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Amine Bendaoud, Jean-Eudes Maigret, Eric Leroy, Bernard Cathala, Denis Lourdin. Cellulose-xyloglucan composite film processing using ionic liquids as co-solvents. 32. International Conference of the Polymer Processing Society (PPS 32), Polymer Processing Society. Akron, Ohio, USA., Jul 2016, Lyon, France. 10.1063/1.5016735 . hal-02733662

HAL Id: hal-02733662

<https://hal.inrae.fr/hal-02733662>

Submitted on 2 Jun 2020

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Citation: [AIP Conference Proceedings](#) **1914**, 070008 (2017); doi: 10.1063/1.5016735

View online: <https://doi.org/10.1063/1.5016735>

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Cellulose-Xyloglucan Composite Film Processing Using Ionic Liquids as Co-Solvents

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Abstract. The aim of the present work is to develop a high-performance composite using biomimetic approaches that will exploit the interactions between two biopolymers, cellulose and xyloglucan, and these interactions play an important role but still not fully understood in the biomechanical properties of primary plant cell walls [1]. In this study, the co-solubility of cellulose and xyloglucan in an ionic liquid (1-ethyl-3-methylimidazolium acetate (EMIMAC)) is used to prepare regenerated films by subsequent precipitation with a non-solvent. Films of pure cellulose, pure xyloglucan and various cellulose/xyloglucan blends were obtained and characterized by Fourier transform-infrared spectroscopy (FTIR), X-ray diffraction (XRD) and hygro-mechanical analysis. The biopolymer blends show an increase of the storage modulus comparatively to the regenerated pure biopolymers.

Keywords: cellulose, xyloglucan, ionic liquids, polymers blends, biomimetic approaches, hydro-mechanical properties.

PACS: 83.85, 87.15, 87.14, 83.85, 82.35, 83.80, 87.15

Introduction

The use of natural polymers to design new environment-friendly materials is a promising solution to overcome the environmental concerns and decrease of petroleum resources [2]. Cellulose is one of the most abundant polymers, and it has a number of interesting characteristics, such as renewability, low price and biodegradability [3]. However, cellulose cannot be melt processed [4]. This drawback is due to the native crystalline structure involving a compact network of intra- and intermolecular hydrogen bonds.

Consequently, solvents based process are used to transform cellulose. Since the fact that cellulose is difficult to dissolve, a number of adequate solvents have been developed [5]. Ionic liquids are currently a promising solvents, for the processing of cellulose by dissolution and regeneration [6]. However, the regenerated cellulose materials present some drawbacks, like low thermal stability, high sensitivity to relative humidity and poor mechanical properties [7]. To address these issues, a number of authors have used the solubilization step to blend cellulose with other polymers [8].

In the present study, we combine cellulose with xyloglucan. This hemicelluloses biopolymer is acknowledged to be an important constituent of primary plant cell wall. Our objective is to obtain a bioinspired material by taking advantage of the interactions occurring between cellulose and xyloglucan [9, 10].

The developed blend films are characterized by FTIR, XRD and hygro-mechanical analysis in order to study the effect of xyloglucan addition on the properties of the cellulosic materials and increase our knowledge on interactions between plant biopolymers.

Materials and Methods

Microcrystalline cellulose (Avicel PH-101, 50 μm) was purchased from Sigma Aldrich. Non fucosylated xyloglucan (Tamarind, 225 Kd (MAALS), purity 95%) was purchased from Megazyme. An ionic liquid, EMIMAC, (purity 98%), was purchased from Solvionic.

Dissolution and Regeneration Process

The cellulose, xyloglucan and EMIMAc were first dried (80°C-24h) in a vacuum oven. These components were used to prepare biopolymer(s) solutions (~1%wt in EMIMAc) of pure cellulose and blends with the following weight cellulose/xyloglucan ratio: 0.5, 0.75, 1, 1.25, 1.5, 2 and 3. The biopolymer powders were dispersed in EMIMAc under stirring at 100 °C until homogenous solutions were obtained. After this solubilisation step, the different solutions were casted in glass petri dishes. These dishes were placed in a water saturated box for 24h in order to obtain films. These films were then immersed in a distilled water bath during 3 days in order to remove the ionic liquid. Finally, the films were dried at 40°C during 12h. Homogenous and transparent films were successfully obtained for all initial solutions using this method.

FTIR Spectroscopy

Fourier transform-infrared spectroscopy studies of the initial powders and the regenerated films were carried out by using ATR Perkin FTIR spectrophotometer. The spectra's were recorded from 4000 cm^{-1} to 400 cm^{-1} .

X-Ray Diffraction Analysis

The X-ray diffraction measurements were provided by using an XRD analyzer (Bruker D8). Wide-angle X-ray intensities were recorded from 3° to 40° in 2 θ with a scanning rate of 2°/min. An approximation of the degree of crystallinity of the different samples was calculated as the ratio of crystalline area to the total area under the diffraction peaks.

Dynamical Mechanical Analysis (DMA) with Controlled Humidity (RH)

The dynamical mechanical analysis is conducted using a Metravib DMA 50N connected to a humidity controller. The thicknesses of films (average of three measurements) were measured using a micrometer. The sample films (20 m x 5 mm x 0.02 mm) were loaded in the testing chamber at 1 Hz frequency, 0.5 N preload force, 0.01% strain and the storage modulus is recorded with the increase of relative humidity from 10% to 70%.

Results and Discussion

The regeneration process gives homogenous, thin (~20 μm) and transparent films. No visual differences were observed between the different samples.

In order to have informations about the absence of ionic liquid and presence of xyloglucan in the blend films, infrared spectroscopy measurements are carried out.

Figure 1 shows the spectra of cellulose, xyloglucan, EMIMAc and an example of a blend films, here, Cellulose(CE)-Xyloglucan(XG)-Ratio(R)=1.

Comparatively to native cellulose, XG shows a characteristic peak at 940 cm^{-1} related to the presence of side chains [11,12]. This characteristic peak could be used in the blend films spectras in order to show the presence of xyloglucan.

For the blend films (CE-XG-R1), we can observe the presence of a peak around 940 cm^{-1} , which is linked to the presence of xyloglucan. This result confirms the effectiveness of the process and suggest that interactions between cellulose and xyloglucan occur, indeed xyloglucan remains in the films, despite the fact that xyloglucan is soluble in water, used here as a solvent to remove the ionic liquid.

X-ray diffraction analysis is used to determine the crystallinity of the different samples. The values of the crystallinity related to the different samples are given in the table 1.

Native cellulose shows a typical diffraction spectra of cellulose I. The solubilisation and the regeneration process of cellulose in ionic liquid leads to the transformation of cellulose I to cellulose II [13]. The blend films show an amorphous halo with a small intensity peak at around 20°.

Furthermore, the degree of crystallinity of cellulose films are greatly reduced comparatively to native cellulose, respectively lower than 10% and as high as 50% (table 1). For blend films, the value of crystallinity is low and close to that obtained for the regenerated cellulose film.

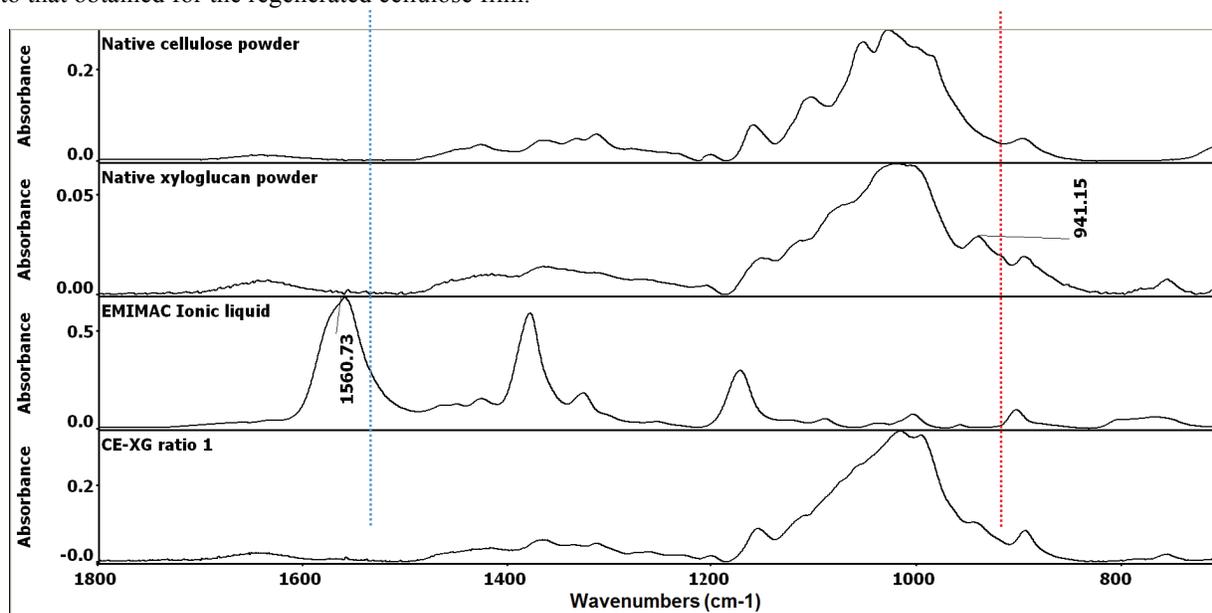


FIGURE 1. FTIR spectra of native cellulose and xyloglucan, EMIMAc and regenerated blend film

TABLE (1). The value of crystallinity of the different studied samples

| Samples | Crystallinity (%) |
|------------------|-------------------|
| Cellulose powder | 50 |
| Cellulose Film | <10 |
| CE-XG-R2 Film | <10 |
| CE-XG-R1 Film | <10 |
| CE-XG-R0.5 Film | <10 |
| CE-Xg-R0.7 Film | <10 |
| CE-XG-R1.5 Film | <10 |

In order to analyze the hygro-mechanical properties of the different films, a dynamic mechanical analysis with controlled relative humidity is used.

Figure 2 shows the evolution of the storage modulus as a function of the relative humidity for regenerated cellulose, xyloglucan and an example of a blend films (Here, CE-XG-R1.5).

For all formulations, the storage modulus decreases with the increase of relative humidity. This phenomenon is related to the plasticizing role of water, which reduces the polymer polymer interactions. Moreover, we note that the blend cellulose-xyloglucan formulation has a higher storage modulus than the modulus of pure cellulose or xyloglucan films over all the relative humidity range. For example, at 10% RH, CE-XG-R1.5 film shows a storage modulus of 4.8 GPa, while pure cellulose and xyloglucan films, gives respectively 4.3 GPa and 3.6 GPa.

This synergy between the two biopolymers could be ascribed to the interactions between cellulose and xyloglucan. Nevertheless, it is striking that these interactions take place between the two (mainly) amorphous polymers in the present materials. As an opposition, interactions between xyloglucan and cellulose microfibrils crystalline surface are known to occur in plants [9]. Consequently, the new model material produced open possibilities for a better understanding of the interactions between the two biopolymers.

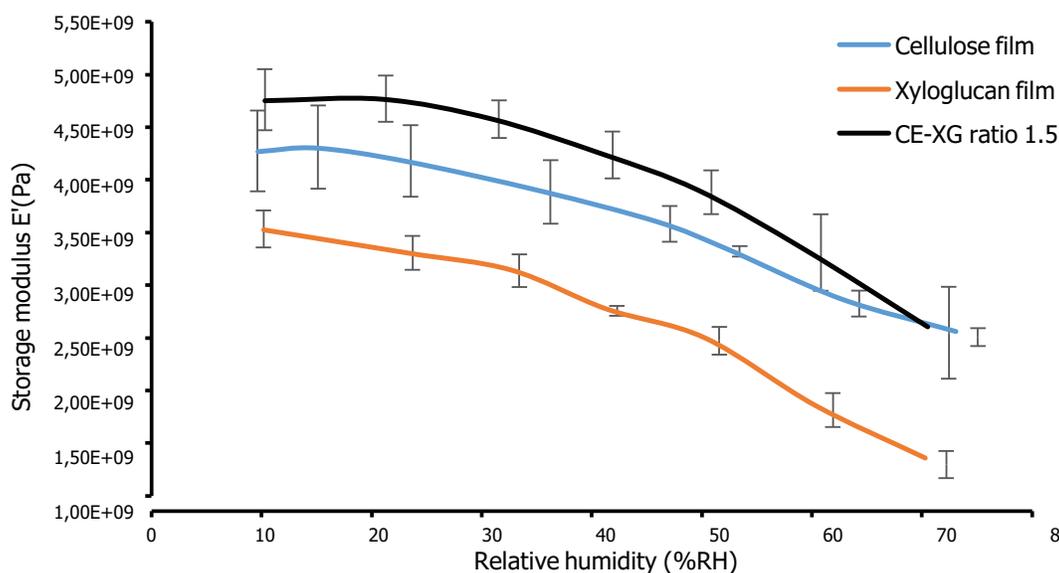


FIGURE 2. Evolution of storage modulus (E') with the increase of relative humidity (%RH) for different regenerated films.

Conclusion

In this present work, we successfully obtained thin films of quasi amorphous CE-XG blends. Anionic liquid is able to dissolve both biopolymers (EMIMAC) was used as a processing aid. The obtained CE-XG films are transparent and homogeneous. The FTIR analysis shows that the regenerated films are free of ionic liquid. Moreover, the presence of XG in the blend films can be observed, even after 3 days washing in water. This indicates strong interactions with cellulose, since XG itself is water soluble.

In addition, the blend films show better mechanical properties than cellulose pure films. These new materials thus potentially open new question about XG/CE interactions that have to be questioned in relation the role of XG in plant cell walls. They could be used in applications where there would have interest in modulating the mechanical properties by changing the relative humidity.

ACKNOWLEDGMENTS

We are grateful for the financial support from the MATIERES (Materials and Interfaces for Environment and Resources Exploitation) project funded by the “Région Pays de la Loire” council. We are grateful for the financial support from the project MATIERES. We also thank Sylvie DURAND and Bruno PONTOIRE for their technical support on FTIR and XRD analysis, respectively.

REFERENCES

- [1] Y.B. Park and D.J. Cosgrove. *Plant Cell. Physiol.* **56**, 180-194 (2015).
- [2] R.J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood. *Chem. Soc. Rev.* **40**, 3941-3994 (2011).
- [3] D. Klemm, B. Heublein, H.P Fink and A. Bohn. *Angew. Chem. Int. Ed. Engl.* **44**, 3358-3393 (2005).
- [4] B. Medronho, A. Romano, M.G. Miguel, L. Stigsson and B. Lindman. *Cellulose.* **19**, 581-587 (2012).
- [5] B. Medronho and B. Lindman. *Curr. Opin. Colloid Interface Sci.* **19**, 32-40 (2014).
- [6] H. Wang, G. Gurau and R.D Rogers. *Chem. Soc. Rev.* **41**, 1519-1537 (2012).
- [7] Y. Cao, H. Li, Y. Zhang, J. Zhang and J. He. *J. Appl. Polym. Sci.* **116**, 547-554 (2010).
- [8] N. Hameed and Q. Guo. *Cellulose.* **17**,803-813 (2010).
- [9] K. Mazeau and L. Charlier. *Cellulose.* **19**, 337-349 (2012).
- [10] F.L. Hatton, M. Ruda, M. Lansalot, F. D'Agosto, E. Malmstrom and A. Carlmark. *Biomacromol.* (2016).
- [11] M. Kacurakova, P. Capek, V. Sasinkova, N. Wellner and A. Ebringerova. *Carbohydr. Polym.* **43**, 195-203 (2000).
- [12] M. Kacurakova, A. Ebringerova, J.Hirsch and Z. Hormadkova. *J. Sci. Food. Agric.* **66**, 423-427 (1994).
- [13] M. Adsul, S.K. Soni and V. Bansal. *Biomacromol.* **13**, 2890-2895 (2012).