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에어레이드 실크부직포의 제조, 구조특성 및 성질

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Preparation, Structural Characteristics, and Properties of Airlaid Nonwoven Silk Fabric

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초록: 본 연구에서는 실크 단사를 공기 분산 후 습윤 및 열압착 처리를 통하여 새로운 에어레이드 실크부직포를 제조하고 그 구조특성과 성질에 대해 살펴보았다. 실크사의 길이가 증가할수록 웹에서 실크사의 분산성은 나빠지고, 실크웹의 인장강도는 감소하였다. 열압착 온도가 200 °C까지 증가함에 따라 에어레이드 실크부직포의 강도와 신도가 증가하였다가 그 이후에는 감소하여 200 °C가 부직포의 기계적 물성을 위한 최적의 압착온도로 밝혀졌다. 2.5% 세리신 수용액을 실크웹에 6 mL 첨가 시까지는 실크부직포의 기계적 물성 향상에 도움이 되었으나 그 이후에는 물성 개선에 도움이 되지 못하는 것으로 나타났다. 본 연구결과를 통해 새로운 실크부직포가 공기분산법을 이용하여 제조가능함을 확인할 수 있었고, 다만 향후에 실크단사보다는 실크섬유를 이용하는 등 제조 공정조건에 대한 개선이 필요할 것으로 생각된다.

Abstract: In this study, short silk yarns were manually airlaid, wetted, and hot-pressed to fabricate new airlaid nonwoven silk fabric. Furthermore, the structural characteristics and properties of the nonwoven fabric were examined. As the length of silk yarn increased, the dispersion of silk yarn in the web worsened and the tensile strength of the resultant nonwoven silk fabric decreased. As the press temperature was increased to 200 °C, the tensile strength and elongation of the airlaid nonwoven silk fabric increased. However, it subsequently decreased with further increase in the press temperature, indicating that 200 °C is the optimum press temperature for obtaining the best mechanical properties of the nonwoven silk fabric. An addition of a 2.5% aqueous sericin solution improved the mechanical properties of the nonwoven silk fabric up to a certain point (i.e., 6 mL); however, further addition of the sericin solution was not helpful. This study demonstrated that nonwoven silk fabric can be fabricated using the airlaid method, although the process should be further improved by controlling preparation conditions, such as using short silk fiber rather than short silk yarn.

Keywords: nonwoven silk fabric, airlaid method, sericin, mechanical properties.

Introduction

Silk is a naturally occurring biocomposite fiber in which sericin covers two fibroin strands. Recently, useful properties of silk, such as its blood compatibility,[1] excellent cytocompatibility,[2,3] and biodegradation,[4-6] were reported. Discovery of these properties has prompted investigation into the applicability of silk in biomedical applications, such as in the fabrication of artificial bone substitute,[7,8] wound dressing,[9] artificial ear drums,[10] membranes for guided bone regeneration,[11,12] and nerve conduits.[13]

For biomedical and cosmetic applications, silk is fabricated in various forms including microsized fibers,[14-16] webs,[17-20] films,[21-23] gel,[24-27] sponge,[3,26,28,29] nonwoven fabric,[30-33] and beads/particles.[34,35] Among these, the structure and performance of electrospun silk web have been extensively investigated for the past 20 years[17-20] because silk web can be easily manufactured by electrospinning and its porous structure facilitates water-holding and promotes cell adhesion and proliferation.

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However, the mass production of electrospun silk web is challenging owing to the low flow rate of electrospinning. Also, too many steps, including degumming, dissolution, dialysis, redissolution, and electrospinning, are required to obtain silk web. More importantly, the high molecular weight and crystallinity of raw silk deteriorate during degumming and dissolution.[36-40] Therefore, the high production cost and limited mechanical properties of the electrospun silk web pose as obstacles to its extensive use.

Recently, it has been reported that a porous natural nonwoven silk fabric with good mechanical properties can be fabricated simply by utilizing the binding properties of sericin.[31-33] In other words, a natural nonwoven silk fabric can be fabricated by winding (reeling) silk filaments and subsequently wetting and hot-pressing them. It was also reported that the porosity and mechanical properties of natural silk web can be adjusted by controlling process variables, suggesting the possibility of its use in various biomedical and cosmetic applications.

Although the existing method using winding, wetting, and hot-pressing succeeded in the fabrication of natural silk web, our research group has explored various alternative fabrication methods for producing natural nonwoven silk fabric because differently prepared nonwoven fabrics could lead to more diverse applications of silk. For example, the previous natural non-woven silk fabric was fabricated using winding silk filaments. Therefore, the silk filaments in the web was arranged regularly resulting in anisotropic properties. On the other hand, silk can be randomly arranged in the airlaid non-woven silk fabric providing isotropic properties. Thus, in this present study, airlaid non-woven silk fabric will be studied.

Based on previous studies,[31-33] it was found to be convenient to first manually prepare nonwoven silk fabric on a small scale and later mechanically fabricate it on a large scale.

Owing to the above-mentioned findings, as a fundamental study, a small batch of the airlaid natural silk web was manually prepared and hot-pressed to fabricate the airlaid nonwoven silk fabric. Effects of the silk yarn length, press temperature, sericin solution addition to the preparation, molecular conformation, and mechanical properties of the nonwoven silk fabric were examined herein.

Experimental

Preparation of the Airlaid Nonwoven Silk Fabric. Twenty eight denier raw silk yarns were provided by Sanju Myungju, South Korea, for this study. The raw silk yarns were arranged in a straight, disentangled manner and then cut into 0.5, 1, and 2 cm raw silk yarns. To prepare an airlaid silk web, 0.2 g of the short raw silk yarns were randomly dropped into an open cylinder.

The airlaid silk web was wetted and hot-pressed to bind the short silk yarns and manufacture the airlaid nonwoven silk fabric. The silk web was wetted by spraying distilled water or an aqueous sericin solution. Distilled water was sprayed on the airlaid silk web for 5 min to steep the whole silk web to facilitate swelling of the sericin in the raw silk prior to hot-pressing. In the case of wetting with the aqueous sericin solution, different amounts (1-12 mL) of a 2.5% (w/w) aqueous sericin solution were sprayed on the airlaid silk web to improve the binding between silk fibers. The 2.5% (w/w) aqueous sericin solution was obtained by treating silkworm cocoons at 120 ºC for 30 min in an autoclave (JSAC-60, JSR, Japan) with a liquor ratio of 1:10.[28]

The wetted silk web was pressed twice in a flat, smooth-surface hot-presser (HK 2008-1-5, Hankuk Industry Co., South Korea) at 150–250 ºC for 10 s to fabricate the nonwoven silk fabric. Nonwoven polyester fabric was placed over and under the silk web to prevent the silk web from sticking to the plate of the hot-presser (Figure 1).

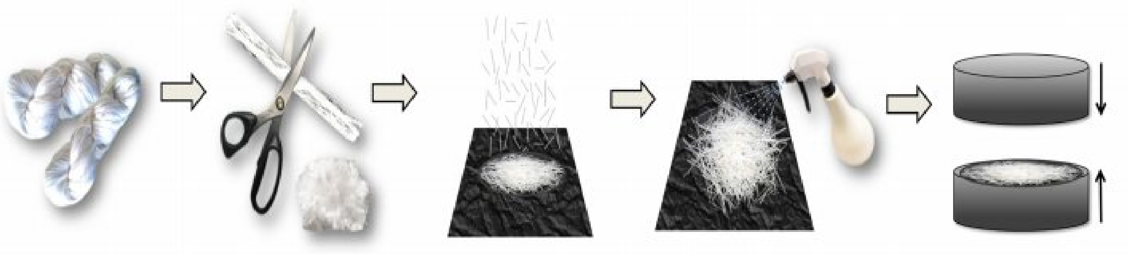

Figure 1. Preparation of the airlaid nonwoven silk fabric.

Measurement and Characterization. A photograph of the nonwoven silk fabric was captured with a digital camera (Canon PowerShot A2000 IS, Canon Inc., Japan). Fourier transform infrared (FTIR, Nicolet 380, Thermo Fisher Scientific, USA) spectroscopy was employed in the attenuated total reflection mode to examine the molecular conformation of the airlaid nonwoven silk fabric.[41-44]

The tensile strength and elongation of the airlaid nonwoven silk fabric were measured using a universal testing machine (UTM) (OTT-03, Oriental TM, South Korea) to evaluate the mechanical properties of the nonwoven silk fabric.[32,33] The tensile tests were performed using a 3 kgf load cell at an extension rate of 10 mm/min. The nonwoven silk fabric was cut into 50×5 mm^2 pieces and the gauge length was 30 mm. All samples were preconditioned at 20 °C and 65% R.H. for 24 h. Seven samples were tested for each condition and the average and standard deviation of the measurements were obtained.

Results and Discussion

Effect of Silk Yarn Length. Fiber length is one of the important factors affecting the preparation and properties of nonwoven fabric. Silk yarn is industrially produced; however, no products made of a single silk filament or single silk staple fibers are commercially available. Therefore, in this study, short silk yarns of different lengths were prepared by cutting commercial silk yarn products and used to fabricate the airlaid nonwoven silk fabric to examine the effect of yarn length on its properties.

The homogeneity of fiber dispersion in the web is important because it strongly affects the web properties. A homogeneous fiber dispersion in the web leads to a homogeneous porous structure, resulting in an even water uptake performance and better mechanical properties of the web. Therefore, the effect of silk yarn length on the homogeneity of yarn dispersion in the web was examined and the results are shown in Figure 2.

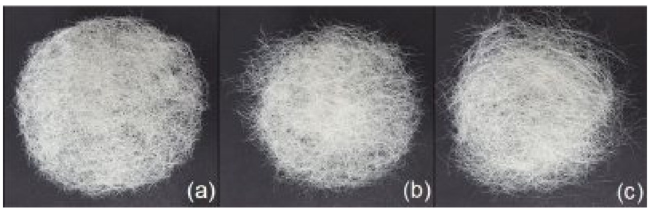

Figure 2. Airlaid nonwoven silk fabric with different yarn lengths: (a) 0.5 cm; (b) 1 cm; (c) 2 cm.

As seen in the figure, in the case of the 0.5-cm silk yarn (Figure 2(a)), the silk yarns were well-dispersed throughout the silk web. Furthermore, the silk fiber and yarn tended to entangle with the neighboring silk. Owing to this characteristic, as the silk yarn length increased, the silk yarns became more entangled, resulting in an inhomogeneous dispersion within the silk web.

Figure 3 shows the effect of silk yarn length on the mechanical properties of the airlaid nonwoven silk fabric prepared by hot-pressing the airlaid silk web at 200 °C. The tensile strength did not change up to a yarn length of 1.0 cm and decreased with further increase in the yarn length up to 2.0 cm. The elongation slightly increased with the increasing yarn length up to 1.0 cm and did not change afterward. It was observed that yarn entanglement and the homogeneity of yarn dispersion have a combined effect on the mechanical properties of the airlaid nonwoven silk fabric; as the yarn length in the nonwoven fabric increased up to a certain point (i.e., 1.0 cm), the entanglement of yarn increased, resulting in a positive impact on the

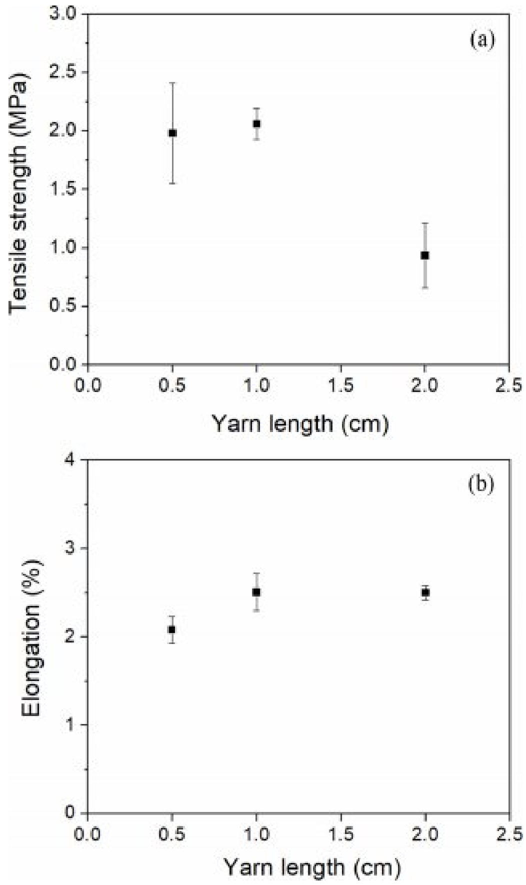

Figure 3. Mechanical properties of the airlaid nonwoven silk fabric with different yarn lengths: (a) tensile strength; (b) elongation.

Figure 4. Airlaid nonwoven silk fabric prepared at different press temperatures: (a) 150 ℃; (b) 180 ℃; (c) 200 ℃; (d) 220 ℃; (e) 250℃.

tensile strength. However, as the length of silk yarn increased further, the homogeneity of yarn dispersion deteriorated, leading to a decreased tensile strength (i.e., a negative effect). As a result of the combined effect of the yarn entanglement and dispersion homogeneity, the tensile strength of nonwoven silk fabric was constant up to a yarn length of 1.0 cm and then markedly decreased as the yarn length increased up to 2.0 cm. The unchanged tensile strength for a yarn length of 1.0 cm despite the worse dispersion homogeneity could be attributed to the positive effect of yarn entanglement on the tensile strength.

When considering the elongation of the nonwoven silk fabric, it is assumed that it does not change significantly with the yarn length owing to the combined effects of yarn entanglement and dispersion homogeneity. Compared with that on the tensile strength, it seems that the negative effect of dispersion inhomogeneity on elongation is less significant.

Despite the similarity in the mechanical properties of the nonwoven silk fabric with yarn lengths of 0.5 cm and 1.0 cm, a yarn length of 0.5 cm was used in the subsequent experiments considering that the homogeneity of yarn dispersion is related to the consistency in the properties of the nonwoven fabric.

Effect of Hot-press Temperature on the Airlaid Nonwoven Silk Fabric. In a previous study,[31] it was reported that the press temperature significantly affected the external features and mechanical properties of nonwoven silk fabric because the binding effect of sericin varies with the press temperature. Therefore, in this study, the silk web composed of short yarns was pressed at different temperatures to examine the effect of the hot-press temperature on the airlaid nonwoven silk fabric. Figure 4 shows the external features of the silk webs.

For a press temperature of 150 ºC (Figure 4(a)), the short silk yarns did not attach well to the neighboring silk yarns, indicating that this temperature is not suitable for preparing the nonwoven silk fabric, although this not been clearly illustrated in the figure. As the press temperature increased, the binding of silk yarns with their neighbors strengthened, leading to the formation of strong nonwoven silk fabric. However, when the press temperature was increased to 220 ºC (Figure 4(d)), the color of the nonwoven fabric turned slightly yellow, which became more evident at a press temperature of 250 ºC (Figure 4(e)). A similar trend has been reported for nonwoven silk fabric prepared by winding silk filaments previously.[31] Setoyama reported that the yellowing index of silk increases with the increasing temperature and owing to the loss of hydroxyl amino acids upon the application of heat.[45]

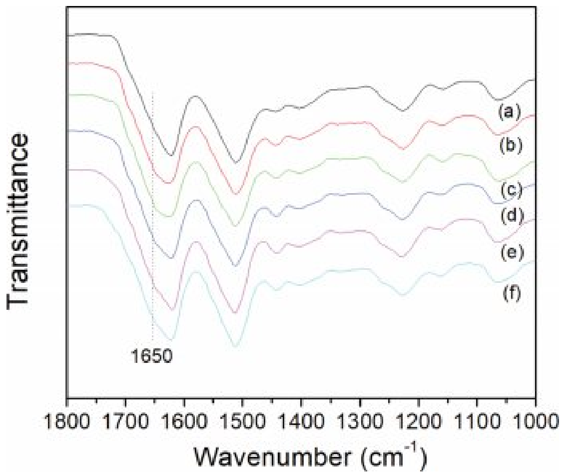

Figure 5. FTIR spectra of airlaid nonwoven silk fabric prepared at different press temperatures: (a) untreated; (b) 150 ℃; (c) 180 ℃; (d) 200 ℃; (e) 220 ℃; (f) 250 ℃.

FTIR spectroscopy has been used to examine the molecular conformation of silk polymers (fibroin and sericin) because the molecular conformation strongly affects their properties.[42,43,46,47] The effect of press temperature on the molecular conformation of nonwoven silk fabric was examined using FTIR spectroscopy and the results are shown in Figure 5. Regardless of the press temperature, all nonwoven silk fabrics showed IR peaks at 1620 and 1510 cm^{-1} in the amide I and amide II bands attributed to the β-sheet crystallite.[42,43,46,47] This is natural considering the silk yarn used in this study is made of raw silk that contains the β-sheet crystallite.[48] It is worth noting that an IR shoulder at 1650 cm^{-1} due to the random coil conformation grew slightly with increasing press temperature. This indicates that more of the random coil conformation was formed at a higher press temperature and is consistent with the hypothesis that it is related to the conformational transition of the β-sheet crystallite to a random coil conformation of sericin upon the application of heat treatment.[31]

Figure 6 shows the mechanical properties of the nonwoven silk fabric prepared at different press temperatures. As the press temperature increased to 200 ºC, the tensile strength and elongation of the nonwoven silk fabric increased, and then they both significantly decreased with a further increase in the press temperature. The trend noted for the mechanical properties of the airlaid nonwoven silk fabric was extremely similar to that observed previously in the nonwoven silk fabric manufactured by winding silk filaments.[31] These results reconfirmed that the optimum press temperature required for achieving good mechanical properties of nonwoven silk fabrics is 200 ºC. The improvement in the strength and elongation of the nonwoven silk fabric up to 200 ºC is due to the increased binding effect of sericin. The remarkable loss of strength and elongation above 200 ºC can be attributed to the reduced binding strength of sericin owing to its thermal degradation at high temperatures (i.e., 220-250 ºC).[31]

Effect of Adding Sericin Solution. In this study, the airlaid nonwoven silk fabric was fabricated with the help of the binding properties of sericin using wetting and hot-press treatments. The sericin in the silk yarn swelled upon water wetting. The swollen sericin in the silk yarn was reformed and bound to the neighboring silk yarns through the hot-press treatment, forming the nonwoven silk fabric. The maximum tensile strength of the airlaid nonwoven silk fabric was 2.0 MPa (Figures 3 and 6). In previous studies,[31,32] nonwoven silk fabrics were fabricated using winding silk filament from the silk cocoon on a roller. Considering that the nonwoven silk fabric demonstrated tensile-strength values higher than 50 MPa in previous studies, the tensile strength of 2.0 MPa observed in this study was relatively low, which is believed to be primarily attributed to the lower amount of sericin available in the silk yarn to bind the neighboring silk yarns than that in the silk filament in the previous study.[31]

The silk yarn used herein comprised 9–10 silk filaments of 2–3 denier, whereas silk filaments of 2–3 denier were used in the previous study. As seen in Figure 7, most of the sericin in the silk filament bound the neighboring silk filaments (Figure 7(A–B)). On the other hand, the sericin outside the silk yarn was involved in binding the neighboring silk yarns (Figure 7(C–D)). In other words, a much lower amount of sericin in silk yarns was used to bind neighboring silks than that in silk filaments. Lee *et al*. reported that the tensile strength of nonwoven silk fabric increased on increasing the sericin content in the silk filament, indicating that the amount of sericin is an important factor affecting the tensile strength.[31] Considering these observations, the low tensile strength of the nonwoven silk fabric in this study could be intimately related to the low amount of sericin available for binding in the silk yarn.

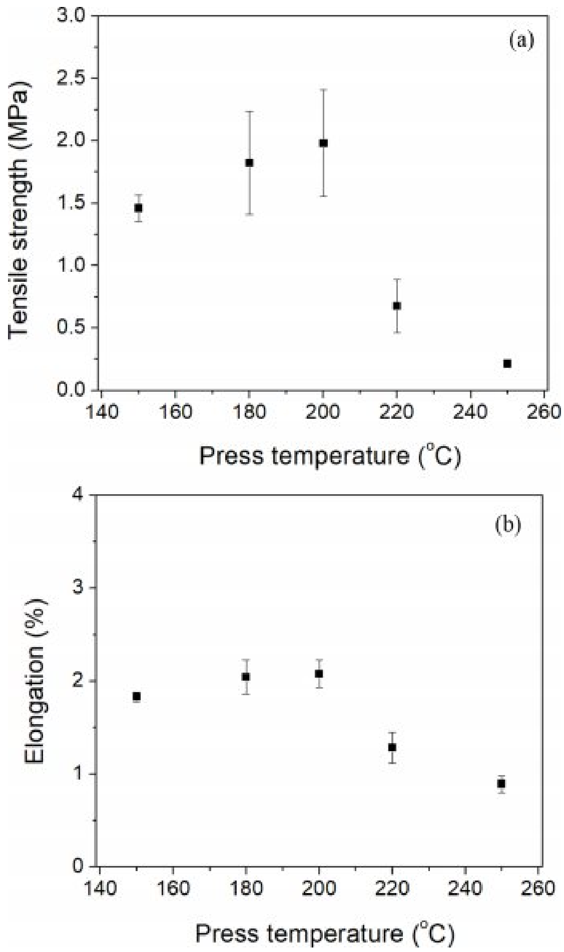

Figure 6. Mechanical properties of the airlaid nonwoven silk fabric prepared with different press temperatures: (a) tensile strength; (b) elongation.

Therefore, to improve the mechanical properties of the airlaid nonwoven silk fabric, different amounts of the 2.5% aqueous sericin solution (3–12 mL) were added to the airlaid silk

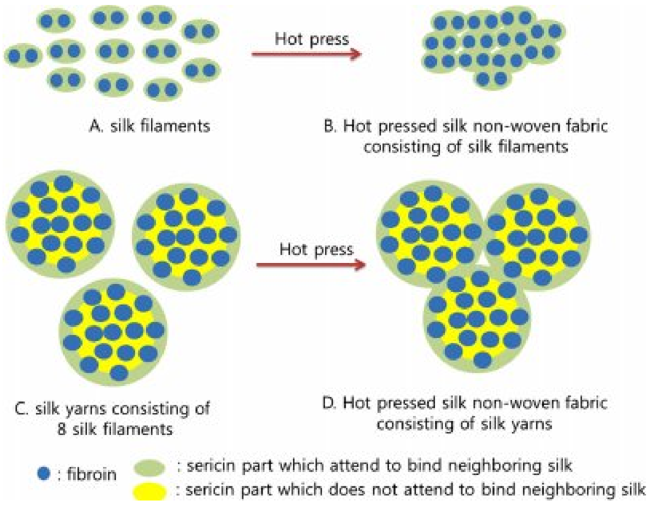

Figure 7. Difference in the binding of sericin in silk filament and silk yarn.

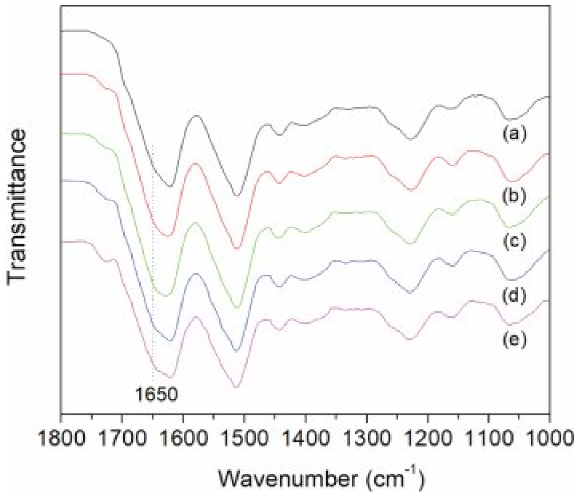

Figure 9. FTIR spectra of airlaid nonwoven silk fabric prepared with different amounts of 2.5% (w/w) aqueous sericin solution: (a) 0 mL; (b) 3 mL; (c) 6 mL; (d) 9 mL; (e) 12 mL.

web and the resultant material was hot-pressed to increase the binding effect of sericin in the preparation of the airlaid nonwoven silk fabric. Figure 8 shows the external feature of the nonwoven silk fabric samples with different amounts of added sericin solution. Although the nonwoven silk fabric with 3 mL of added sericin solution (Figure 8(b)) showed no difference compared with the nonwoven silk fabric without added sericin solution (Figure 8(a)), other nonwoven silk fabric showed irregular arrangements of silk yarns, particularly around the edges of the nonwoven specimens. This is due to the extra amount of sericin solution being squeezed out during the hot-press treatment.

Figure 9 shows the FTIR spectra of the airlaid nonwoven silk fabric added with different amounts of sericin solution. As the amount of added sericin solution increased, the IR shoulder at 1650 cm^{-1} became more evident, indicating the presence of a higher amount of random coil conformation in the nonwoven material. As previously mentioned, the IR shoulder at 1650 cm^{-1} can be attributed to the random coil conformation of sericin resulting from the disruption of the β-sheet crystallite upon heat treatment. Considering this, it can easily be inferred that the IR intensity at 1650 cm^{-1} increased by adding a higher amount of sericin.

Figure 10 illustrates the mechanical properties of the airlaid nonwoven silk fabric after adding different amounts of the sericin solution. As the amount of sericin solution was increased to 6 mL, both the tensile strength and elongation increased; however, they subsequently decreased with further addition of the sericin solution. It is interesting to note that the tensile strength and elongation of the nonwoven silk fabric both increased up to 6 mL of added sericin solution, considering that the strength and elongation of materials often show opposite trends (i.e., the elongation decreases with of the increasing strength). This behavior can be attributed to the effect of additional sericin that increases the bonding between

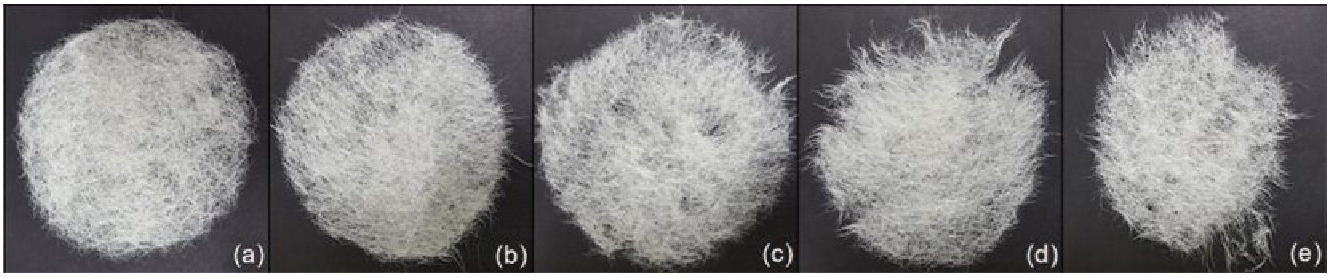

Figure 8. Airlaid nonwoven silk fabric prepared with different amounts of 2.5% (w/w) aqueous sericin solution: (a) 0 mL; (b) 3 mL; (c) 6 mL; (d) 9 mL; (e) 12 mL.

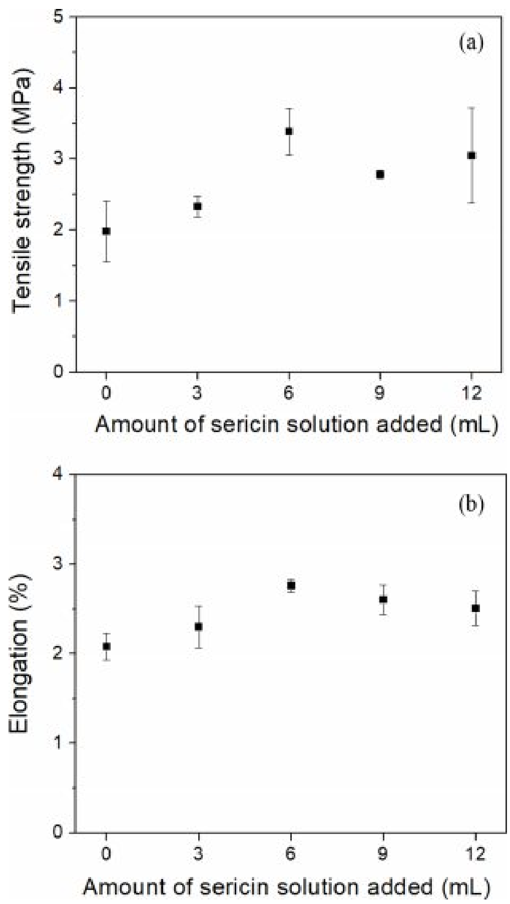

Figure 10. Mechanical properties of the airlaid nonwoven silk fabric prepared with different amounts of 2.5% (w/w) aqueous sericin solution: (a) tensile strength; (b) elongation.

silk yarns in the silk web. However, when an extensive amount of sericin solution was added to the silk web (i.e., 9 or 12 mL), the extra sericin solution was squeezed out during the hot-press treatment. Therefore, additional amount of sericin solution does not improve the mechanical properties of the nonwoven silk fabric. Furthermore, an irregular arrangement of silk yarn in the silk web occurred during the squeezing out of the excess sericin solution (Figure 8), resulting in the decreased tensile strength and elongation.

Conclusions

In this study, the airlaid nonwoven silk fabric was manually prepared by free-falling short silk yarns and the effect of preparation conditions on the molecular conformation and mechanical properties of the nonwoven silk fabric was examined to explore the potential of industrial fabrication of the airlaid nonwoven silk fabric.

As the length of silk yarn decreased, the dispersion of silk yarn became more homogeneous, resulting in better mechanical properties of the nonwoven silk fabric. Similar to the case of the nonwoven silk fabric prepared by winding silk filament in a previous study,[31] the press temperature was one of factors affecting the mechanical properties of the nonwoven silk fabric. A press temperature of 200 ℃ provided the highest tensile strength and elongation. The airlaid nonwoven silk fabric showed a lower tensile strength and elongation than that of the nonwoven fabric prepared by winding silk filaments owing to the low amount of sericin available for binding silk yarns. However, the mechanical properties of the airlaid nonwoven silk fabric were somewhat improved by adding a sericin solution to the airlaid silk web.

Thus, this study demonstrated that it is possible to prepare nonwoven silk fabrics through the airlaid method. Although satisfactory mechanical properties of the nonwoven silk fabric have not been yet achieved, it is envisaged that those can be improved by changing the preparation conditions (e.g., using short silk fiber instead of short silk yarn). Considering the potential of nonwoven silk fabric in biomedical and cosmetic applications, more detailed relevant studies should be conducted to enhance the preparation methods and properties of the airlaid nonwoven silk fabric in the near future.

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