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Morphological and Physico-mechanical Properties of Finished Cotton Fabric by Regenerated Bombyx Mori Silk Fibroin

Vo Thi Lan Huong[1,2], Duong Thi Thom[1], and Nguyen Ngoc Thang[1,*]

[1] Hanoi University of Science and Technology - No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam; thang.nguyenngoc@hust.edu.vn
[2] Hanoi Industrial Textile Garment University - Le Chi Ward, Gia Lam District, Ha Noi City, Viet Nam; huongvtl@hict.edu.vn

* Correspondence: thang.nguyenngoc@hust.edu.vn; Tel.: +84-904309930

Abstract: Silk is one of the natural protein fibers used widely all over the world. This material has been found to be smooth and shiny, exhibits good mechanical strength, and is biocompatible. It has been shown that fibroin may be dissolved into an aqueous solution, and then formed into a number of different geometrical forms. This paper presented the dissolving process of Vietnam Bombyx mori silk fibroin by an aqueous lithium bromide solution and regenerated it onto cotton fabric via padding method. The fibroin coated cotton fabrics were characterised by scanning electron microscopy (SEM), Fourier transform infrared spectrophotometry (FTIR) and color measurement. The air permeability, wrinkle recovery angle and breaking strength of the fibroin treated fabric were determined as representative physico-mechanical properties. The analysed results presented no change of the air permeability values, noticeable increase in the wrinkle recovery angle values, and slight improvement of the breaking strength when the fabrics were treated with higher silk fibroin concentration.

Keywords: Bombyx mori silk; Fibroin solution; Regenerated fibroin; Padding; Cotton fabric

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1. Introduction

The raw Bombyx mori silk consists of two main components named fibroin and sericin. However, the raw silk could not be used directly for textile application due to allergic problem of the human skin with sericin [1,2]Therefore, degumming process is applied to remove sericin from silk fibroin. Silk fibroin has a long history of use as textile material due to its mechanical robustness, high biocompatibility, biodegradability, morphologic flexibility, and good water vapor permeability [1]In recent years, regenerated silk fibroin

from Bombyx mori silk has been widely studied as a biomaterial for tissue engineering and regenerative medicine [4,5], environmentally sensitive hydrogel [3,7,8], bone repair [5,7], fracture fixation [6,8]. Dissolution and regeneration of the silk fibroin form the central steps to shape the polymer for different functional applications. It has been shown that fibroin could be dissolved in a number of different highly concentrated salt solutions, e.g., calcium chloride/water/ethanol, calcium nitrate/methanol/water, and lithium bromide/water/ethanol [8,9,11,12]. These solutions are subsequently dialyzed to remove the salt and regenerated fibroin can be formed.

The use of silk fibroin solution as a finishing agent for the treatment of textile fabrics has been reported [9,10], however, the effect of different chemicals and organic solvent on the fibroin regeneration from its solution have not studied yet in detail. In this investigation, the dissolving process of Vietnam Bombyx mori silk fibroin by aqueous lithium bromide solution, and the fibroin regeneration onto cotton fabrics using several chemical solutions have been demonstrated. The fixation of silk fibroin onto cotton fabrics were characterised by scanning electron microscopy (SEM), Fourier transform infrared spectrophotometry (FTIR) and color measurement. To clarify the influence of the fibroin on the physico-mechanical properties of treated cotton fabrics, the selected samples were characterised with regard to air permeability, wrinkle recovery angle and breaking strength. The results contributed to the understanding of deposition and properties of the cotton fabric coated regenerated silk fibroin. Such an approach would open new perspectives in application of regenerated silk fibroin on textiles.

2. Materials and Methods

2.1. Materials

Raw Bombyx mori silk (Vong Nguyet village, Bac Ninh province, Vietnam) were degummed in a solution of 5 g/l Na2CO3 at 98^{0}C for 30 min at a liquor ratio of 1:20 (mass in gram per volume in mL). The silk fibroin was rinsed five times by warm and cold distilled water, then dried at 40^{0}C and stored at 65% relative humidity and 20^{0}C. Cotton fabric was used in this study (100% cotton, Ne32, woven plain, scoured and bleached, Hungyen Textile and Dyeing Co.,Ltd, Vietnam). Other chemicals (Na2CO3, C2H5OH, LiBr, Al2(SO4)3.18H2O) purchased from Aladdin Shanghai Biochemical Technology Co.,Ltd, China, were analytical graded.

2.2. Methods

Dissolution of Fibroin

A LiBr/C_2H_5OH/H_2O (LiEtW) solution with a weight ratio of 45:44:11 was used as a solvent for dissolution of silk fibroin. To prepare the solvent, 6.6g of LiBr was dissolved in 8.3ml ethanol and 1.7 ml distilled water [1]. Fibroin solutions were prepared by dissolving a

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maximum amount of degummed fibroin in 10g LiEtW at 80□C for 1 h.

In this research, the maximum amount of degummed fibroin dissolved in the given LiEtW solution was 1.4 g and the obtained solution contained of 12 wt% fibroin.

The process of degumming and dissolving silk fibroin was given in Figure 1.

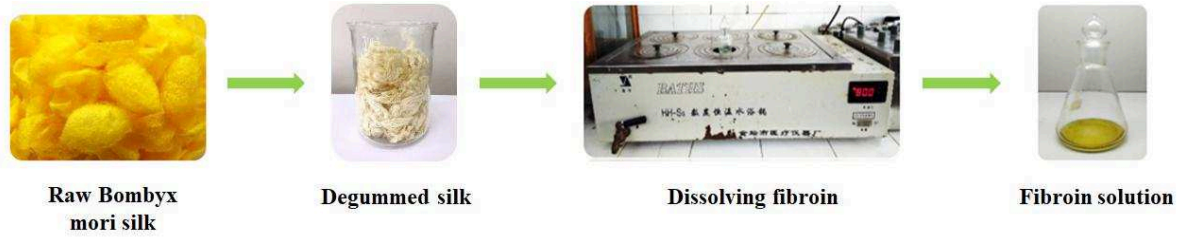

Figure 1. Scheme of degumming and dissolving silk fibroin.

Table 1. The aqueous solutions used for regenerating silk fibroin solution

Solutions used for fibroin regeneration	Abbreviations
Calcium chloride ($CaCl_2$)	ReS.Ca
Aluminum sulfate ($Al_2(SO_4)_3$)	ReS.Al
Methanol (CH_3OH)	ReS.Me
Ethanol (C_2H_5OH)	ReS.Et
Acetone ($(CH_3)_2CO$)	ReS.Ax

Regeneration of Fibroin

To find out a suitable condition for the regeneration of silk fibroin, the solution was treated with different salt solutions and solvents listing in Table 1. In a typical process, 10 g of the fibroin solution in LiEtW was mixed with 70 mL of the regenerated agent. The solution was rested overnight to allow the regenerated fibroin to settle. The regenerated fibroin appeared as a white substance, adhering to the glass subject and partly dispersed in the solution. Three independent repetitions were performed for each experiment protocol. The selected condition for the regeneration of silk fibroin was used to finish cotton fabrics.

Finishing of cotton fabric with silk fibroin solutions

In a typical experiment, 100ml of various concentration of fibroin solutions (0.5, 1, 1.5 wt % fibroin) were prepared to finish cotton fabric. Cotton fabric samples with size of 35 × 35 cm were impregnated with the fibroin solution using a laboratory padder (nip pressure 0.6kg/cm^2, 10rpm, Atlas, model D394A, China). The treated fabrics were then rested for 10 mins, and dried in a laboratory dryer (110^{0}C, 2 mins; SDL mini dryer, model 398, England). The dried samples were treated with Acetone solvent and dried in an oven. In the subsequent step, the samples were soaked in an aluminum sulfate solution for two hours. This process was repeated for the second time for permanent fixation of silk fibroin onto

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cotton samples. The samples were washed in distilled water to remove residual LiBr salt and dried at 60^0C. The process of finishing of cotton fabric with silk fibroin solutions was illustrated in Figure 2.

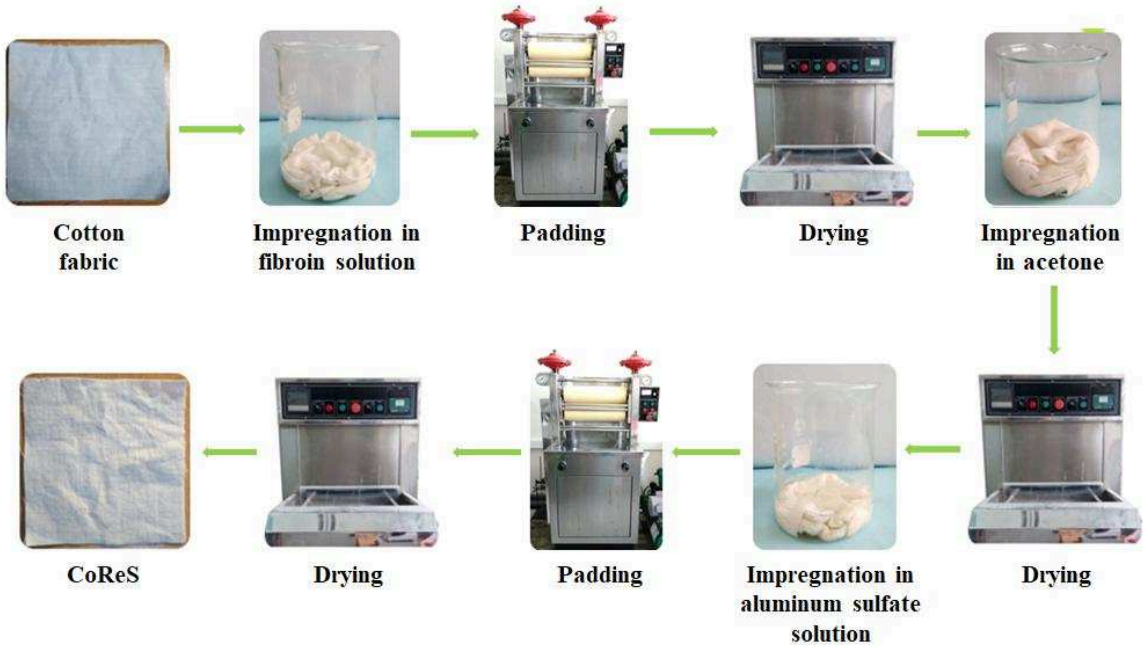

Figure 2. Scheme of finishing of cotton fabric with silk fibroin solutions.

Analytical Methods

Scanning Electron Microscope (SM-6510LV Jeol, Japan) and Fourier transform infrared spectrophotometry (Nicolet iS10, Thermo Scientific, America) were used to confirm the regeneration of silk fibroin onto cotton fabric.

The color change of the treated sample with the untreated sample was evaluated using a Data color 800 spectrophotometer (Data color, USA). The ΔL*, Δa*, Δb* values of the samples over the range of 400-600nm were used to calculate the color-difference value of ΔE using the equation 1.

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (1)$$

Physico-mechanical property measurements

The air permeability measurement was performed according to DIN 53887:1977 using a SDL ATLAS tester (M021A SDL ATLAS, USA). The wrinkle recovery angle of the samples was evaluated according to ISO 2313:1972, using a wrinkle recovery tester (HUST, Hanoi, Vietnam). The breaking strength of the samples was tested in warp and weft directions, according to TCVN 1754 – 1986, using a Universal Material Testing Machine (RT- 1250A,

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Japan).

3. Results and discussion

3.1. Solubility of silk fibroin in Lithium bromide/ Ethanol/Water

It was reported in the literatures that the degumming silk fibroin dissolves only in a limited number of solvents and alcoholic aqueous salt solutions, due to the presence in fibroin of a large amount of inter- and intra-molecular hydrogen bonds, and its high crystallinity and specific physicochemical properties. In this research, we chose the LiEtW (weight ratio of Lithium bromide/ Ethanol/ Water was 45:44:11) solution as a co-solvent to dissolve the silk fibroin because lithium halides solutions exhibited high solvency with silk fibroin [1,13-14] The interaction of solvent ions in the alcoholic aqueous salt solution with functional groups of the fibroin macromolecules leaded to dissolution of fibroin. It had been assumed that the inter- and intra-molecular hydrogen bonds in the chains of fibroin were broken as a result of the nucleophilic attack by the anion [13,14] .

In order to use the fibroin solution for finishing textile fabrics, high content of silk fibroin in the fibroin solution should be made. As the previous reports, the solubility of silk fibroin in the LiEtW system is quite good; however, the concentration of resulted silk fibroin solution is not high. Thus, we tried to increase the amount of fibroin dissolving in the LiEtW solution by increase of the temperature. In this work, 1.4 g silk fibroin was completely dissolved in 10 ml of the given LiEtW solution at 80^0C for 1h. As shown in the Figure 1, the obtained fibroin solution was transparent, dark yellow and high viscosity. The fibroin concentration in the obtained solution was much higher than that reported in previous studies [1, 11,13,14] .

3.2. Fibroin regeneration

To recover silk fibroin from salt-containing aqueous solutions, the dialysis process was applied. This process removed the inorganic salt (LiBr) and organic solvent (EtOH), and destabilised the Li-fibroin complex leading to coagulation of silk fibroin. The main disadvantage of the dialyzed process is the long preparation time (aqueous fibroin solutions should be dialyzed for several days). Thus, to apply the regeneration of silk fibroin from its solution for coating textile material in the large scale, replacement of dialysis by mores simple operations should be considered.

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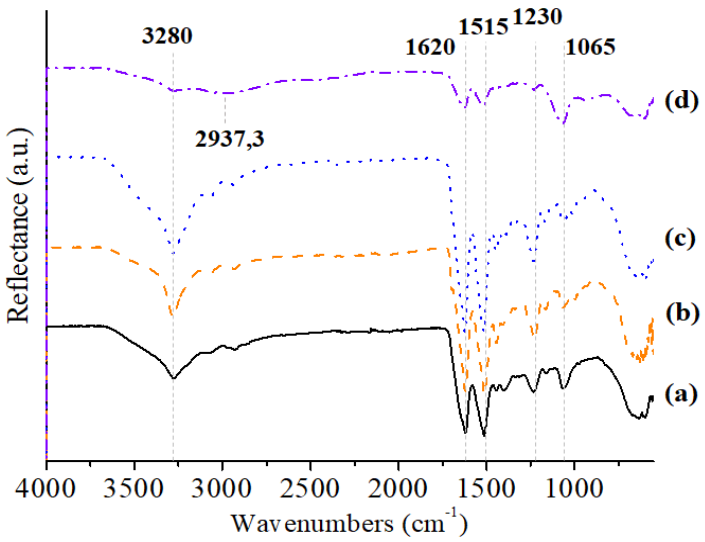

Figure 3. FTIR spectra of the samples: (a) Silkworm cocoon; (b) Degummed silk fibroin; (c) Regenerated silk fibroin in acetone solvent; (d) Regenerated silk fibroin in $Al_2(SO_4)_3$ aqueous solution.

In this study, various regenerated fibroin solution systems were investigated, and the results showed that the best condition for the regeneration of silk fibroin were treated the fibroin solution with both acetone solvent and $Al_2(SO_4)_3$ solution. Acetone solvent acted as a poor solvent in which silk fibroin molecules shrink when the fibroin solution was poured into the acetone solvent. The collected coagulation of fibroin was then treated with $Al_2(SO_4)_3$ solution to replace Li^+ ions in the fibroin-Li^+ complex by Al^{3+} ions to form stable fibroin-Al complex. It means that this coagulation method could be applied to deposit directly silk fibroin onto surface of cotton fabric.

In order to determine the change of functional groups of silk fibroin in each step of dissolved and regenerated fibroin processes, the infrared spectroscopic measurements of silkworm cocoon, degummed silk fibroin, regenerated silk fibroin in acetone solvent and regenerated silk fibroin in $Al_2(SO_4)_3$ aqueous solution samples were performed, and the spectra were given in Figure 3. The characteristic peaks of silk fibroin at 3274 (cm^{-1}), 1619 (cm^{-1}), 1514 (cm^{-1}) and 1231 (cm^{-1}) are associated with N-H in amino group, C = O (amide I), C = O (amide II) and C = O (amide III), respectively [1, 9-11]. Compare to the raw silk fibroin and the regenerated fibroin, the silk fibroin in LiEtW solution shown a significant shift in N-H group. The amide I and amide II absorbance shifted toward higher wavenumbers of 3280 (cm^{-1}) for N-H group, 1621 (cm^{-1}) for amide I and 1515 (cm^{-1}) for amide II, while amide III absorbance slightly blue shifted from 1231(cm^{-1}) to 1230 (cm^{-1}). The shift of the amide absorbance could be due to the interaction of Li^+ ions with amino groups of fibroin molecules to form the fibroin-Li^+ complex. The peak at 2937.3 (cm^{-1}) was confirmed the C-H group, and peaks at 1604-1608 (cm^{-1}) were C-N groups of amino acid [1, 9, 11]. On the basis of the FTIR observations, the mechanism of fibroin regeneration was elucidated in light of Figure 4.

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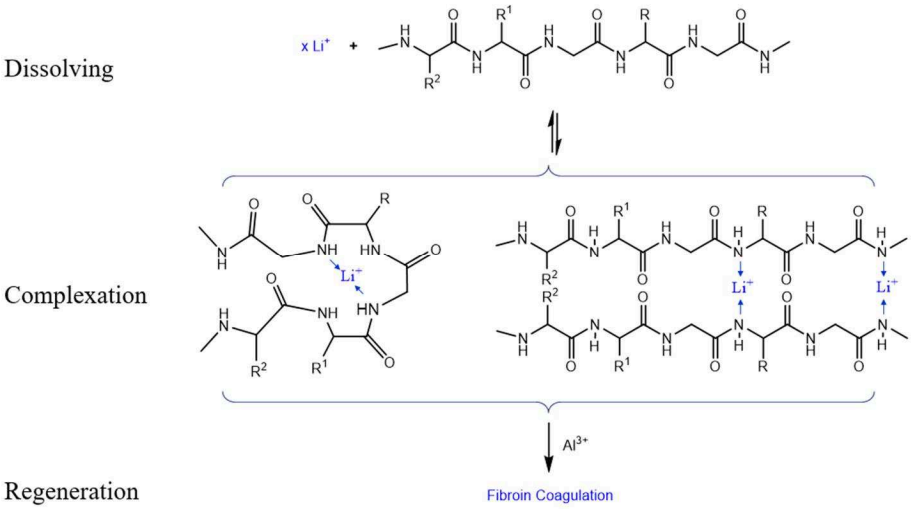

Figure 4. Reaction scheme for fibroin regeneration

3.3. Silk fibroin fixation on cotton fabric

To observe the fibroin regeneration onto the cotton fabric, SEM measurements have been performed. The SEM images of untreated cotton fabric and representative samples after deposition of fibroin were shown in Figure 5. Figure 5a-c shown the micro-morphology of untreated cotton samples with different magnification. The images clearly revealed a plain weave structure of the fabric, and a specific microstructure of cotton fiber. After padding the cotton fabric with the silk fibroin solution and regenerating fibroin to solid stage, the treated cotton fibers were covered by a layer of the regenerated silk fibroin, Figure 5d-f. It should be note that the coagulated fibroin films deposited onto surface of cotton fibers were uniform, and they did not fill in the space between the fibers.

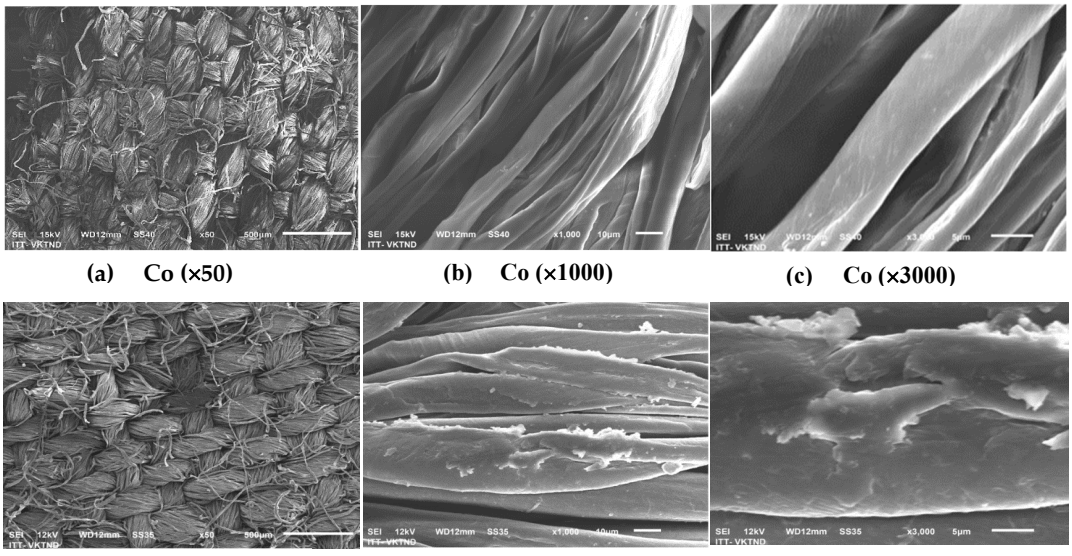

Figure 5. SEM image of the cotton samples: (a, b, c) Untreated cotton fabric with magnification of 50, 1000 and 3000, respectively; (d, e, f) Treated cotton fabric with 1.5

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wt% fibroin (CoReS3) with magnification of 50, 1000 and 3000, respectively.

In order to evaluate the influence of regenerated fibroin to the color of the treated cotton fabric, the color of the untreated cotton fabric and treated fabric with fibroin were measured according to the CIELAB color scale relative to the standard illuminant D65.

Table 2 showed the difference values of ΔL*, Δa*, Δb* and ΔE the samples before and after treatment with the silk fibroin. The negative values of ΔL* and Δa*, and positive value of Δb* indicated that the treated sample were slightly darker, greener and yellower than original cotton fabric. However, these absolute values were small, and the color-difference value of ΔE was less than 1.0 confirming no color change of the treated cotton fabric. It is difficult to distinguish the color-difference of the fabric samples before and after treatment by naked eyes. The results could open a potential application of this technique for functionalizing textile materials due to no color change of final products.

Table 2. Color measurement comparison of selected samples

Sample	ΔL*	Δa*	Δb*	ΔE
Untreated cotton fabric	-1,40	-0,05	0,15	0,53
Treated cotton fabric (CoReS3)				

3.4. Physico-mechanical properties of cotton fabric treated with silk fibroin

The formation of a silk fibroin layer on cotton fibers would change the physical and mechanical properties of the fabric. To confirm this assumption, several analytical testes including air permeability, wrinkle recovery angle and breaking strength were carried out.

As shown in Figure 6a, the air permeability of untreated and treated cotton fabrics were not change and its values were around 98 to 99 l/m2.s. The air permeability values were unchanged due to silk fibroin only covering the cotton fibers. This assumption was correlated with the observations of SEM images.

The wrinkle recovery angle of untreated and treated cotton fabrics were presented in Figure 6b. It is clearly observed that the values of wrinkle recovery angle of all cotton samples were not high, meaning low crease recovery ability. However, the crease recovery ability had been slightly improved by increasing concentration of fibroin solution (from 0.5 to 1.5 wt%).

The breaking strength of untreated and treated cotton fabrics were illustrated in Figure 6c. The breaking strength values of the untreated cotton in warp and weft directions were 482.85 N and 287.85 N, correspondingly. There were an insignificant decrease in the breaking strength of CoReS1, CoReS2 samples by approximately 3% and 10% in warp and weft directions, respectively. However, the breaking strength of the treated fabric with high concentration of silk fibroin solution (1.5 wt%) was increase. This could be due to the fibroin layer deposited on cotton fibers leading to restriction of fiber mobility, and thus result in

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increasing the breaking strength.

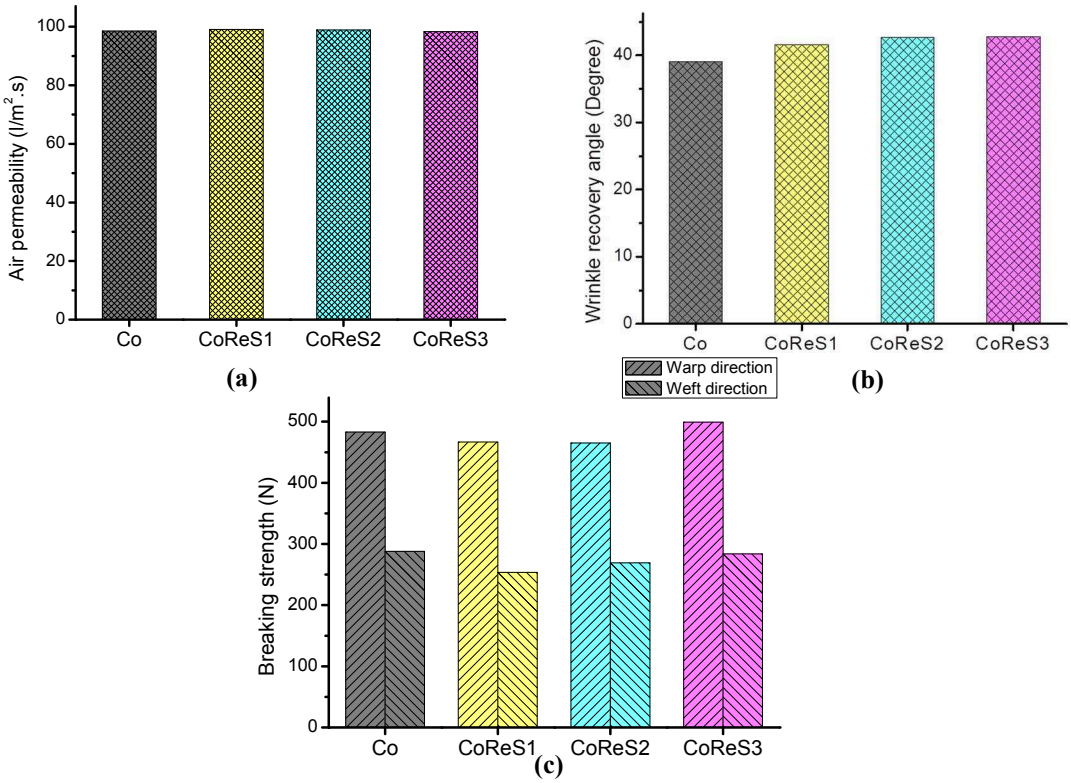

Figure 6. (a) Air permeability, (b) Wrinkle recovery angle and (c) Breaking strength of untreated and treated cotton fabrics.

4. Conclusions

Degummed silk was effectively dissolved by aqueous LiEtW system with enhanced dissolution rate which was significantly shorter than that in the conventional method. The fibroin solution was dissolved from degummed silk could be used to form fibroin coatings on cotton fabric using the pad-dry-cure technique. In addition, a following acetone and aluminum sulfate treatment was introduced to regenerate silk fibroin. The presence of silk fibroin on the cotton fabric was confirmed by SEM, physical and mechanical testes. The silk fibroin concentration in the solutions affected the physico-mechanical properties of treated cotton fabric. Higher silk fibroin concentration improved the wrinkle recovery angle and breaking strength values of the samples, but insignificantly affected to the air permeability of the treated fabrics. This investigated method would bring new perspectives in application of regenerated silk fibroin on textile materials.

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Conflicts of Interest: The authors declare no conflict of interest.

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