkiness of the treated silk fabric specimens.

5. In this series of treatments of silk fabric specimens, the air permeability of the treated fabric increased as the thickness increased up to some optimum treatment condition(0.18mm) with the maximum air permeability of ca. 165$cm^3/cm^2/s$ due to the structural changes.

Based on the findings of this study achieved through objective measurement, several treatment conditions for desirable silk fabric results may be selected for the parameters of the physical and mechanical properties of the fabric specimens.

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