The properties of sericin/poly(vinyl alcohol) films modified by boric acid

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Abstract: A group of films mainly composed of sericin and poly(vinyl alcohol) (PVA), using boric acid (BA) as a modifier, were prepared by a technique of solution casting. In this work, the effect of BA and sericin on the mechanical properties and water resistance of the films was analyzed, the interior morphology of the films were described by a scanning electron microscopy (SEM), the thermal stability of the films was characterized by differential scanning calorimetry (DSC), and the reaction mechanism was proposed according to the previous literature and the test of Fourier transform infrared spectrum (FTIR). Results indicated that, the properties of the membrane were the functions of the blend ratio of sercin to PVA and the content of BA. The use of BA increased the tensile strength, improved the water resistance and the thermal stability, and varied the interior morphology of the films. The content of sericin greatly influenced the combination of properties of the films, especially the mechanical properties, interior morphology, thermal stability, and water resistance reducing with the increasing of sericin content. The films have potential to be used in materials, such as skin-care coatings for beauty, percutaneous drug delivery systems for exterior intact skin, due to the characteristics of the components and the good mechanical properties of the films.

Introduction

Sericin is a natural macromolecular protein derived from silkworm and is usually discarded in silk processing wastewater. However, recently the outstanding properties of sericin have attracted the attention of people [1-7]. Especially, its skin-care characteristics is revealed due to its high content of serine which is the major component of the natural moisturizing factor (NMF); the moisture absorbing and desorption properties of sericin, depending on the amount of serine presented in the protein, render it suitable for production of cosmetics and biodegradable materials [8]. Considering economics and environmental impact, sericin protein is anticipated to be a promising natural resource for novel applications, such as enzyme immobilization, biomaterials, films, functional fibers [9]. However, sericin protein also has some drawbacks such as poor mechanical properties, high solubility in aqueous solutions and instability at high temperatures. Various modifications have been used to overcome its drawbacks [10-12].

PVA is widely used in practical investigations of functional polymers due to its ease of modification through its hydroxyl groups. And the applications of PVA, in a form of film have been intensively studied due to its properties of film-forming, highly hydrophilic, nontoxicity and good chemical resistance [13]. It seems that the mechanical properties of pure sercin film can be surely improved through
blending or cross-linking with PVA [14-16], but no reports have been found using BA as a modifier of the blend system of sericin and PVA according to the available literature.

BA is a kind of inorganic reagent, usually used as a cross-linking reagent of PVA with the purpose of improving the water resistance and the stability of PVA. In addition, aqueous solutions of BA with a low concentration usually find applications in skin-care ointments and membranes which can inhibit the growth of the bacteria and help the recovery of the lightly irritated skin [17, 18]. Therefore, BA used in skin-care materials with PVA may be a promising selection.

In this article, many films made from sericin and PVA, modified by BA, have been prepared and studied in detail. Such films may find potential applications in products such as skin-care coatings for beauty, percutaneous drug delivery systems for exterior intact skin, and so on.

**Result and discussion**

As shown in Figure 1, the tensile strength gradually increases and then decreases with increasing BA content, however, the fracture strain rate only has a minor variety limited in the range 2.5-3.0%. The variety of the tensile strength suggest that the use of BA did not always do a positive contribution to improve the tensile strength. The phenomenon is primarily due to the amounts of phase separations, as noted later, caused by the excess amount of BA used leading to cross-linking of intramacromolecules, and the partially inherent crystallinity of PVA deteriorating the miscibility of the two components, thus, the films may be easy to fracture under a smaller stress. The variety of fracture strain rate indicates that, the effect of modifier on the elongation property was insignificant, meaning that, the use of BA in small scale did not produce enough cross-linking sites between the two components to effectively change the elongation property.

![Figure 1](image_url)

**Fig. 1.** Effect of BA content on mechanical property of the films.
The Young’s modulus gradually decreases with increasing BA content as represented in Figure 2, the phenomenon suggests that, the more the use of BA, the weaker became the elasticity. It is generally true that Young’s modulus is suitable for estimating the degree of cross-linking, and the higher the degree of cross-linking, the bigger becomes the modulus in theory. But in practice, Figure 2 gives a information that, the degree of cross-linking decreases with increasing BA content. It seems to be inconsistent with the theory mentioned above, because people usually assume the more the cross-linking reagent, the bigger is the degree of cross-linking. However, it should be taken into consideration that, the longer PVA macromolecules actually cross-link easier than the globular and shorter sericin macromolecules in dilute aqueous solution, providing PVA more opportunities to cross-link than sericin, thus, between PVA and sericin, worse miscibility with some extent cross-linking appeared in the form of phase separations at the expense of the effect of cross-linking, resulting in a decrease in Young’s modulus. It is clear that, the slight cross-linking did not do enough positive contribution to the elongation property, and on the contrary, the miscibility of the two components deteriorated as increasing the content of BA, resulting in a similar elasticity.

![Graph showing Young's modulus vs. BA content](image)

**Fig. 2.** Effect of BA content on Young’s modulus of the films.

Figure 3 shows that, the dissolution degree of the films, as a function of BA content, firstly decreases and then increases with increasing BA content, this illustrates that BA was not continuously a positive factor to the improvement of water resistance, but there is a smallest dissolution when the BA content is 0.4wt% of the solutes. Obviously, the variety was the result of the combination of the effect of cross-linking and crystalinity preventing the dissolution, and the effect of phase separation facilitating the dissolution as previously discussed. The smallest dissolution was a compromise of the two opposite effects.

The tensile strength firstly increases and then decreases with increasing sericin content as shown in Figure 4. The strengths are bigger than others when the content of sericin are 20wt% and 30wt% of the solutes, which indicates that the cooperated
effect of cross-linking and miscibility would be better when the content of sericin were 20wt% and 30wt%.

![Graph showing dissolution degree vs. B.A. content](image1)

**Fig. 3.** Effect of BA content on the dissolution degree of the films.

It is clear that sercin is a water-soluble protein with more than 74% polar side groups on the macromolecular chains, and PVA was also a hydrophilic and water-soluble polymer, this determines that the two macromolecules will have good miscibility either in aqueous solutions or solid blends.

![Graph showing tensile strength and fracture strain rate vs. sericin content](image2)

**Fig. 4.** Effect of sericin content on mechanical property of the films.
However, the molecular weight of sericin, 35000-40000Da, is smaller than that of PVA, 75000. And the state of proteins in aqueous solution was globular random coil which was difficult to entangle with the macromolecules of PVA. Therefore, it is easy to understand why the tensile strength of the films did not increase with increasing sericin content. Actually, a film, with a sericin content of 50 wt%, could not appear in a homogenous state, which is absent in the paper but produced in the lab.

In the films containing sericin, the fracture strain rate greatly decreases and has little difference compared to the pure PVA film, this indicates that, the use of sericin had a negative effect on the elongation property of the films, possibly because the sericin macromolecules with irregular chain structures, has inferior miscibility with PVA macromolecules with relatively regular chain structure.

As shown in Figure 5, with increasing sericin content, the Young’s modulus first increases and then decreases, and the biggest modulus appears when sericin content is 30wt% of the solutes, this indicates that, a suitable content of sericin did contribution to the Young’s modulus, and the best one was 30 wt%. The increasing trend of Young’s modulus in the previous section of the curve is primarily due to the effect of cross-linking and the crystalinity of PVA, and the decreasing trend is primarily due to the effect of phase seperation as previously mentioned, the two opposite effects reach an equilibrium when sericin content was 30wt%.

![Figure 5](image-url)

**Fig. 5.** Effect of sericin content on Young’s modulus of the films.

Figure 6 illustrates the effect of sericin on the dissolution, the dissolution degree gradually increases with increasing sericin content, and the curve seems to be a straight line before 30 wt%, but the dissolution degree of the last one is severe than the previous four. This suggests that, when the sericin content was less than 30 wt%, sericin had been homogenously distributed into the films, nevertheless, when the sericin content was more, the sericin macromolecules preferred to gather together, resulting in a worse miscibility between sericin and PVA macromolecules, thus the water molecules easily penetrated the film, and a severe dissolution occurred.
Fig. 6. Effect of sericin content on the dissolution degree of the films.

The interior morphology of different samples exhibits different structures as described in Figure 7 and 8.

Fig. 7. SEM photographs of films with different B.A. content; a) 0% B.A. b) 0.2% B.A. c) 0.4% B.A. d) 0.6% B.A.

It's clear that, sericin protein with more than 74% (mol/mol) hydrophilic side groups such as amido, carboxyl and hydroxyl, which usually appear outside of the random coil in polar surrounding, is miscible with PVA which is also hydrophilic. However,
there are many granular phase domains in the sample without BA, which disappear with increasing BA content, and the interior morphology of sample c is the most homogenous one as shown in graph a of Figure 7. This indicates that the use of BA improved the miscibility of sericin and PVA. Moreover, graph d shows a worse morphology than graph c, which suggests that excess use of BA was likely to produce more heterogeneous structure. Graph I of Figure 8 also shows many granular phase domains, which meant an imperfect miscibility between sericin and PVA when the blend ratio of PVA to sericin was 8/2. The miscibility greatly improved when the blend ratio of PVA to sericin changed to 7/3 as shown in graph II. However, graph III represents a inferior morphology with many layer-like phase separations when the blend ratio of PVA to sericin was 6/4, this indicates more content of sericin may do harm to the homogeneity of the blend film.

Fig. 8. SEM photographs of films at different blend ratios of PVA to Sericin.

The thermal stability of the films was shown as Figure 9, the decomposition of PVA occurred accompanying with the melting of PVA at temperatures ranging from 220 °C to 300 °C. It was different from other three samples, 2#, 3# and 4#, which had lower melting temperatures at about 220 °C and higher decomposition temperatures. The lower melting temperatures indicates that, the intrinsically capability of crystallization of PVA was diminished by adding BA or sericin or both, suggesting that the macromolecules of PVA have strong interactions with the molecules of BA or sericin. After comparing the curve of sample 2# with the curve of sample 4#, it is clear that in the curve of sample 2# appears two endothermic peaks at 257 °C and 286 °C. This is due to the decomposition of polyvinyl alcohol, and indicates that the films containing sericin had better thermal stability.

After comparing the curve of sample 3# with the curve of sample 4#, it is discovered that the curve of sample 3# has a faint endothermic peak at 250 °C, possibly caused by the decomposition of a small quantity of sericin, however, sample 4# do not have this absorption at 250 °C. This suggests that the use of BA improved the thermal stability of sericin. The result is testified by the comparison among curve 3#, curve 4# and curve 5#, the decomposition temperature of sericin rose after blending with PVA and reached 330 °C after using BA in the blend of PVA and sericin.
According to the comparison of the three FTIR curves in Figure 10, there are two new absorption bands at 1575.84 cm\(^{-1}\) and 1261.44 cm\(^{-1}\) in the curve c, which are the bands of C-N bending and N-H stretching vibrations of the amides II and III, respectively. Curve c has a bigger absorption band of C=O stretching vibration of amide I at 1660.70 cm\(^{-1}\), which is different from curve a and curve b. Considering sample b and sample c were washed in running nonionic water for 24 h, the BA and sericin without incorporating into cross-linking had already been dissolved out, so the differences among the curves are due to the existence of sericin. This indicates that, as a cross-linking agent, BA has the ability to connect sericin and PVA together to a certain extent.

**Fig. 9.** DSC analysis of the films.

**Fig. 10.** Fourier infrared spectrum analysis.
It is clear that, the macromolecules of PVA have many hydroxyls, 38.9% of sericin residues also have hydroxyls, and BA can be used as cross-linking agent of PVA through the reaction with hydroxyls, therefore, there is possibility that BA can react with the hydroxyls of the sericin. In addition, the amido groups of the sericin macromolecules are easy to react with BA by a reaction of nucleophilic substitution due to the literature, thus, the reaction mechanism may be supposed as scheme 1:

\[
3R-O-H + HOB-OH \rightarrow ROBO-R + 3H_2O
\]

(R represents the residues of PVA molecules or sericin proteins)

\[
2R-O-H + H_2N-R' + HOB-OH \rightarrow \]

\[
R-O\]

\[
R' \]

\[
B-NH-R'
\]

(R represents the residues of PVA molecules, R' represents the residues of sericin proteins)

**Scheme 1.** Reaction mechanism of PVA/SS with BA.

**Experimental part**

**Materials**

Water-soluble sericin powder (M$_w$: 3.5×10$^4$~4.0×10$^4$, Purity Degree: 95-97%), was from Huzhou Xintiansi Bio-tech Co. Ltd, Zhejiang Pro., P. R. China. PVA (Dp: 1700±50, >99% hydrolyzed) was obtained from Beijing Organic Chemistry and Engineering Corp., Beijing City, P. R. China. Boric acid (M$_w$: 61.83), from Tianjin Chemical reagents wholesale Corp. Tianjin City, P. R. China.

**Preparation of the films**

Firstly, a 10 weight percent (wt%) PVA aqueous solution and a 10 wt % sericin aqueous solution were prepared. The above two solutions were mixed together by agitating at room temperature in a predetermined weight ratio (sericin/PVA was 3/7)[19]. A 5 wt% BA aqueous solution was added dropwise at ratios of 0wt%, 0.2wt%, 0.4wt%, 0.6wt%, and 0.8wt% of the solutes, in the above mixed solutions to prepare five modified solutions, respectively. Then they were agitated for 1 hour at 65 °C. The solution mixtures were kept still for 30 min at the same temperature for excluding the air bubbles caused by agitating, then they were cast to plain glass plates, dried for 48 hours at room temperature, and packed away for testing.

In addition, other four solution mixtures were prepared, which the blend ratios of sericin to PVA were 0 to 10, 2 to 8, 3 to 7, and 4 to 6, with a same BA content 0.4wt% of the solutes, in the above four kinds of solutions, respectively.

**Mechanical properties**

A electronic textile strength instrument YG065 was employed, the drawing speed was 200 mm/min; the textile force, fracture strain rate, and Young’s modulus were
recorded by the computer controlling the instrument; every sample was tested five times, and the average value was taken as the final data. The thickness of the films was tested via a outside micrometer, then the tensile strength of the films was given by:

\[ T_s = \frac{F}{l \times d} \]  

(1)

where \( F \) (N) is the tensile force, \( l \) (mm) is the width the sample with a shape of 100 mm×10 mm, and \( d \) (mm) is the thickness of the film.

**Rate of water content and solubility of the films**

The test of rate of water content: the film samples were weighed and then vacuum-dried for 2 h, then the rate of water content is given by

\[ q = \frac{w_1 - w_2}{w_1} \times 100\% \]  

(2)

where \( w \) (g) is the weight of the film, and subscripts 1 and 2 refer to the weight of the original film and the vacuum-dried film, respectively.

The test of dissolution degree: the film samples were cut into the shape of 50 mm×50mm and weighed, then were put into nonionic water 100 times weightier than that of films to dissolve with shaking for one hour at 37 °C, after that, they were vacuum-dried for 2 h at 105 °C, the dissolution degree is given by:

\[ S = \frac{m_1 - m_2}{m_1} \times 100\% - q \]  

(3)

where \( m \) (g) is the weight of film, and subscripts 1 and 2 refer to the original film and the film after dissolving and drying, respectively; the quantity \( q \) (wt\%) is the rate of water content, as noted above.

**SEM**

The film samples were first vacuum-dried at 50 °C for 24 h, then quickly frozen in liquid nitrogen, and the frozen dried samples were carefully fractured and mounted onto aluminum studs and sputter-coated with gold for 240 s. The interior morphology was investigated using a scanning electron microscope (Quanta 200, FEI, CZECH).

**DSC**

Three representative film samples were tested using a thermal analysis instrument (DSC7, PERKIN-ELMER Corp. USA). Sample 2# was made from PVA modified by BA with a content of 0.4wt% of PVA, sample 3# was made from PVA and sericin at a blend ratio of 7 to 3, sample 4# was made from PVA and sericin at a blend ratio of 7 to 3 and modified by BA with a content of 0.4wt% of the macromolecules. Furthermore, in order to compare with above three samples, the PVA feed named sample 1# and the sericin powder named sample 5# were tested, respectively.

For each measurement, about 15 mg of sample (along with its water) was placed inside a hermetic aluminum pan, then sealed tightly with a hermetic aluminum lid. The thermal analysis was performed from 40 to 350 °C on the samples at a heating rate of 10 °C min\(^{-1}\) under dry nitrogen (flow rate of 50 mL min\(^{-1}\)).
**FTIR-ATR**

Three FTIR-ATR curves of representative films were gained for comparing analysis (VECTOR22, **BRUKER** Corp., GERMANY). The first one (a) was a dry film of pure PVA, the second one (b) was a dry blend film of PVA and sericin washed for 24 h in running water at room temperature, the third one (c) was a dry film of PVA and sericin modified by BA which was also washed in running water for 24 h at room temperature.

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**References**