

STRUCTURE AND PROPERTIES OF CELLULOSE/*SOLIDAGO CANADENSIS L.* BLEND

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By dissolution of cellulose (9% weight) and *Solidago canadensis L.* (SCL) (1% weight) in ionic liquid, IL, we prepared a cellulose/SCL blend. Taking pure cellulose as reference, polar microscopy analysis suggested that the SCL was well dissolved in the IL solution. The cellulose/SCL/IL solution has been found to present increased viscosity at a lower shear rate, which could be rapidly reduced to a similar value as that of the pure cellulose solution with a shear rate increase. DSC analysis indicated that this cellulose/SCL blend reduced the glass transformation temperature, T_g , by about 15 °C, as compared to that of the pure cellulose. TG analysis indicated that the cellulose/SCL blend presented a greatly enhanced thermal stability – by about 75 °C higher than that of the pure cellulose. The presence of SCL in cellulose has been also found to increase the stress with about 7%, while reducing the strain by about 35%, as compared with those of the pure cellulose.

Keywords: cellulose, *Solidago canadensis L.*, blend, structure, properties

INTRODUCTION

Solidago canadensis L. (SCL) is a natural plant with therapeutic applications due to its high content of (–)-cyclocolorenone,^{1,2} most of its extracts being applied in diseases of the urinary tract, nephrolithiasia, prostate, for antibacterial and antifungal activity.³⁻⁵ SCL grows rapidly and its composition is similar to that of most plants,⁶ comprising cellulose, hemicelluloses and lignin.

Cellulose is the most abundant macromolecule and it has been extensively exploited throughout human history. Since it can be easily dissolved in a lot of solvents or solutions, this property allows creating cellulose products with the desired shape and size for applications in various areas. Cellulose is easily incorporated with some functional materials to form novel celluloses.⁷⁻⁹ For example, recently we have prepared cellulose-based drug fiber by loading persimmon herb leaves,⁸ and a phase change controllable drug film,⁹ respectively.

The aim of this work has been to prepare a cellulose/SCL blend and study its structure and

properties to compare them with those of pure cellulose. Considering that an ionic liquid, IL, is able to dissolve lignocellulosics, including wood,^{5,10-14} we used an IL experimentally to dissolve both cellulose and SCL and then formed a cellulose/SCL blend film by casting. The structure and properties of the cellulose/SCL blend were studied and compared with those of pure cellulose.

EXPERIMENTAL

Materials

SCL was obtained from a local field in Songjiang. Only the middle trunk was used. After peeling the bark, the SCL trunk was milled to powder. Before dissolution, the SCL powder was dried in an oven for some days at 80 °C for removing moisture.

Similarly to our previous studies,^{8,9} commercial cellulose was obtained from Shanghai Chemical Fiber Co. with a known degree of polymerization of about 500 and α -cellulose component above 90%.

A [Bmim]Cl type IL provided by Hebei Normal University, China, was used. Before use, the IL solution

was prepared by heating the solid IL in an oil bath at 80 °C.

Preparation of cellulose/SCL blend

The solid IL (52.907 g) was initially heated in an oil bath at 95 °C for several hours, and then the cellulose (4.873 g) and SCL (0.588 g) were added to start the dissolution under stirring. After dissolution of about 10 h, the fluid presented amber color. A cellulose/SCL blend film was cast on a clean glass surface and washed by distilled water twice, then oven dried at 80 °C for several days. The as-obtained cellulose/SCL blend film had a transparent appearance.

Characterization

The dissolution was characterized using a polar microscope (XPN-203, JVC), by observing the formed film directly.

The rheological properties were studied by a Brookfield viscosimeter (Brookfield Engineering Laboratories Inc.). Double-gap (40/50) geometry was used for these cellulose solutions, and cone and plate geometry (4°/40 mm) for the remainder. The viscosimeter was equipped with Peltier elements to control the temperature. By pouring the cellulose/SCL solution into a concentric cylinder fixture at a constant temperature, 90 °C, the shear rate-based rheological properties were recorded between 1-3000 s⁻¹.

Thermogravimetric analysis was performed using a 209F1 Netzsch Instrument. Each sample was analyzed in a platinum pan with nitrogen as purge gas at a flow rate of about 30 ml/min. In all experiments, the temperature was increased from 25 to 700 °C at a rate of 10 °C/min.

The thermal properties were also characterized by a Mettler-Toledo 822e Differential Scanning Calorimeter, DSC. In this test, the temperature was increased from 0 to 300 °C at a rate of 10 °C/min.

The FTIR spectra were recorded from 400 to 4000 cm⁻¹, using a Nicolet NEXUS-670 FTIR spectrometer. For each spectrum, a 50-scan interferogram was collected corresponding to a single beam mode with a 4 cm⁻¹ resolution.

The morphology was imaged by a scanning electron microscope, SEM (JSM-5600LV), with an accelerating voltage of about 10 kV and magnification of 500-160,000×.

The mechanical properties were determined using several instruments, e.g., XQ-1, YG086, and YG001A (Donghua University, China). During the measurements, the gauge length and crosshead speed were chosen as 500 mm and 7.5 mm/min, respectively. All reported values were averaged based on 10-30 independent measurements.

RESULTS AND DISCUSSION

Cellulose/SCL solution

After casting the polymer solution on the glass surface, polar microscopy images of cellulose/SCL/IL were taken and compared with those of the pure cellulose/IL, as shown in Figure 1. The comparison revealed that the cellulose was distributed uniformly, suggesting that it dissolved well in IL (Figure 1 left), which is in agreement with the results reported by Swatloski *et al.*¹⁰ Also, it was noted that the SCL was dissolved well, since the polar microscope image of the cellulose/SCL solution presents only a few white dots corresponding to undissolved components. This could be expected since the SCL also contains lignin, which is hardly dissolved in IL, as has been also found for the dissolution of wood in IL.¹¹⁻¹⁵ This is not surprising considering the structural matrix of the SCL cell walls, which is made up primarily of tightly associated cellulose and lignin chains, and therefore it is significantly more complex than that of the cellulose sample used in this study with high α -cellulose content, i.e. above 90%. In fact, SCL has been known to contain about 19% of the lignin component.¹⁶

The rheological behavior of the cellulose/SCL/IL solution is presented in Figure 2. It was remarked that the cellulose/SCL solution showed a shear thinning behavior similar to that of the pure cellulose solution (Figure 2), suggesting that the addition of a low amount of SCL to the cellulose solution has little influence on the processing behavior. According to Figure 2, the cellulose incorporated with SCL would have increased viscosity at low shear rate conditions, and this high viscosity would be rapidly reduced to a value similar to that of the pure cellulose solution with an increase in shear rate. This rheological behavior suggests that the incorporation of the biofunctional SCL into cellulose is feasible. In other words, this implies that one can add SCL to cellulose to obtain cellulose with biobehavior.

The non-Newtonian index, n , was found to be 0.16 for the cellulose/SCL solution and 0.61 for the pure cellulose solution.

Structure of cellulose/SCL blend

The FTIR spectra of the cellulose/SCL blend and of the pure cellulose are presented in Figure 3.

A comparison of the control cellulose revealed that the cellulose/SCL blend presented some visible peaks located at about 753, 1168, 1464, 1573, 1639 and 1068 cm^{-1} corresponding to cellulose, and some new peaks located at 638, 753 and 1067 cm^{-1} contributed by SCL in relation to its components: lupeol, lupeyl acetate, ursolic acid, cycloartenol, cycloartenyl palmitate, α -amyrin acetate and

stigmasterol.⁵ Obviously, this demonstrates that the SCL molecules were incorporated well in the cellulose. According to Figure 3, the incorporation of SCL in cellulose has enhanced the hydrogen interactions, as evidenced by the band between 3300-3400 cm^{-1} . The assignments of the IR peaks of the cellulose/SCL blend are summarized in Table 1.

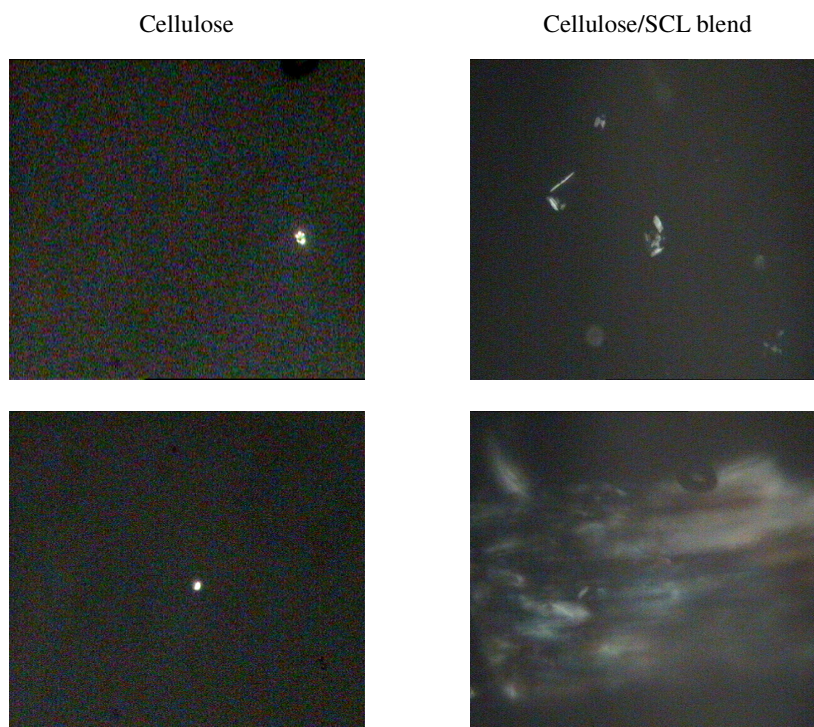


Figure 1: Polar microscope photographs of control cellulose (left) and cellulose/SCL blend (right)

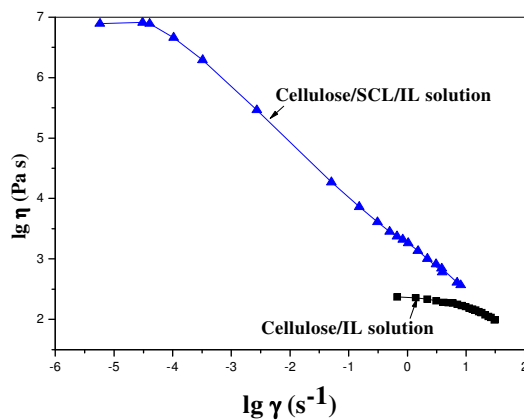


Figure 2: Plot of viscosity vs. shear rate for cellulose/SCL/IL blend solution and control cellulose/IL solution at 90 °C

Table 1
IR peak assignments for cellulose/SCL blend and reference cellulose

cm ⁻¹	Assignments	
	Cellulose	Cellulose/SCL blend
753		C-H bending
867	CH ₂ , C-OH stretching	
1026		C-H bending
1068		C-C, C-O stretching
1158	CH ₂ , C-OH bending	
1168		C-O-C stretching
1374		C-H bending
1464		C-H bending
1573		C=O stretching
1639		Ring stretching
2902	C-H stretching	
2964		C-H stretching
3388	O-H stretching	

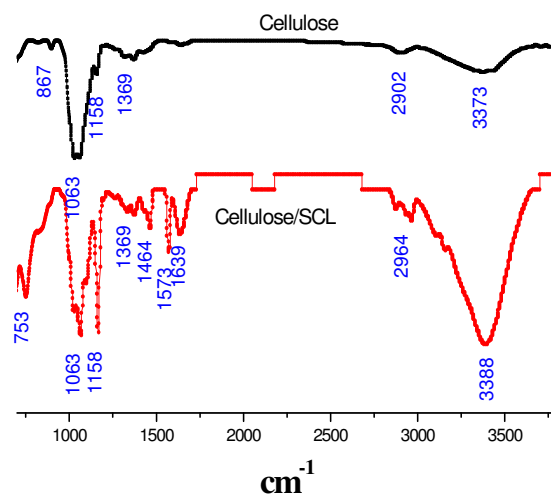


Figure 3: FTIR spectra of cellulose/SCL blend and reference cellulose

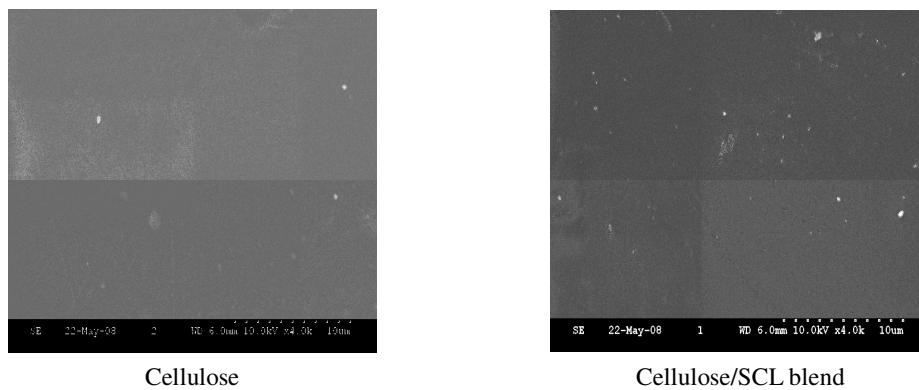


Figure 4: SEM images of reference cellulose (left) and cellulose/SCL blend (right)

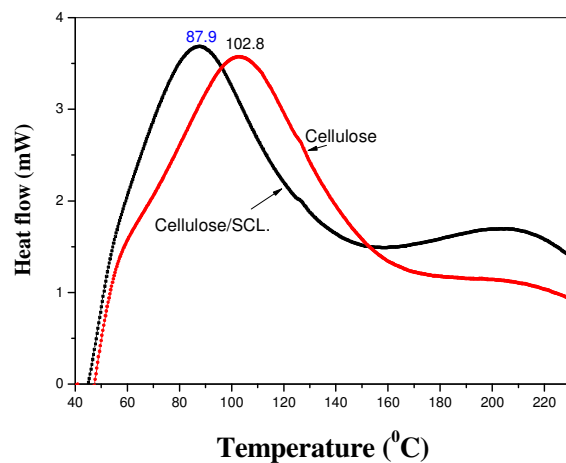


Figure 5: TG curves of reference cellulose and cellulose/SCL blend

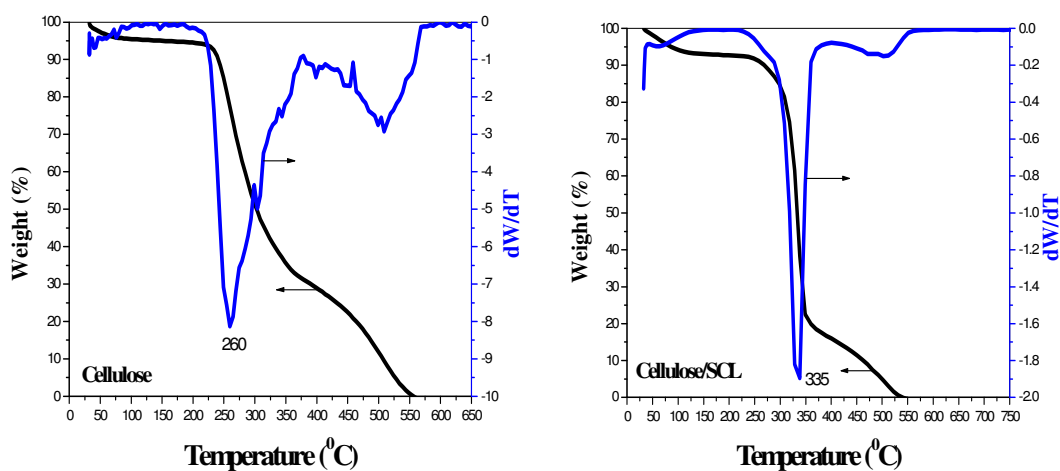


Figure 6: DSC curves of reference cellulose and cellulose/SCL blend

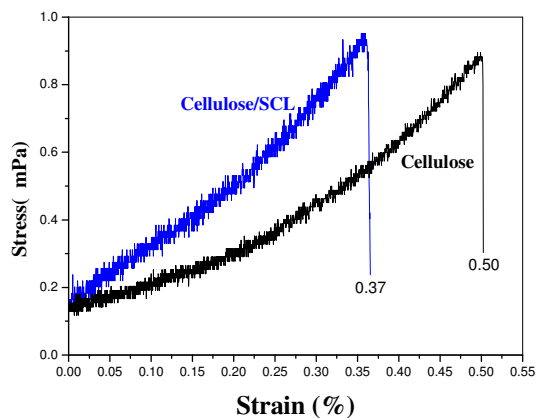


Figure 7: Mechanical properties of cellulose/SCL blend and reference cellulose

The morphology of both the cellulose/SCL blend film and of the pure cellulose film is illustrated by

the SEM images presented in Figure 4. It is worth noting that the pure cellulose film presents a few

white dots corresponding to undissolved substances, while the cellulose/SCL blend film presents more white dots, probably due to the lignin component or other undissolved components.¹¹⁻¹⁵

Properties of cellulose/SCL blend

The thermal stability of the cellulose/SCL blend was studied by TG and the corresponding curves are presented in Figure 5, where the pure cellulose is given as reference. In terms of these DTG results, the cellulose/SCL blend has been found to have enhanced thermal stability – by about 75 °C higher than that of the pure cellulose.¹² According to the DSC curves (Figure 6), the cellulose/SCL blend has a lower glass transformation temperature, T_g , than that of the pure cellulose, which is in good agreement with literature reports on T_g of lignocellulosics.¹²

The mechanical properties of the cellulose/SCL blend and those of the pure cellulose film are illustrated in Figure 7. Their comparison leads to the conclusion that the cellulose/SCL blend has a small increase in stress and a small reduction in strain. This suggests that the insoluble SCL components affect the mechanical properties of cellulose.

CONCLUSION

Experiments have proven that the SCL can be mostly dissolved in an IL solution together with the cellulose to form a blend. The blend formed by incorporation of 10% SCL with 90% cellulose showed visible enhancement in thermal stability, e.g. by about 75 °C, and a reduction in the glass transformation temperature, T_g , i.e. by about 15 °C, as compared with the respective values for the pure cellulose. SCL incorporation into cellulose also reduced the strain of cellulose, but not the stress. The obtained cellulose/SCL blend had an increased stress value by about 7%, and reduced strain by about 35%, as compared to those of the pure cellulose.

REFERENCES

- ¹ K. Hiller, G. Bader, *Zeitschr. Phytother.*, **17**, 123 (1996).
- ² L. Skrzypczak, M. Wesolowska, B. Thiem, J. Budzianowski, in "Biotechnology in Agriculture and Forestry", edited by Y. P. S. Bajaj, Berlin and Heidelberg, Springer-Verlag, vol. 43, 1999, pp. 384-403.
- ³ D. Kalembe, B. Thiem, *Flavour Fragr. J.*, **19**, 40 (2004).

- ⁴ J. M. Jacyno, N. Montemurro, A. D. Bates, H. G. Cutler, *J. Agric. Food Chem.*, **39**, 1168 (1991).
- ⁵ V. S. P. Chaturvedula, B. N. Zhou, Z. Gao, S. J. Thomas, S. M. Hecht, *Bioorg. Med. Chem.*, **12**, 6271 (2004).
- ⁶ J. F. Hu, T. L. Zuo, H. Zhang, Q. Shen, *J. Inner Mongolia Polytechnic University*, (in Chinese), **21**, 272 (2002).
- ⁷ Y. Nishio, *Adv. Polym. Sci.*, **205**, 97 (2006).
- ⁸ Z. X. Wang, Q. Shen, Q. F. Gu, *Carbohydr. Polym.*, **57**, 415 (2004).
- ⁹ Q. Shen, D. S. Liu, *Carbohydr. Polym.*, **69**, 293 (2007).
- ¹⁰ R. P. Swatloski, S. K. Spear, J. D. Holbrey, *J. Am. Chem. Soc.*, **124**, 4974 (2002).
- ¹¹ M. B. Turner, S. K. Spear, J. D. Holbrey, R. D. Rogers, *Biomacromolecules*, **5**, 1379 (2004).
- ¹² D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna *et al.*, *Green Chem.*, **9**, 63 (2007).
- ¹³ I. Kilpelainen, H. Xie, A. King, M. Granstrom, S. Heikkinen *et al.*, *J. Agric. Food Chem.*, **55**, 9142 (2007).
- ¹⁴ O. A. ElSeoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules*, **9**, 2629 (2007).
- ¹⁵ H. Xie, A. King, L. Kilpelainen, M. Granstrom, A. D. S. Argyropoulos, *Biomacromolecules*, **12**, 3740 (2007).
- ¹⁶ Q. L. Li, *Research on Applied Techniques*, (in Chinese), **5**, 15 (2002).