Preparation and characterization of transparent silk fibroin/cellulose blend films

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Abstract

Both silk fibroin (SF) and cellulose are considered as potential substitutes of synthetic polymers because of the problems for the exhaustion of fossil resources and the pollution of environment. In order to obtain a material that exhibits both the advantages of SF and cellulose, ionic liquid (IL) was introduced to prepare blend films of SF and cellulose in the present work. We found that by our new fabricate method, i.e. coagulating SF/cellulose IL mixture solution by vaporized methanol and cold pressing during vacuum dry, the resulted SF/cellulose blend films were transparent owing to the significant compatibility between cellulose and SF. The mechanical properties of the blend films in dry state is better than other reported counterparts, while those in wet state is good enough for further applications. Our results also confirms that the miscibility of SF and cellulose was induced by the intermolecular interactions between the components in the same blend system but with different fabricating methods in the literature. In addition, mouse fibroblast L929 cells was found to show the significant adhesion and proliferation on the blend film, which suggested that the treatment of IL and methanol may not affect the biocompatibility of SF/cellulose blend films.

1. Introduction

Recently, most of polymeric materials are produced from fossil resources derived monomers, and the gap between the continuously increasing demand and decreasing availability of crude oil or coal based products is enlarging along with the booming economy. Besides that, environmental problem arisen from synthetic polymer has attracted much more attentions of the human being. Therefore, one of the main challenges faced to the researchers is the development of those sustainable materials. Bio-product, as the gift from nature, is obviously best candidates by its advantages including environment friendly, low cost, renewable, nontoxicity, degradability, and biological compatibility etc., and is especially suitable for the applications in biotechnological and biological area [1–6].

SF, a fibrous protein delivered from silkworm silk, has been explored as a versatile biomaterial in the forms of fiber, microsphere and porous scaffold for various applications, due to its great biocompatibility and slow degradability [4,7–10]. However, the regenerated SF material with various shapes is either too brittle in dry state or too weak in wet state to promise its applications within a broad area [11–15]. Although it was reported that mechanical properties of SF dried film in the direction of pre-stretching was significantly improved after uniaxial extension of its wet film [16], the obtained SF film still has poor mechanical properties in perpendicular direction and the biaxial oriented SF film was very difficult to produce. On the other hand, cellulose, mainly produced by photosynthesis of plants, certain strains of bacteria and the marine animals, is the most abundant polysaccharide on the earth. Various shapes of regenerated cellulose materials with high mechanical strength, excellent hydrophilic properties, good thermal resistance and biodegradability have been produced [5,6,17]. However, the cellulose based material needs to be further modified for its good appetency with living agents, such as cell, enzyme, functional polypeptide, etc. [18–21].

It is well known that the blending is an effective possible way to combine advantages of each component [3,22]. Thus, blends of SF and cellulose have been prepare to acquire biomaterials that are able to deliver good performance both at mechanical and biological aspects [11,13,14,23,24]. However, it has to be noticed that solvent resistance of crystalline structure of both nature cellulose and silk fiber requires harsh chemistry procedures for their dissolution. For
example, cuoxam [23,24], N-methyl morpholine N-oxide (NMNO) [11], N,N-dimethylacetamide (DMAC)/LiCl [14], were applied to dissolve SF and cellulose in the literature. Several drawbacks of those solvents, including environmental pollution, toxicity and cost, etc. are against to the principal of green chemistry [2,25]. Meanwhile, the molecular weight of the biomacromolecule is often significantly reduced during such rigorous procedures [26,27].

Ionic liquids (IL), which is considered as the green solvent by features of nonflammable, negligible vapor pressure and recyclable, etc. has been implied to separately dissolve various natural products, including SF, cellulose, chitosan, starch, keratin, soybean protein and so on [2,17,28–36]. It has been proved that only slight decomposition and negligible deviation occurs during the dissolving process, even in the high concentrations [17,28,35]. Apparently, the employment of IL provides new approach to mix SF and cellulose at molecular level in an efficient way. It was reported that mechanical properties of SF/cellulose blend films from IL solution were better than the one from NMNO solution [26]. However, owing to inappropriate fabricating procedures including coagulating bath, coagulating rate and post treatment that have great effects on the regenerated materials [37,38], mechanical properties of these blend films in dry state were still even worse than that of pure SF film obtained from aqueous solution, according to published data [16,26,33,39]. Moreover, it is worth to mention that mechanical performance of the material in wet state as well as its biocompatibility are essential for the medical applications [4,7].

In the present work, in order to combine beneficial features of SF (e.g. biocompatibility) and cellulose (e.g. mechanical performance), ionic liquid was employed as co-solvent to mix SF and cellulose. The mixture solution was placed into a methanol atmosphere for precipitating the blend materials. After a developed “cold pressing” process, the transparent blend films of SF and cellulose with significantly improved mechanical properties as well as satisfied biocompatibility were produced to suggest their promising application in the biomedical field.

2. Experimental section

2.1. Materials

Bombyx mori silkworm silk cocoon was degummed by the established process [40]. The degummed silk fiber was dried at 60 °C for 24 h prior to use. Microcrystalline cellulose (DP = 360) powder was purchased from Sigma–Aldrich (USA), and was dried at 60 °C in vacuum for 24 h. The IL, 1-butyl-3-methylimidazolium chloride (BmimCl), was purchased from Lanzhou Institute of Chemical Physics, China, and was freeze-dried to remove the residual IL and methanol in the cake was removed later by repeated vacuuming to 0.06 MPa and kept at room temperature for 48 h. The oven was vacuumed to 0.06 MPa and kept at room temperature for 48 h. Owing to the effect of vaporized methanol, cellulose and SF were coagulated and formed gel-like cake in the Teflon petri dish. In such a case, BmimCl was squeezed out from the material. Both of the residual IL and methanol in the cake was removed later by repeated soaking and washing with distilled water. The dried blend films were finally acquired by cold press which stands for a processing including clamping the gel-like cake between two glass plates by binder clip and drying under reduced pressure at room temperature. The wet blend films were prepared by swelling those dried films in distilled water until the thickness was constant.

2.2. Dissolution of cellulose and SF

5 g dried cellulose was added into a flask containing 45 g BmimCl, and the mixture was magnetic stirred in an oil bath at 100 °C for 4 h under vacuum-pumping. Completely dissolving of cellulose was checked by polarized light microscope on a 100 °/C hot stage. The dissolving procedure for degummed silk is similar to cellulose except for heating temperature was 90 °C and duration was 1.5 h. Both cellulose and SF solution in IL with the concentration of 10 wt% were kept at drying condition for further mixing.

2.3. Manufacturing of blend films

The SF and cellulose solutions were mixed and magnetic stirred in a flask at 80 °C for 3 h with the desired ratios of cellulose to SF as 100/0, 75/25, 50/50, 25/75, and 0/100, which are marked as C100, C7525, C5050, C2575 and S100 accordingly. The mixed solution was poured into a Teflon petri dish and put into a vacuum drying oven with several beakers contained methanol. The oven was vacuumed to 0.06 MPa and kept at room temperature for 48 h. Owing to the effect of vaporized methanol, cellulose and SF were coagulated and formed gel-like cake in the Teflon petri dish. In such a case, 8mimCl was squeezed out from the material. Both of the residual IL and methanol in the cake was removed later by repeated soaking and washing with distilled water. The dried blend films were finally acquired by cold pressing which stands for a processing including clamping the gel-like cake between two glass plates by binder clip and drying under reduced pressure at room temperature. The wet blend films were prepared by swelling those dried films in distilled water until the thickness was constant.

2.4. Characterization of the films

High-magnification image of fragile fracture on cross section of freeze-dried cake and blend films was pictured on a Hitachi S4800 field emission SEM after sputtered with gold. The crystallization pattern of the dried films was recorded on a wide-angle X-ray diffraction (XRD) instrument (D8 Advance, Bruker AXS, Germany) with CuKα radiation (λ = 0.154 nm). XRD data were collected from 2θ = 5–40 at a scanning rate of 2°/min.

All infrared spectra were collected using a Nicolet Nexus 6700 Fourier transform infrared spectroscopy (FTIR) spectrometer. To eliminate spectral contributions due to atmospheric water vapor, the instrument was continuously purged with dry air. For each measurement, 64 interferograms were co-added with a nominal resolution of 4 cm⁻¹. Deconvolution and peak separation of amide I bands was carried out using PeakFit 4.12. The position of peaks was defined from the result of second derivative spectrum and fixed during the deconvolution process. A Gaussian model was selected for the band shape, and the bandwidth was automatically adjusted by the software.

The thermal stability of obtained film was examined up to 700 °C through Perkin Elmer Pyris-1 thermogravimetric (TG) analyzer at a heating rate of 5 °C/min in nitrogen. The dried sample was placed in pressure tight aluminum cells heating from 50 to 400 °C with a rate of 10 °C/min in nitrogen atmosphere by Netzsch, F3 for implementing analysis of differential scanning calorimetry (DSC).

Dynamic mechanical thermal analyses (DMA) of the obtained films was executed on TA-Q800 in tension mode from 50 to 400 °C with a heating rate of 5 °C/min at 1 Hz load frequency, 1 N maximum dynamic tension and 0.8% initial strain in nitrogen atmosphere.

The mechanical properties of the films (20 mm × 5 mm × 0.15 mm) were measured on an Instron 5565 mechanical testing instrument in tensile mode at 25 °C and 40 ± 5% RH for dried film or 95 ± 5% RH for wet film. The gauge length and the drawing speed were preset as 10 mm and 10 mm/min, respectively.

2.5. Cell culture

L929 (mouse fibroblast, NCTC clone 929, derivative of Strain L, Chinese Academy of Sciences Type Culture Collection, Shanghai, China) cells were cultured in Dulbecco’s modified Eagle’s medium (DMEM medium, Gibco, USA) supplemented with 10% fetal bovine serum (Gibco, USA) and 1% Ul/ml streptomycin–penicillin (Sigma, St Louis) incubated at 37 °C and 5% CO₂. Obtained gel-like cakes were cut into dimension of flat cylinder (i.e. 10 mm in diameter and 7.5 mm in height) and sterilized with 75% ethanol for 2 h, then thoroughly washed with sterilized PBS and finally rinsed with...
culture medium for 4 h before cell seeding. Each film was seeded with $1 \times 10^5$ cells in 24-well plate. The culture medium was changed every other day. The cell-film constructs at day 7 were washed with sterilized PBS, fixed with 2.5% glutaraldehyde at 4 °C for 24 h, then quenched in liquid nitrogen and freeze-dried. Cell morphology on the materials was investigated using scanning electron microscopy Tescan 5136 MM after sputtered with gold.

3. Results and discussion

3.1. Morphology of the blend material

In general, IL solutions of cellulose and SF, as well as their mixtures with various ratios were homogenous and transparent under observation of naked eyes. After placed into methanol atmosphere, the solutions turned to gel-like cake (Fig. 1-“gel-like cake” column) rather than hydrogel, although it was reported that cellulose IL solution could be coagulated as transparent hydrogel in distilled water [41]. It is suggested that gel-like cake acquired here is composed by hydrated cellulose and SF domains and water. In our case, pure cellulose cake is transparent, but the opacity of blend cakes was continuously increasing along with the content of SF. In addition, the cross section of those freezing dried gel-like cakes showed that the size of pore in blend cakes resemble to each other (Fig. 1-“cross section of cake” column). Therefore, variation of transparency among these gel-like cakes with different blend ratios indicated the refractive index of hydrated SF domains in the blend cake differs from that of hydrated cellulose domains which must be similar to water. Moreover, on the account of the transparency of SF/cellulose blend cake does not sharply decrease with the adding of SF, it is inferred that cellulose and SF are homogenous distributed in the blend cakes and interactions between their molecular chains give rise to a gradual change of difference in refractive index between SF/cellulose and water. On the other hands, cold pressing give rise to a gradual change of difference in refractive index between the blend cakes and interactions between their molecular chains.

3.2. Secondary structure of SF and cellulose in the blend film

FTIR is one of the techniques to investigate the specific interactions in multi-component polymer blends. Herein, the spectra from 1600 cm$^{-1}$–1700 cm$^{-1}$ (amide I) of obtained SF/cellulose blends were collected for illustrating secondary structure of SF. The assignment of adsorption peaks in the amide I band is generally agreed upon: the broad peak centered at 1655–1660 cm$^{-1}$ to random coil, or helical conformation, or both; the peak around 1620–1630 cm$^{-1}$ to β-sheet conformation; and the small peak nearby 1700 cm$^{-1}$ to β-turn conformation of the hairpin-folded antiparallel β-sheet structure [42,43]. As the treatment of methanol can induce conformational changes of SF from random coil or α-helix to β-sheet [42,43], three kinds of secondary conformation of SF stated above are detected in the blend films (Fig. 2). For the sake of further comparison of secondary conformation among these films, data processing of FTIR spectroscopy, which is consisting of drawing second derivative spectra, deconvolution and peak separation, were executed to give more detailed information of relative content of β-sheet in all conformations. As in our previous studies [42,44], a Gaussian model was selected for the band shape; the band position was set at 1625, 1655, and 1698 cm$^{-1}$ according to results of second derivative spectra, which represented β-sheet, random coil or helix, and β-turn associated with β-sheet; and the bandwidth was automatically adjusted by the software. The detailed information about deconvolution of one of spectrums (C50S50) is presented at Supporting Information as Fig. S1. The increase of absorbance of the 1623 cm$^{-1}$ band was used as a probe for the β-sheet formation during the conformation transition process. It is estimated that the proportion of β-sheet + β-turn has been raised from 0.13 ± 0.04 of S100 to 0.41 ± 0.09 of C75S25 (Table S1), indicating the blending with cellulose has promoted conformational transition of SF from random coil or helical content to β-sheet, which is presumably resulted by strong interactions between molecular chains of SF and cellulose.

In order to investigate the crystalline structure of both components, XRD of obtained films was carried out, and the acquired patterns are showed at Fig. 3. It can be seen that the pure regenerated SF (S100) displays two higher diffraction peaks around 2θ = 20° and 2θ = 28°, and a smaller one at 2θ = 8°. Obviously, it is indicated that silk II (mainly β-sheet conformation) dominates in crystalline structure of SF film [33] after coagulating at vapored

![Fig. 1. Gel-like cake, transparent film, and their cross section acquired by FE-SEM.](image-url)
methanol and cold pressing treatment, similar to the observation of Philips et al. in the regenerated SF fiber spun by SF IL solution in the coagulation bath of methanol [31]. On the other hand, it was well defined that typical cellulose I crystalline structure displays diffraction peaks at 2θ of 15.1 (110), 16.8 (110), 21.0 (012), 22.8 (200), and 34.6° (004), while cellulose II emerges at 2θ of 12.2 (110), 20.0 (110), and 22.2° (200) [45]. However, XRD pattern of regenerated cellulose in this work is inconsistent with that of neither cellulose I nor cellulose II. It was reported that treatment with IL could induce the transformation of crystal domain of cellulose from cellulose I to cellulose II, and modified or intermediated crystalline structure of cellulose also could be found at certain of processing conditions or several kinds of original materials [45–48]. Therefore, it is more likely that the diffraction pattern of regenerated cellulose (C100) shown in Fig. 3 is close to cellulose II even though diffraction of (110) and (200) lattices have merged into one peak and (110) become a shoulder at left side of the peak. The crystalline transformation of cellulose component possibly affects miscibility between cellulose and silk fibroin. It also can be found that the peaks at 2θ = 19° (silk I) and 2θ = 28° (silk II) of blend films gradually disappears during the increasing of cellulose, suggesting that ordering of SF in the blend film was reduced along with severity of disturbance of cellulose molecular chains. Meanwhile, the diffraction from (110) lattice of cellulose in blend films becomes weaker due to the existence of SF molecular chains.

### 3.3. Thermo properties of the blend film

To investigate the thermal stability, TG and corresponding derivative DTG of the blend films were performed. From curves presented in Fig. 4, it can be found that temperature at maximum rate of thermal decomposition (T_{max}) and onset temperature of decomposition (T_{onset}) of the regenerated cellulose is higher than that of SF. Consistently, thermo stability of blend film varies depending on the composition of two components, and the residual weight of blend film is increasing along with the proportion of SF.

DSC curves of the blend films were obtained from room temperature to 400 °C for investigating the possibility of interactions between the components. As shown in Fig. 5 and presented in Table 1, both regenerated SF and cellulose films display a weak and progressive endothermic shift from room temperature to nearly 220 °C, which is caused by desorption of water and motivation of molecular chain in amorphous region [49,50]. And then, an intense endothermic peak at temperature (T_{endo}) of 274 °C comes out in SF film, representing the thermal decomposition of SF [51,52]. However, DSC curve of cellulose presents a change of from endothermic to exothermic after heating above 250 °C, and a typical exothermic peak (T_{exo}) appears at 320 °C later. It was reported that the exothermic peak around this temperature is associated with the onset of thermal degradation of cellulose, which consists of a sequence of events starting with rearrangement of chains in the...
amorphous regions, followed by the dehydration, decarboxylation and decarbonation, accompanied by increase of crystallinity and intermolecular cross-linking [53,54]. It can be seen in Fig. 5, both of endothermic and exothermic peaks which were normalized by the weight of scanned sample clearly appear in the blend films. It is found that the change of $T_{\text{endo}}$ and $T_{\text{ex}}$ peak intensity is not proportional to the increment of cellulose content, suggesting the cellulose and SF in the blend film is not just physical mixed with each other, and there are certain degree of interactions between their molecular chains which is able to affect the efficiency of releasing or absorbing heat of SF and cellulose. Meanwhile, the $T_{\text{endo}}$ increases with the increasing of cellulose content and the $T_{\text{ex}}$ displays a reverse way (Table 1). These results demonstrate that decomposition of SF is hampered by the adding of cellulose, and carbonization of cellulose is also prevented by the existence of SF. One of possible reasons for the phenomenon above is due to a fact that char barrier formed by decomposition of one component would affect the following endothermic or exothermic behavior of another component in the blend system. The effectiveness of char barrier to prevent heat flow in the film is based on a precondition, namely cellulose and SF well disperse with each other. If the premise is sound, the compatibility between SF and cellulose should be induced, mainly due to their intermolecular interactions.

It was widely accepted that dynamical loss tangent ($\tan \delta$), the ratio of loss modulus to storage modulus in the measurement of DMA, is associated with the behavior of relaxation or damping of materials. $\tan \delta$ versus temperature curve can also be used to illustrate the molecular response of a polymer chain with others in blends [55]. Therefore, the $\tan \delta$ curves of blend films (Fig. 6a) are depicted for detecting the changes of internal molecular mobility of SF and cellulose after blend with each other, while the storage modulus curves are illustrated at Fig. 6b for providing more information of thermal relaxation.

The $\tan \delta$ of SF in this work shows a slight increasing from room temperature to 150 °C, and then the main relaxation peak $\alpha_1$ appears at 196 °C, which is higher than so called glass transitional temperature of amorphous regenerated SF film ($T_g$-SF, around 177 °C) reported [56,57]. Conformation transition of SF from random coil or helix to $\beta$-sheet induced by ethanol or methanol treatment was proved to be effective for reducing relative content of the amorphous domains, and its behavior of thermal relaxation was modified accordingly [42,56,58]. In addition, Yuan et al. demonstrated that both treatment of water annealing and axial stretch increased the temperature of main relaxation peak $\alpha_1$ of SF film [57]. As illustrated at experimental part, coagulating at vapor methanol atmosphere and cold pressing were executed for preparing the regenerated SF film, therefore, it is suggested that $T_g$-SF in our work is increased by a reorganization of the disordered domains to more stable and ordered structures of SF that was caused by cold pressing and methanol treatment.

It is well known that regenerated cellulose have five kinds of micro-Brownian movement of molecular chains in amorphous, named $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_h$ and $\alpha_{H2O}$ from higher temperature to lower temperature, respectively. The $\alpha_1$ relaxation corresponds to the molecular motion of cellulose chains, in which intra- and intermolecular hydrogen bonding are strongly and densely formed. The $\alpha_2$ relaxation is due to the micro-Brownian movement of cellulose chains in the amorphous region, in which intra- and intermolecular hydrogen bonding are completely ($\alpha_h$ and $\alpha_{2.2}$) or partially ($\alpha_{2.1}$) destroyed. The $\alpha_{H2O}$ Relaxation corresponds to the cooperative motion of cellulose chains and water molecules in the amorphous region [59,60]. However, it was also claimed that $\alpha_1$ relaxation is associated with decomposition of cellulose, which results in motion of molecular fragments [61–63]. In our case, four relaxation peaks, including $\alpha_1$, $\alpha_2$, $\alpha_h$ and $\alpha_{H2O}$, emerged at the $\tan \delta$ curve of C100 from room temperature to 400 °C (Fig. 6). When DMA test was accomplished at temperature higher than 350 °C, char at the exterior face of film was found, indicating parts of thermal decomposition of cellulose took place here. Thus, $\alpha_2$ relaxation of cellulose is considered to be the main relaxation in this work for providing more reliable information about the mobility of molecular chains of cellulose.

The blend films contain most relaxation peaks of cellulose and SF (Fig. 6a), and the detail information of relaxation peaks is listed in Table 1. It can be seen that $T_g$-SF is elevated sharply by adding of cellulose, and then keeping a slight increment from C25S75 to C75S25. This means that the associations between SF and cellulose molecular chains can stabilize amorphous area of SF and its mobility is reduced accordingly. Temperature of $\alpha_2$ relaxation of cellulose ($T_{\alpha_2}$) is significantly reduced after mixing with SF, and remains nearly as a constant from C50S50 to C25S75. The phenomena indicates that cellulose chains become more mobile when

<table>
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<th>Film codes</th>
<th>DSC</th>
<th>DMA</th>
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<tr>
<td></td>
<td>$T_{\text{endo}}$ (°C)</td>
<td>$T_{\text{ex}}$ (°C)</td>
</tr>
<tr>
<td>C100</td>
<td>—</td>
<td>320</td>
</tr>
<tr>
<td>C75S25</td>
<td>264, 285</td>
<td>325</td>
</tr>
<tr>
<td>C50S50</td>
<td>281</td>
<td>325</td>
</tr>
<tr>
<td>C25S75</td>
<td>275</td>
<td>331</td>
</tr>
<tr>
<td>S100</td>
<td>274</td>
<td>—</td>
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</table>

Table 1: Thermo Characterization of the blend films.
it contacts with SF molecular chains. Therefore, it is possibly inferred that the hydrogen bonds between cellulose chains are partly substitute by the hydrogen bonds between cellulose and SF chains, and miscibility between two component is confirmed consequently. In addition, it is should be noticed that decomposition of SF around $T_{g, C}$ is able to affect the relaxation behavior of cellulose while cellulose and SF homogenously disperse in the blend film. Free volume created by emission of by-products gas and H$_2$O during thermal degradation of SF is capable of improving the mobility of adjacent cellulose molecular chains, and decreasing $T_{g, C}$ of blend film accordingly.

3.4. Mechanical properties of the blend film

Tensile test was carried out to evaluate the mechanical properties of SF/cellulose blend film, both in dry and wet states. The representative stress–strain curves are presented in Fig. 7 and summaries of the mechanical properties are listed in Table 2. It can be found that dried film of cellulose is robust and tough, while SF is weak and fragile. Although the Young’s modulus show slight fluctuation, both breaking stress and strain of blend film are continuously increasing along with the proportion of cellulose, exhibiting the typical features of a miscible multi-component polymer material. Obviously, the interactions between cellulose and SF molecular chains are attribute to the gradual change of tensile properties among different component ratios. It was reported that the cellulose film coagulated from IL solution was considered to exert higher toughness than the film from other organic solution because less methanol to be atmosphere rather than directly adding into the mixture solutions is favorable to obtain more flatten “gel-like” cake and prevent crust on the interface between methanol and mixture solutions. On other hand, the alignment of both cellulose and SF molecular chains and the formation of crystalline structures also improved during this gentle coagulating process. Moreover, cold pressing promotes the organization of the chains in blend film further. In all, the gentle coagulation and then cold pressing developed in our work deliver sufficient improvement on the mechanical performance of SF/cellulose blend film.

As the mechanical properties of material in wet state are essential for its application in biomedical field, the tensile measurement of SF/cellulose blend film was carried out in a humid condition (RH = 95 ± 5%) after the film was swollen by water until its thickness reached constant. As the results listed in Table 2, the wet SF film obtained in such a way is too fragile to be tested, however, the wet cellulose film still holds strength at a certain extent and become more stretchable than the dried one. Along with the decreasing of cellulose proportion, the mechanical properties of the blend films are decreasing, indicating the reinforcement of cellulose still works at wet state of the film. Indeed, it makes the blend films are suitable to be practice in water and qualified for biomedical utilization in terms of mechanical aspect.

3.5. In vitro cell culture of blend materials

In order to evaluate the biocompatibility of obtained blend materials of SF and cellulose, cell adhesion and proliferation of

![Fig. 7. Tensile properties of obtained dried (a) and wet films (b).](image)

Table 2

<table>
<thead>
<tr>
<th>Film codes</th>
<th>Dried film</th>
<th>Wet film</th>
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<tr>
<td></td>
<td>Breaking stress (MPa)</td>
<td>Breaking strain (%)</td>
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<tr>
<td>S100</td>
<td>31.9 ± 5.1</td>
<td>2.1 ± 0.7</td>
</tr>
<tr>
<td>C25S75</td>
<td>49.8 ± 7.4</td>
<td>22.0 ± 0.3</td>
</tr>
<tr>
<td>C50S50</td>
<td>106.9 ± 8.9</td>
<td>7.7 ± 3.0</td>
</tr>
<tr>
<td>C75S25</td>
<td>120.2 ± 12.1</td>
<td>17.6 ± 2.6</td>
</tr>
<tr>
<td>C100</td>
<td>146.9 ± 18.8</td>
<td>37.8 ± 8.5</td>
</tr>
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a: The SF film in wet state was too fragile and weak to be clamped during the test.
4. Conclusion

SF/cellulose blend films were prepared through dissolving and mixing in BmimCl, one kind of ILs, and coagulating in methanol. A special procedure for the preparation of SF/cellulose blend film from IL solution was developed, i.e. slow precipitation by vapored methanol and then cold pressing on water swelling materials. Characterizations of these films by FTIR, XRD, TGA, DSC and DMA determined the existence of strong interactions between SF and cellulose molecular chains. There was no obvious phase separation in the films was observed both on macroscopic and microscopic levels, suggesting the miscibility between SF and cellulose. The mechanical properties of SF/cellulose films we prepared were significantly higher than those films reported in the literature, which use the similar methods for dissolving and blending. The results presented not only demonstrated that the cellulose component enhanced the mechanical performance of these blend films in both dry and wet states, but also showed that the SF component promoted the adhesion and proliferation of L929 cell on the blend materials. Therefore, it implies that SF/cellulose blend films have the great potential in the biomedical field.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.07.002.

References


