Novel Cellulose/SPI Blend bio-fibers Prepared via Direct Dissolving Approach

Shuai Zhang , Faxue Li, Jian Yong Yu

Donghua University, Shanghai, CHINA

Correspondence to:
Faxue Li email: lifaxue@gmail.com

ABSTRACT
We have successfully prepared the biodegradable and biocompatible blend fibers from cellulose and soy protein isolate (SPI) in NaOH/thiourea/urea aqueous solvent by coagulating with 10 wt % H_2SO_4/12.5 wt %Na_2SO_4 aqueous solution. The rheological behavior and the spinnability of the prepared complex solution were analyzed by the rheometer in detail. The structure analysis of the prepared blend fibers indicated that there were strong interaction and good miscibility between cellulose and soy protein isolate. The values of tensile strength and elongation at break for the blend bio-fibers with 10 wt % of SPI reached 1.86 cN/dtex and 10.3%, respectively. It provides promising application in biomedical fields of cellulose/SPI blend fibers as the functional materials while keeping its mechanical characteristics. The morphology of the blend fibers reveals a certain level of phase segregation, that is, the blend fibers displays a smooth, fibrillar nature with homogeneous blends properties but some micro voids in cross-section. Biodegradable cellulose/SPI blend fibers with good mechanical properties and compatibility combine the beneficial characteristics of the individual components and may be useful for biomedical applications, especially for the tissue engineering scaffold.

Keywords: Cellulose/SPI; blend bio-fibers; spinnability; wet spinning; properties

INTRODUCTION
Bio-macromolecules from various renewable biomass resources, such as Polysaccharides and proteins have been considered as alternatives for petroleum-based polymers. Cellulose are the most abundant and important bio-macromolecules in nature, which have been considered as inexpensive and yearly renewable resource for various applications and the ideal substances of developing biodegradable materials. Soy protein, generally regarded as one of the most important groups of plant protein, has great potential to be used as plastics in many applications, which will reduce environmental waste and add value to agriculturalproducts. Considering that the combination of proteins and cellulose can express many biological functions and constitute the tissues of plants and animals, the composites based on biocompatible polysaccharides and proteins show a potential as biomedical materials. [1]

Polymer blending is of considerable importance as an alternative to graft copolymerization and the high cost to develop new homo-polymers. Extensive research has been undertaken in blending different polymers to obtain new products having some of the desired properties of each component. The blend films prepared from cellulose with animal protein such as casein and silk fibroin have been investigated by Zhang.[2-5] Their Studies regarding the behavior of blend materials, often in form of film. The cellulose films containing 10 wt% W_{SPI} were found have special porous properties and higher tensile strength and elongation at break than other cellulose films.[6] The preparation of fibers with a variety of functions and properties has attracted the interest of scientists for many years. In particular spinning of polymers blends is followed to get high-performance fibers and composite materials.[7, 8] However, the cellulose/SPI blend fibers based on the directly dissolving methods had never been mentioned, furthermore, the rheological properties of blend solutions are scarcely investigated to date. There is no doubt that the blend bio-fibers have great potential as a kind of biological and medical materials.

In this work, we attempted to prepare blend fibers from cellulose and SPI through the renewable and friendly solvent -NaOH/thiourea/urea aqueous solution for the first time. This novel solvent could be used to directly dissolve cellulose and SPI. Blending cellulose with SPI is expected to be a useful method to introduce amino acid groups into cellulosic

materials.[9] The properties of the cellulose/SPI blend solution, the characteristics of the prepared blend fibers, as well as the interaction between cellulose and SPI throughout various characterizations were investigated and discussed.

Literature has showed that blend films of SPI and cellulose have biocompatibility.[6] Therefore, the aim of the present work is to determine the blend ratio of two kinds of polymers and whether the polymers are compatible and if the resulting fibers have structural and physical-mechanical properties comparable to those of pure regenerated cellulose fibers. The novel blend fibers of complex system of cellulose/SPI are expected to be an important method for combining the advantages of both components and may have better properties than either component.

EXPERIMENTAL
Materials
The cellulose (cotton linter pulp) was supplied by Shanghai Cellulose Pulp Factory, China. The viscosity-average molecular weight ($\overline{M}_\eta$) of the cellulose was determined by viscometry in cadoxen to be 10.02×10^4. Cellulose samples were shredded into powder, and dried in a vacuum oven at 70 for 24 h before use. Commercial soy protein isolate (SPI) was purchased from kayon biological technology Co, Ltd (shanghai, China), and vacuum-dried at 60 °C for 4 h to contain 2% water content. All chemicals employed were of analytical grade and were purchased from commercial sources in China.

Preparation Of Blend Solution And Fibers
5 wt % cellulose solution was prepared by dissolving Cotton linter in 8 wt % NaOH/6.5 wt % thiourea/8 wt % urea aqueous solution as described in the previous work.[9] SPI was dissolved in the 6 wt % NaOH aqueous solution at room temperature to get a slurry with 10 wt % of SPI content. After both solutions were filtered, the cellulose xanthate solution was blended with the chitin xanthate solution according to different mass ratios (0 : 100, 5 : 95, 10 : 90, 20:80 and 40 :60 weight ratios of SPI to cellulose). The resulting blend solution was stirred at room temperature for 30 min and degassed at 10 by centrifuging. Homogeneous, transparent solutions were obtained and kept at 0 until they were tested.

The blend solution containing 10 wt % of W_{SPI} (10:90 weight ratio of SPI to cellulose) was adopted as the spinning dope.
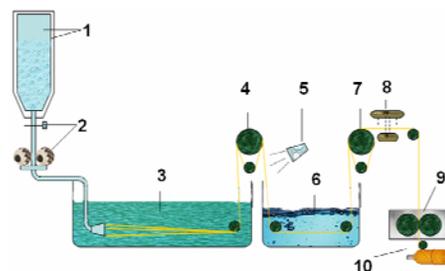

FIGURE 1. Sketch of multifilament spinning machine; 1-A pressure extruder with a stainless cylinder having cooling jacket, 2-gauging device, 3-coagulation bath (10 wt% H_2SO_4/12.5 wt% Na_2SO_4 aqueous solution, 20 ℃), 4-Nelson-type roller, 5-water spray device, 6-washing bath(hot water, 70), 7-post drawing roller, 8-post treatment device (finishing oil bath), 9-heating roller, and 10-take-up device

A laboratory scale wet-spinning apparatus was used to prepare the blend fibers, as schematically shown in *Figure* 1. The blend solution was introduced into the cylinder at room temperature. A pressure of 0.1 MPa was applied to the spinning dope to extrude it into coagulation bath using a spinneret of 12 orifices. The 10 wt% H_2SO_4/12.5 wt% Na_2SO_4 aqueous solution was selected as the coagulation bath. The temperature of the coagulation bath was preset for 20 ℃. The apparent jet stretch ratio (the ratio of the take-up velocity to the dope extrusion velocity) was 90%, the fibers were subsequently washed in water at boil and further drawn up, while the post-drawing ratio was adjusted as 120%. After spinning and washing thoroughly, the blend fibers were gradually dried by a heating roller (surface temperature 65-80 ℃) and wound on a spool.

CHARACTERIZATION
Rheological Properties Of Blend Solutions
The rheological properties of cellulose/SPI blend solutions were investigated to provide data for further fiber spinning.

The rheological properties of the solutions were measured on an RVDV-II+rheometer (Brookfield Instruments, USA). The realized region of the shear rate (γ) was in the range of 0.5–100 S^{-1}.

The slope of the flow curve in the form of $\lg \sigma = f(\lg \gamma)$ is the non-Newtonian index (n): σ is the shear stress, and γ is the shear velocity. n indicates the extent of fluid deviation from a Newtonian fluid. For shear thinning fluids n is less than one and for shear thickening fluids n is greater

than one, that is, for Newtonian fluids, $n = 1$; for dilatant fluids, $n > 1$; for pseudoplastic fluids, $n < 1$. The structure viscosity index ($\Delta\eta$), which was obtained at infinitesimal γ, was calculated on the basis of the equation (1):

$$\Delta\eta = \left(-d\lg\eta_a \big/ d\gamma^{1/2}\right) \times 10^2$$

(1)

A large amount of polymers belong to shear-thinning fluid, where $\Delta\eta$ is larger than 0. The higher $\Delta\eta$, the worse the spinnability for the polymer solution, and the more difficult for thefi ber formation and then the lower mechanical pro perty for the fiber.

Characterization Of Blend Fibers
The FTIR spectrums (4000-400 cm^{-1}) of blend fibers were recorded using a Nicolet 410 spectrometer with a resolution of 4 cm^{-1} and 64 scans per sample. Wide-angle x-ray diffraction (WAXD) data were obtained at 20 ℃ using an X-ray diffractometer (Rigaku/Dmax-B, Japan). X-ray diffraction patterns with Cu-Kα at 40 kV and 50 mA were recorded in a range of 2θ from 5 to 40°. The degree of crystallinity (χ_c) was calculated according to the peak separation method. The fiber was frozen in liquid nitrogen, snapped immediately, and vacuum-dried. SEM characterization was performed by using a JEOL JSM-5600LV microscope, at an acceleration voltage of 10 kV and 15 mm working distance. The tensile property of the as-spun fiber was measured on a universal tensile tester (XQ-1, Donghua University, China) according to ASTM method D2256-80.

RESULTS AND DISCUSSION
Dependence Of The Rheological Properties On The Blend Composition
The dependence of viscosity index on the composition of the mixture could reveal different types of interaction between macromolecular components of blends.
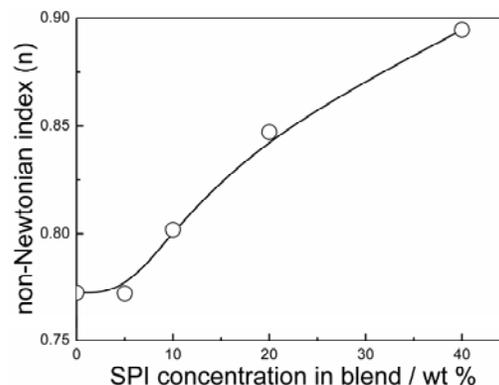

FIGURE 2. Dependence of non-Newtonian index on the SPI content of blend solutions at 20.

Dependence of non-Newtonian index (n) on the composition for the investigated solutions can be found in *Figure 2*. As the case stands, n increases with increasing SPI content. For one hand, there exist hydrogen bonds among hydroxyl groups in cellulose macromolecules and amine, amide, carboxyl, and hydroxyl groups in SPI macromolecules, the interaction in or among SPI macromolecules is stronger than that of cellulose, so the addition of SPI macromolecules would destroy the crosslink among cellulose macromolecules, and the resistance among flow fields decreases; Furthermore, the addition SPI aqueous will dilute the cellulose solution *Figure 3*. This may also lead to an increase in n, and this tendency increases with increasing SPI content in the blend solution.
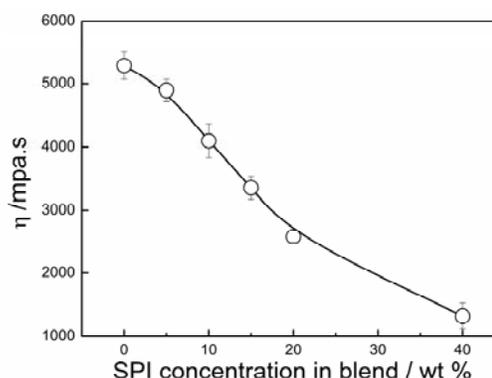

FIGURE 3. Dependence of apparent viscosity on the SPI content of blend solutions at 20.

Structure viscosity index ($\Delta\eta$) indicates the extent of solution structuralization. As can be figured out in *Figure 4*, all blend solutions appear as shear-thinning fluids, and $\Delta\eta$ of the blend solutions decreases with increasing SPI content. The addition of SPI destroys the network that is formed through cellulose

macromolecules, and this leads to a decrease in $\Delta\eta$.

As we know, the solution viscosity determines the spinnability and maximum spinneret stretching of a spinning solution. On the one hand, a solution cannot be used for spinning if the solution viscosity is too low. On the other hand, the elasticity of the viscose increases with viscosity, and this leads to an increase in the spinnability and maximum spinneret stretching of the solution. When the solution viscosity reaches a certain range, the shear stress and extent of extrusion swelling of the solution also increase, and this leads to a decrease in the maximum spinneret stretching and spinnability. When the viscosity reaches its highest value, the filtration of the solution is difficult to carry out, and this leads to difficulty with filtration and deaeration, high energy consumption, a low spinning velocity, and so forth. The solution at such a high viscosity is not fit for spinning.

Combine the consideration of viscosity and spinnability; the SPI content in the blend solution should be controlled in a given interval of 5 wt %-20 wt % during the wet-spinning process.
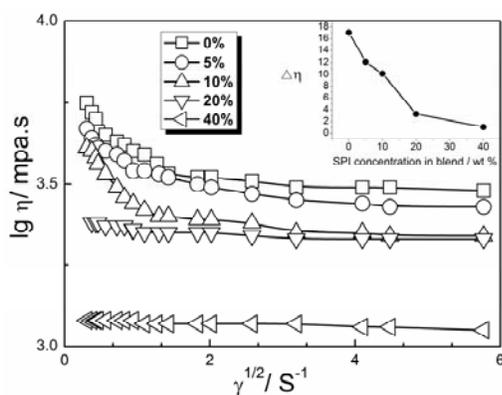

FIGURE 4. The $\lg\eta_a - \overset{\bullet}{\gamma}^{1/2}$ curve of blend solution at 2 0

Moreover, according to the reference,[4-6] the cellulose/SPI blend film with 10 wt % of SPI content exhibited the higher intensity in comparison with the films with other SPI contents. Therefore, the blend bio-fibers containing 10 wt % of SPI was prepared and their properties were investigated in the following parts.

Structure And Morphology Of The Blend Fibers

For thermodynamic reasons most polymer pairs are immiscible and, as a result, phase separation could occur. Accordingly the dispersed phases could exist in different forms of spheres, ellipsoids, fibrils and lamellas, depending on the compositions, chemical,

and physical structures of polymer blends, as well as processing conditions. Nevertheless, the degree of compatibility may vary widely.

IR spectroscopy is useful to study the hydrogen bonding and other interactions as well as the miscibility. The IR spectrum of blend fibers is shown in *Figure 5*. In the blend fibers, the peaks at 3350cm^{-1}, 2900cm^{-1}, 1644cm^{-1}, 1369cm^{-1}, 692cm^{-1} and 1158cm^{-1}, 1028cm^{-1}, 896cm^{-1} were assigned, respectively, to the characteristic absorption bands of SPI and cellulose. These peaks also reflect a certain level of miscibility for the blend fiber. The broad band at 3423 cm^{-1} in pure cellulose fiber was ascribed to the stretching absorbance of $-$OH. However, it shifted to a lower wavenumber in the blend fibers, which reflected a reasonably wide distribution of hydrogen-bond distances and geometries because of the new intermolecular interactions.[3, 10]

It also can be found in *Figure* 4 that cellulose and SPI exhibit carbonyl groups at 1,637 and 1,661 cm^{-1}, respectively. However, when they were blended, an apparent absorption bands (around 1,650 cm^{-1}) appeared, indicating the presence of intermolecular hydrogen bonds.
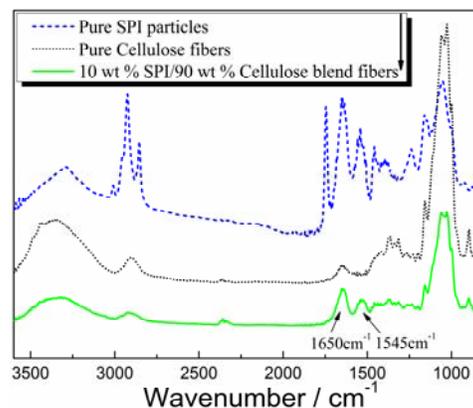

FIGURE 5. FTIR spectra of Cellulose/SPI blend fibers, SPI particles and pure cellulose fibers

Cellulose and SPI molecules. Moreover, with the addition of SPI, the relative intensity at 1,545 cm^{-1} can be found in the blend membranes (1554 cm^{-1} for pure SPI), further indicating the formation of hydrogen-bonding interactions between amide, carbonyl groups in protein and hydroxyl groups in cellulose molecules.
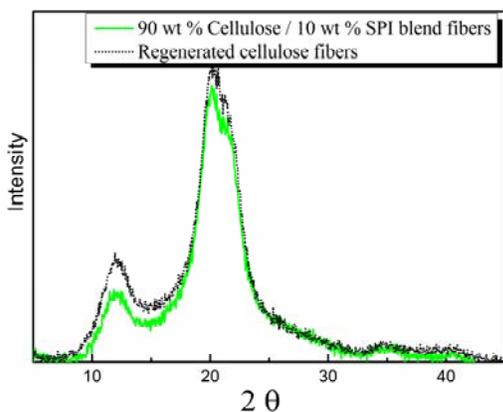
FIGURE 6. The X–ray diffraction curves of cellulose/SPI blend fiber and pure regenerated cellulose fiber

The X-ray diffraction curves of fibers are shown in *Figure* 6. Similarly, the diffraction apexes of regenerated cellulose fibers and blend fibers appears at 2θ =11.9°, 20.0°, 21.8°, all these peaks clarify the presence of cellulosic chains in the structure of cellulose II and in accordance with the reference.[1] It surely means that the incorporation of SPI did not obviously change the crystal range of type II crystalline cellulose in the blends. However, the peak at 2θ =11.9° of the blends decreased slightly, suggesting that intermolecular hydrogen bonding of cellulose was destroyed as a result of the strong interaction between SPI and cellulose molecules. It also indicates that the course of cellulose crystallization was interfered by the addition of SPI and the degree of crystallinity of cellulose/SPI blend fibers was slightly lower than the pure cellulose fibers (*Table* 1). Even if the differences between the values are included in the error limits of the calculation method and thus they must be considered not significant. Similar phenomena also can be found in 80 wt % cellulose/ 20 wt % SPI blend films prepared by using ionic liquid as cosolvent. Compared with the peak of original biopolymer, the blend films did not show any characteristic crystalline peak and only showed one broad dispersion peak around 2θ = 20°, indicating that the blend films were predominantly amorphous.[14] In 90 wt % cellulose/ 10 wt % casein blend films, it was found that casein promoted the arrangement of hydrogen bonding in the cellulose, crystallinity value for cellulose/casein blends increased when compared to pure cellulose films.[2] However, crystallinity decreased with the increase of the silk component (0-25%) in the cellulose/ silk fibroin blends fibers.[16]

It is well known that the mechanical properties of fibers, especially the blend fibers are strongly dependent on their morphologies and, therefore, the control of the morphology of polymer blend is extremely important for the tailoring of the final product properties.[11, 12] The SEM micrographs of blend fibers are shown in *Figure* 7. The Cellulose/Soy Protein Isolate blend bio-fibers showed a circular shape with fairly regular size along the fiber axis. However, the SPI particle can be found along the surface of the blend fibers and the micro void can be seen in the cross-section of the fibers, which can be consider as the evidences of partly phase separation. According to Flory theory,[13] a phase separation occurs upon blending rigid and coil polymers, beyond a critical concentration, in the absence of strong intermolecular interactions. This behavior was detected in all the cellulose/SPI blends, irrespective of composition and, therefore, the presence of a phase separation in the fibers at every prepared composition could be hypothesized. In addition, cellulose has three hydroxyl groups per anhydroglucose unit while SPI is rich in amine, amide, carboxyl, and hydroxyl groups. In the blend solution, SPI partly destroyed the interaction between solvent and cellulose chains by a much stronger interaction between amido groups of SPI, and then the exposed hydroxyl groups of cellulose prompted the formation of a new physical crosslinking network with a bigger pore size than that of pure cellulose itself. [1, 6, 14]
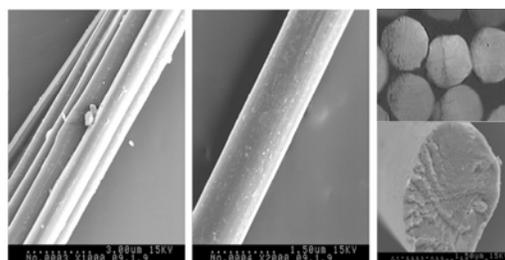

FIGURE 7. SEM images of the surface of the blend fibers (a, b), cross-section of the fibers(c)

Mechanical Properties Of The Blend Fibers
As can be found in *Table I*, 90 wt % cellulose/10 wt % SPI blend fibers presented mechanical properties values similar to those for pure regenerated cellulose fibers. Although the additional amount of SPI was interfere with the crystallization of cellulose macromolecules, long chain cellulose molecules, containing many -OH groups, will form strong intra- and intermolecular interactions with protein molecules. These interactions may include a hydrogen-bonding, dipole-dipole and charge effect, and would cause some rearrangement of hydrogen bonding in the cellulose. The mechanical properties of the blend fibers were improved by this strong

crosslinking consequently. [3,4,11]

TABLE I. Mechanical properties of cellulose/SPI blend fibers and pure regenerated cellulose fibers.

Fibers	Tensile strength cN/dtex	Elongation at break %	χ_c %
Cellulose/SPI blend fibers	1.86 ± 0.33	12.3 ± 1.5	57 ± 3.1
Regenerated cellulose fibers	1.81 ± 0.27	12 ± 1.9	61 ± 2.4

In the SPI composite film reinforced with ramie and flax fiber, strong interfacial hydrogen-bonding interaction was also found.[16-18] However, it can be expected that mechanical properties of the blend fibers would be affected by further addition of SPI. This phenomenon is due to the serious interference of the random coil polymer (SPI) with the mutual orientation of the molecules of the rod-like polymer (cellulose). A qualitative agreement between theory and experimental results is reported in literature for system based on a rigid polymer and a flexible one. [19-20]

CONCLUSIONS

Novel blend fibers of cellulose/SPI were prepared in NaOH/thiourea/urea aqueous solvent by coagulating with 10 wt % H_2SO_4/12.5 wt % Na_2SO_4 aqueous solution. The n and $\Delta\eta$ of the blend solution were investigated to determine the spinnability of a spinning fluid. It found that the optimum value of SPI content in the blend solution should be in a given interval of 5 wt %-20 wt %.The as-prepared blend fibers with 10 wt % of SPI content exhibited smooth topography and cylindrical shape. By addition of SPI, the particle and apparent pore size can be found in surfaces and cross-sections of the blend fibers measured by SEM. The results from FTIR revealed good miscibility between cellulose and SPI in the blend fibers with 10 wt % of SPI content, as a result of the strong hydrogen bonding between hydroxyl groups of cellulose and amido groups of SPI molecules. Good mechanical properties of the blend fibers are another indicator for strong interaction between the two phases and suggesting a good compatibility of these two natural polymers in the blend fibers. To this end, Cellulose/SPI blend fibers have great potential as new regenerated biodegradable fibers with structural and physic-mechanical properties comparable to those of pure regenerated cellulose fibers. Its biomedical application can be expected, especially for the tissue engineering scaffold.

REFERENCES

[1] Zhou, Z.; Zheng, H.; Wei, M.; Huang, J.; Chen, Y.; Structure and Mechanical Properties of Cellulose Derivatives/Soy Protein Isolate Blends; *Journal of Applied Polymer Science* 2008, 107, 3267-3274.

[2] Yang, G.; Zhang, L.; Han, H. W.; Zhou, J. P.; Cellulose/casein blend membranes from sodium hydroxide/urea solution; *Journal of Applied Polymer Science* 2001, 81, 3260-3267.

[3] Yang, G.; Zhang, L.; Liu, Y.; Structure and microporous formation of cellulose/silk fibroin blend membranes. I. Effect of coagulants; *Journal of Membrane Science* 2000, 177,153-161.

[4] Yang, G.; Zhang, L.; Cao, X.; Liu, Y.; Structure and microporous formation of cellulose/silk fibroin blend membranes. Part II. Effect of post-treatment by alkali; *Journal of Membrane Science* 2002, 210, 379-387.

[5] Zhou, J.; Zhang, L.; Solubility of cellulose in sodium hydroxide/urea aqueous solution; *Polymer Journal* 2000, 32,866-870.

[6] Luo, L.; Wang, X.; Zhang, Y.; Physical properties and biocompatibility of cellulose/soy protein isolate membranes coagulated from acetic aqueous solution; *Journal of Biomaterials Science-polymer edition* 2008, 19, 479-496.

[7] Arcidiacono, S.; Mello, C. M.; Butler, M.; Welsh, E. A.; Soares, J. W.; Allen, A.; Ziegler, D.; Laue, T.; Chase, S.; Aqueous processing and fiber spinning of recombinant spider silks; *Macromolecules* 2002, 35, 1262-1266.

[8] Gilbert, R. D.; Hu, X. C.; Fornes, R. E.; Preparation of high-strength/high-modulus regenerated cellulose fibers from lyotropic mesophases; *Journal of Applied Polymer Science* 1995, 58, 1365-1370.

[9] Zhang, S.; Li, F. X.; Yu, J. Y.; Hsieh Y. L.; Dissolution behaviour and solubility of cellulose in NaOH complex solution; *Carbohydrate Polymer,* 2010, 81, 668-674.

[10] Kondo, T.; Sawatari, C.; Manley, R. St. J.; Gray, D. G.; Characterization of hydrogen bonding in cellulose- synthetic polymer blend systems with regioselectively substituted methylcellulose; *Macromolecules* 1994, 27, 210-215.

[11] Martuscelli, E.; Palumbo, R.; Kryszewski, M.; *Polymer Blends: Processing, Morphology and Properties*, Plenum Press: New York, 1979.

[12] Thomas, S.; Groeninckx, G.; Nylon 6/ethylene propylene rubber (EPM) blends: Phase morphology development during processing and comparison with literature data; *Journal of Applied Polymer Science* 1999, 71, 1405-1429.

[13] Flory, J.; Molecular Theory of Liquid Crystal, Springer: Berlin, 1-36, 1984.

[14] Wu, R.; Wang, X.; Wang, Y.; Bian X.; Li, F.; Cellulose/Soy Protein Isolate Blend Films Prepared via Room-Temperature Ionic Liquid; *Industrial & Engineering Chemistry Research* 2009, 48, 7132-7136.

[15] Marsano, E.; Corsini, P.; Canetti, M.; Freddi, G.; Regenerated cellulose-silk fibroin blends fibers; *International Journal of Biological Macromolecules* 2008, 43, 106-114.

[16] Lodha, P.; Netravali, A.; Characterization of phytagel modified soy protein isolate resin and unidirectional flax yarn reinforced "green" composites; *Polymer Composites* 2005, 26, 647-659.

[17] Lodha, P.; Netravali, A.; Characterization of interfacial and mechanical properties of "green" composites with soy protein isolate and ramie fiber; *Journal of Materials Science* 2002, 37, 3657-3665.

[18] Lodha, P.; Netravali, A.; Characterization of stearic acid modified soy protein isolate resin and ramie fiber reinforced 'green' composites; *Composites Science and Technology* 2005, 65, 1211-1225.

[19] Marsano, E.; Bianchi, E.; Ciferri, A.; Ramis, G.; Tealdi, A.; Mesophase formation and polymer compatibility. 4. Cellulose/cellulose acetate/diluent systems; *Macromolecules* 1986, 19, 626-630.

[20] Bianchi, E.; Ciferri, A.; Conio, G.; Marsano, E.; Tealdi, A.; Mesophase formation and polymer compatibility. The poly (p-benzamide)-polyacrylonitrile -diluent system; *Macromolecules* 1984, 17, 1526-1531.

AUTHORS' ADDRESSES

Shuai Zhang
Faxue Li
Jian Yong Yu
College of Textiles
Donghua University
2999 North Renmin Road, Songjiang
Shanghai, Shanghai   201620
CHINA