Preparation and Mechanical Properties of Lignocellulosic Composite Films Based on Poplar Wood Flour and Waste Filter Paper

Zuju Shu,[a,b] Jie Song,[a] Yan Yuan,[a] Jiawei Chen,[a] Sa Zhang,[a] Lili Huang,[b,*] and Shengquan Liu [c,*]

Novel lignocellulosic composite films (LCFs) based on poplar wood flour (PWF) and waste filter paper (WFP) were developed with 1-allyl-3-methylimidazolium chloride ([Amim]Cl) as green solvent. Scanning electron microscopy revealed that the dissolved part acted as the matrix that combined with the insoluble part and reinforced the LCFs. Under the same preparation conditions, there was an increased amount of the insoluble part with an increased amount of PWF. The PWF and WFP mass ratio was a key parameter that influenced the solubility of the raw materials. The differences in the grammage, thickness, and mechanical properties among the groups were related to the dissolution extent of the raw materials. Group A (100 wt% WFP) had the best mechanical properties because of the highest dissolution of cellulose. When the PWF and WFP mass ratio increased, the mechanical properties of the samples decreased and surface bonding became poor. Consequently, the TS of group F (100 wt% PWF) was the lowest. The elongation and elastic modulus showed the same trend as that of the TS.

Keywords: Poplar wood flour; Waste filter paper; Ionic liquid; [Amim]Cl; Lignocellulosic composite film; Mechanical properties

Contact information: a: School of Light Textile Engineering and Art, Anhui Agricultural University, Hefei, Anhui, China; b: School of Engineering, Anhui Agricultural University, Hefei, Anhui, China; c: School of Forestry and Landscape Architecture, Anhui Agricultural University, Hefei, Anhui, China;
** Corresponding author: shuzuju@ahau.edu.cn*

INTRODUCTION

Fast-growing poplar wood, which is widely planted in China, is an environmentally friendly resource and has been modified for applications in a variety of fields, such as furniture, construction, and decoration (Guo *et al*. 2017; Wang *et al*. 2017). During the manufacturing of wood products, large amounts of wastes, such as sawdust, shavings, and damaged boards, are generated, and these are renewable lignocellulosic resources (Kuka *et al*. 2016; Üner *et al*. 2016).

Studies on the development of poplar wood products have mainly focused on wood modifications to improve its overall performance (Qin and Zhang 2012; Lang *et al*. 2013), while studies on residues have mainly focused on conversion into value-added bio-products (bio-fuels, chemicals, pulp and paper, composites, *etc*.) (Iqbal *et al*. 2013; Si *et al*. 2013).

Wood plastic composites (WPCs), which have been used to substitute structural and non-structural wood and other materials, have attracted a great deal of research attention (Mijiyawa *et al*. 2015; Kuka *et al*. 2016; Li *et al*. 2016).

Wood plastic composite manufacturing is regarded as a green technology because recycled plastics and waste wood-based fillers can be used. However, the poor compatibility between hydrophilic wood-based fillers and hydrophobic polymer matrices restricts its applications. This poor compatibility leads to the agglomeration of wood fibers and weak interfacial adhesion between wood-based fillers and polymer matrices and results in a low performance. To solve the interfacial bonding issue, one approach is to add a coupling agent. However, the use of multi-components, which are difficult to dispose of after being discarded, leads to environmental issues (Kaseem *et al*. 2015; Borah and Kim 2016; Sommerhuber *et al*. 2017). Mono-material-based eco-design concepts have attracted remarkable interest to overcome these problems. For example, all-cellulose composite (ACC) was developed by partially dissolving a single cellulose source with a solvent by adjusting the process parameters.

An approach similar to that for ACC production can be used for wood and lignocellulosic fibers, though wood chips and flour are more difficult to dissolve than cellulose (Duchemin *et al*. 2009; Soykeabkaew *et al*. 2009; Shibata *et al*. 2013a,b). Many studies have shown that ionic liquids (ILs) are a new class of non-molecular, ionic solvents with low melting points (< 100 °C), and they have been used successfully to replace traditional solvents employed in a variety of synthetic and manufacturing processes. Furthermore, ILs can be used to dissolve wood chips or flour (Kilpeläinen *et al*. 2007; Mäki-Arvela *et al*. 2010; Shibata *et al*. 2013a,b; Tisserat *et al*. 2015).

In this study, the IL 1-allyl-3-methylimidazolium chloride ([Amim]Cl) was used to partially dissolve the raw materials. The raw materials were composed of poplar wood flour (PWF) and waste filter paper (WFP), which were used to develop new environmentally friendly lignocellulosic composite films (LCFs).

The WFP, which contains a high cellulose content, was obtained from the laboratory of Anhui Agricultural University (Hefei, China). The techniques of hot pressing and coagulation bath were applied to the PWF and WFP mixture (Shu *et al*. 2017). Pure water (PW), a cheap and environmentally friendly anti-solvent, was used to extract the [Amim]Cl from the composites. The effect of the PWF and WFP mass ratio on the mechanical properties of the LCFs was also investigated.

EXPERIMENTAL

Materials and Instruments

Hybrid poplar clones, 5 years to 6 years in age, were randomly collected from the agricultural garden at Anhui Agricultural University. Lumber that was free from flaws, such as knots, holes, cracks, fungi, and insect damage, was processed into PWF to pass through a 30-mesh screen and be retained on a 50-mesh screen. The [Amim]Cl, with a purity of 99.0%, was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China), and used without further purification. The PW was manufactured in the laboratory at Anhui Agricultural University. The WFP (98% α-cellulose) was collected from the laboratory at Anhui Agricultural University and had a density of 88 g/m^2 and thickness of 180 μm; they were originally supplied by General Electric Biotechnology Co. Ltd. (Hangzhou, China). The instruments used in this study are listed in Table 1.

Table 1. Instruments Used for the Experiments and Analysis

Name	Model	Manufacturer
Ball mill	TL-2020	Beijing Haonuosi Technology Co., Ltd. (Beijing, China)
Digital magnetic stirrer	SZCL-3A	Zhengzhou Kehua Instrument and Equipment Co., Ltd. (Zhengzhou, China)
Vacuum drying oven	DZF-6050	Nanjing Tianhuang Machinery Co., Ltd. (Nanjing, China)
Air drying oven	DHG-9070	Shanghai Sanfa Scientific Instrument Co., Ltd. (Shanghai, China)
Hot press	R-3212	Wuhan Qien Science and Technology Development Co., Ltd. (Wuhan, China)
Ion sputter coater	E1010	Hitachi Group (Tokyo, Japan)
Field emission scanning electron microscope	Hitachi S-48	Hitachi Group (Tokyo, Japan)
Electronic universal material testing machine	AG-X plus	Shimadzu Corporation (Suzhou, China)

Preparation of the LCFs

The 30-mesh to 50-mesh PWF was dried to a constant mass in an oven at a 60 °C, and so was the collected and cleaned WFP. The prepared PWF and WFP were separately stored in a desiccator until they were used.

For every group, the mass ratio of the PWF/WFP to [Amim]Cl was 1:4, while the PWF and WFP mass ratios were different (Table 2). Group A was composed of 100 wt% WFP. Groups B, C, D, and E were obtained by decreasing the WFP content and increasing the PWF content. Group F was composed of 100 wt% PWF. The untreated original WFP (CK) acted as the control.

PWF/WFP and [Amim]Cl were placed into the ball mill and sealed for cooling in liquid nitrogen for 30 min. Then it was milled for 15 min at a rotational speed of 1700 rpm. The milled mixture was put into a round-bottomed flask for heating with a temperature of 100 °C for 60 min under moderate magnetic stirring.

The heated mixture was sandwiched between stainless steel molds coated with Teflon film and pressed on the hot press for 15 min at a temperature of 150 °C and pressure of 20 MPa. The molds with the pressed mixture were immediately cooled in PW; then, the cooled film was peeled off. The PW was replaced every 3 h for 48 h to extract the [Amim]Cl from the film. Then, the film was placed between glass plates for drying in the vacuum oven at a temperature of 40 °C until the variation in the mass was within 0.001 g. Before characterization, the films were conditioned for at least 48 h at 23 °C and a 50% relative humidity.

Table 2. Design of Experiment

Group	A	B	C	D	E	F
PWF (wt%)	0	20	40	60	80	100
WFP (wt%)	100	80	60	40	20	0
[Amim]Cl (wt%)	400	400	400	400	400	400

Testing

Morphological study

Scanning electron microscopy (SEM) was used to visualize the microstructure and evaluate the surface morphology of the LCFs. The dried samples were sputter-coated with gold using the ion sputter coater for 15 s with a current of 10 mA prior to observation. Then, the surface topography of the samples was observed with the electron microscope under vacuum at an accelerating voltage of 5 kV.

Physical properties

The dimensions of the samples used for measuring the thickness and grammage were 30 mm × 5 mm. A spiral micrometer and scale were used to determine the thickness and mass, respectively. Each test was repeated on three specimens.

Mechanical properties

The mechanical properties of the LCFs were measured on the universal material testing machine at a cross-head speed of 5.0 mm/min at room temperature. The specimens were rectangular with the dimensions 30 mm × 5 mm. The length between the two grips was 15 mm. Each test was repeated on three specimens, and the mean values and standard deviations were analyzed. The stress, strain, and Young's modulus were calculated according to the testing results, and the tensile strength, elongation at break, and initial Young's modulus of the samples were obtained.

RESULTS AND DISCUSSION

Microscopic Morphology

The SEM images of the morphology of each group are shown in Fig. 1. The raw material in each group was fused into a relatively homogeneous macrostructure. The mixture of WFP and PWF partially dissolved to form a matrix and combined with the insoluble components. Figure 1 also shows that the dissolution rates were different because of the different WFP and PWF mass ratios among the groups. The surface morphology of group A was more homogeneous than that of the other groups because the high cellulose content in the WFP was easy to dissolve (Kilpeläinen *et al*. 2007).

When the proportion of WFP increased, the PWF was not able to be completely dissolved. There were more insoluble cellulose crystal structures in the films, which resulted in the bulk materials not closely bonding with each other. Therefore, the mechanical properties of the films decreased and the surface bonding state became poor.

When the PWF content was less than 60 wt%, dissolved components easily formed continuous matrices to connect undissolved lignocellulose. With an increased PWF content, the network between the lignin and cellulose crystals in the wood flour limited the dissolution of the PWF. Consequently, the undissolved components tended to aggregate, and the bond strength was insufficient to withstand higher loads. For example, the surface morphology of group F showed some aggregated parts that overlapped, which led to a decrease in the mechanical properties of group F. Thus, the results of the SEM analysis supported the results of the analysis of the mechanical properties.

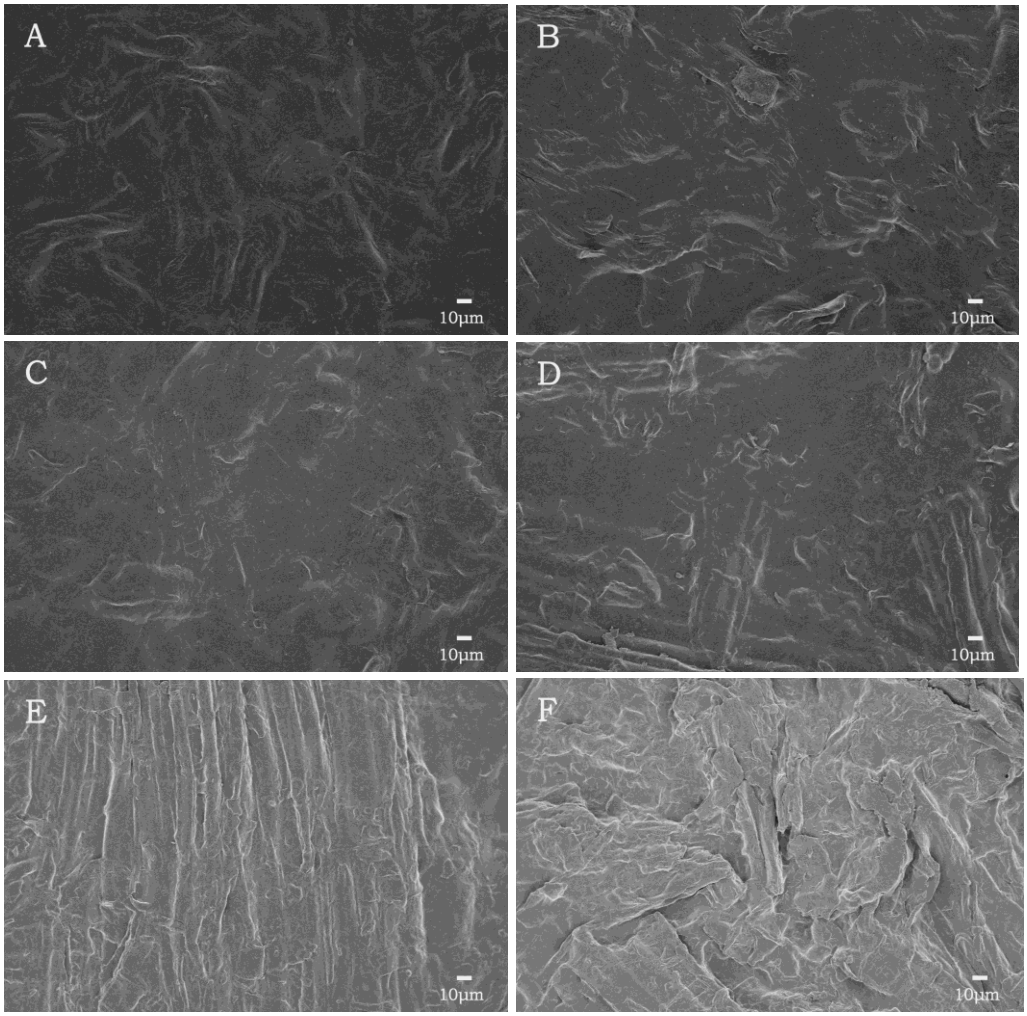

Fig. 1. SEM images of the samples at 400× magnification: (A) Group A; (B) Group B, (C) Group C, (D) Group D, (E) Group E, and (F) Group F

Thickness and Grammage

Figure 2 shows that the grammage of group A was the greatest and its thickness was the lowest among all of the groups, including the CK. This was because of its high cellulose content. The original paper was loosely composed of large pores and cellulose fibers. Also, cellulose dissolves more easily than wood flour (Sun *et al*. 2009; Shu *et al*. 2017). The dissolved cellulose was able to regenerate to form a dense film.

With an increased proportion of PWF, the samples became thicker, although the thickness varied little. Meanwhile, the grammage decreased continuously (except for group F) and the structure became progressively looser. This might have been caused by more insoluble components in the solution system. However, because of the limited dissolution of Group F, its grammage did not follow the decreasing trend, and visible wood powder particles could be seen on the surfaces of the samples. This indicated that different dissolution rates directly influenced the interfacial binding capacity between the regenerated cellulose and insoluble components, which would lead to different mechanical properties (Tisserat *et al*. 2015).

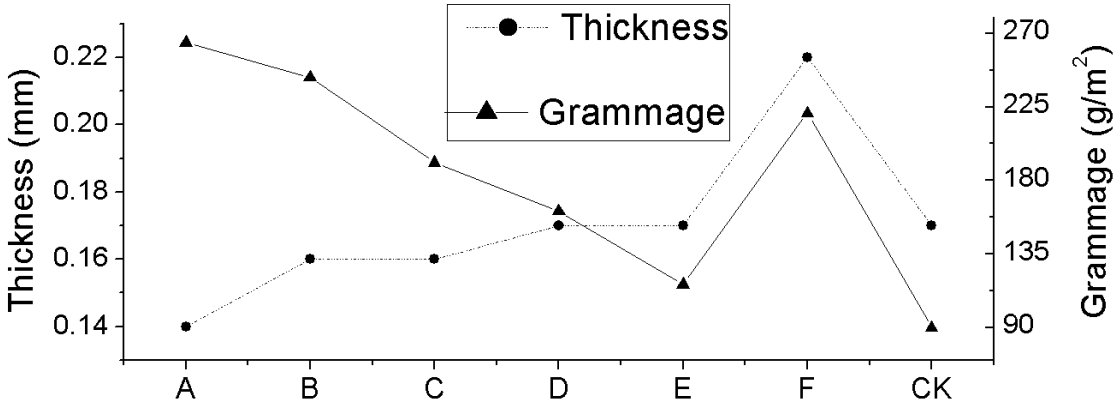

Fig. 2. Thickness and grammage of the samples

Mechanical Properties

Figure 3 shows the mechanical properties of each group. It was evident that the tensile strength, elongation at break, and initial Young's modulus decreased with the incorporation of PWF. The greatest decrease was from group A to group B. For example, the change in the elongation at break was 12.1%. Subsequent decreases were relatively lower. This result was because the cellulose content in group A was the highest. Cellulose could be easily dissolved by [Amim]Cl, but there were cellulose, hemicellulose, lignin, and other macromolecules in the PWF.

The amorphous structure of the lignin acted like a binder connecting the cellulose and hemicellulose, which could be the main influence that made the PWF more difficult to dissolve than the WFP (Shibata *et al*. 2013a). For group A, which had no PWF in the mixture, the dissolved cellulose in the WFP was intertwined closely and the interfacial binding capacity of the regenerated cellulose was greater than that of the other groups (Tisserat *et al*. 2015). Thus, group A exhibited the best tensile properties with the greatest tensile strength (114.4 MPa), elongation at break (19.4%), and initial Young's modulus (4.4 GPa).

When the mass ratio was less than 60 wt%, the network between the carbohydrate and lignin could be broken by the IL, and the dissolved components could disperse and distribute among the undissolved components. Their tensile strengths were better than that of the CK, which did not undergo the IL treatment.

With an increased poplar fiber content in the mixture, it's more difficult for IL to penetrate the network structure formed by cellulose, hemicellulose and lignin, which resulted in a lower percentage of dissolved components. Therefore, there was more uneven fiber dispersion and aggregation in the composite system (Zhao *et al*. 2009).

Group F (100 wt% PWF) had the lowest tensile strength (5.3 MPa), elongation at break (0.5%), and initial Young's modulus (1.4 GPa) of the treatment groups. Clearly, the trends of the tensile strength, elongation at break, and initial Young's modulus were similar. However, the CK showed some differences across the properties. The elongation at break of the CK was 11.0%, which was less than for group A and greater than for any of the groups containing PWF. The initial Young's modulus of the CK was 0.7 GPa, which was less than that of all of the other groups. Meanwhile, the tensile strengths of groups A through D were greater than that of the CK (15.1 MPa).

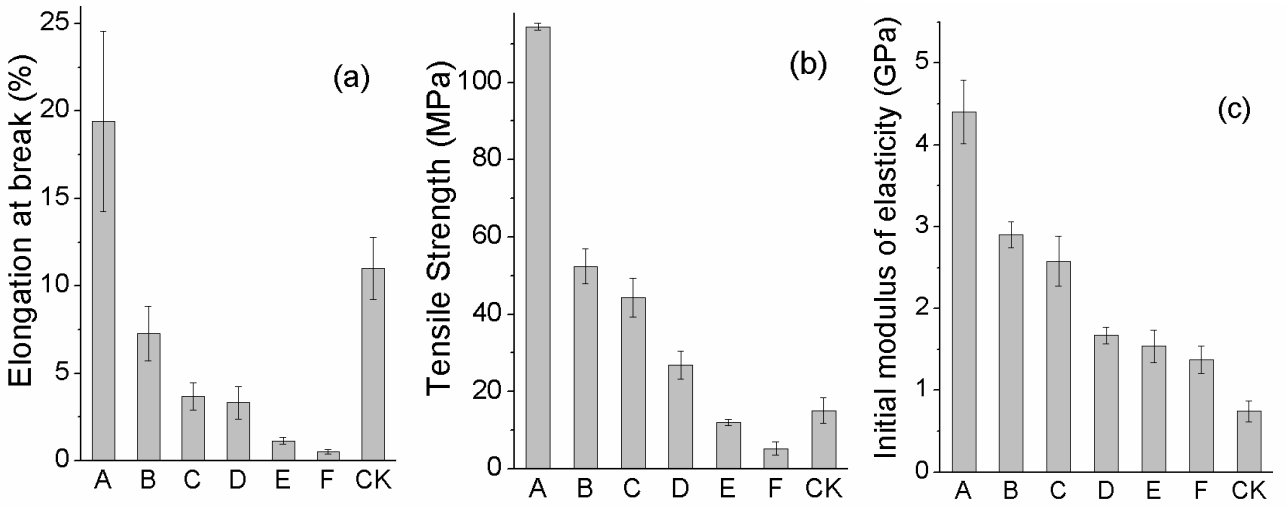

Fig. 3. Mechanical properties of the samples: (a) Elongation at break, (b) Tensile strength, and (c) Initial modulus of elasticity

CONCLUSIONS

1. A novel, environmentally friendly bio-composite lignocellulosic composite films (LCFs) based on renewable low-cost raw materials was developed *via* the ionic liquid [Amim]Cl as green solvent to substitute petroleum-based products.
2. Mixtures with different mass ratio of raw materials showed different solubilities. Therefore, different mass ratios of matrix and reinforcement part led to different surface bonding states. The grammage, thickness, and mechanical properties of LCFs were also related to the dissolution of the raw materials.
3. Group A (100 wt% waste filter paper (WFP)) had the best mechanical properties. This was attributed to the highest dissolution of cellulose in the raw material. When the poplar wood flour (PWF) content was increased, the content of the insoluble components also increased under the same processing conditions. Consequently, the tensile strength decreased with the increasing of PWF content. Even so, that of group D (60 wt% PWF) was greater than that of the untreated original WPF (CK), which indicated the appropriate PWF and WFP mass ratio may meet the needs of application.
4. The elongation and elastic modulus showed the same trend as that of the tensile strength. Thus, the PWF and WFP mass ratio was found to be the main factor that affects the dissolution of the raw materials, and further affects the mechanical properties of the LCFs. Choosing the proper PWF and WFP mass ratio is important for the development of environmentally friendly LCFs with the desired properties.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Natural Science Research Project of Educational Commission in Anhui Province, China (Grant No. KJ2016A231), the 2016 National College Students' Innovation and Entrepreneurship Plan Project (Grant No. 201610364023), the 2016 College Students Innovation and Entrepreneurship Plan Project of Anhui Province (Grant No. 201610364050), and the Discipline Backbone Cultivation Project of Anhui Agricultural University (Grant No. 2014XKPY-57).

REFERENCES CITED

Borah, J. S., and Kim, D. S. (2016). "Recent development in thermoplastic/wood composites and nanocomposites: A review," *Korean J. Chem. Eng.* 33(11), 3035-3049. DOI: 10.1007/s11814-016-0183-6

Duchemin, B. J. C., Mathew, A. P., and Oksman, K. (2009). "All-cellulose composites by partial dissolution in the ionic liquid 1-butyl-3-methylimidazolium chloride," *Compos. Part A-Appl. S.* 40(12), 2031-2037. DOI: 10.1016/j.compositesa.2009.09.013

Guo, X., Lin, Y., Na, B., Liang, X., Ekevad, M., Ji, F., and Huang, L. (2017). "Evaluation of physical and mechanical properties of fiber-reinforced poplar scrimber," *BioResources* 12(1), 43-55. DOI: 10.15376/biores.12.1.43-55

Iqbal, H. M. N., Kyazze, G., and Keshavarz, T. (2013). "Advances in the valorization of lignocellulosic materials by biotechnology: An overview," *BioResources* 8(2), 3157-3176. DOI: 10.15376/biores.8.2.3157-3176

Kaseem, M., Hamad, K., Deri, F., and Ko, Y. G. (2015). "Material properties of polyethylene/wood composites: A review of recent works," *Polym. Sci. Ser. A+* 57(6), 689-703. DOI: 10.1134/S0965545X15070068

Kilpeläinen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., and Argyropoulos, D. S. (2007). "Dissolution of wood in ionic liquids," *J. Agr. Food Chem.* 55(22), 9142-9148. DOI: 10.1021/jf071692e

Kuka, E., Cirule, D., Kajaks, J., Andersone, I., and Andersons, B. (2016). "Wood plastic composites made with thermally modified birch wood residues," *Int. Wood Prod. J.* 7(4), 225-230. DOI: 10.1080/20426445.2016.1214439

Lang, Q., She, Y., Chen, H.-y., and Pu, J.-w. (2013). "Poplar wood-methylolurea composites prepared by *in situ* polymerization," *J. Appl. Polym. Sci.* 130(2), 933-938. DOI: 10.1002/app.39280

Li, J., Li, D., Song, Z., Shang, S., and Guo, Y. (2016). "Preparation and properties of wood plastic composite reinforced by ultralong cellulose nanofibers," *Polym. Compos.* 37(4), 1206-1215. DOI: 10.1002/pc.23285

Mäki-Arvela, P., Anugwom, I., Virtanen, P., Sjöholm, R., and Mikkola, J. P. (2010). "Dissolution of lignocellulosic materials and its constituents using ionic liquids—A review," *Ind. Crop. Prod.* 32(3), 175-201. DOI: 10.1016/j.indcrop.2010.04.005

Mijiyawa, F., Koffi, D., Kokta, B. V., and Erchiqui, F. (2015). "Formulation and tensile characterization of wood–plastic composites: Polypropylene reinforced by birch and aspen fibers for gear applications," *J. Thermoplast. Compos.* 28(12), 1675-1692. DOI: 10.1177/0892705714563120

Qin, C., and Zhang, W. (2012). "Antibacterial property of titanium alkoxide/poplar wood composite prepared by sol–gel process," *Mater. Lett.* 89, 101-103. DOI: 10.1016/j.matlet.2012.08.089

Shibata, M., Teramoto, N., Nakamura, T., and Saitoh, Y. (2013a). "All-cellulose and all-wood composites by partial dissolution of cotton fabric and wood in ionic liquid," *Carbohyd. Polym.* 98(2), 1532-1539. DOI: 10.1016/j.carbpol.2013.07.062

Shibata, M., Yamazoe, K., Kuribayashi, M., and Okuyama, Y. (2013b). "All-wood biocomposites by partial dissolution of wood flour in 1-butyl-3-methylimidazolium chloride," *J. Appl. Polym. Sci.* 127(6), 4802-4808. DOI: 10.1002/app.38047

Shu, Z., Liu, S., Zhou, L., Li, R., Qian, L., Wang, Y., Wang, J., and Huang, X. (2017). "Physical and mechanical properties of modified poplar veneers," *BioResources* 12(1), 2004-2014. DOI: 10.15376/biores.12.1.2004-2014

Si, H., Li, B., Wang, T., Lin, L., and Xu, Z. (2013). "Preparation of cyclodextrin grafting wood flour and investigation of the release characteristics of eugenol," *Wood Sci. Technol.* 47(3), 601-613. DOI: 10.1007/s00226-012-0520-9

Sommerhuber, P. F., Wenker, J. L., Rüter, S., and Krause, A. (2017). "Life cycle assessment of wood-plastic composites: Analysing alternative materials and identifying an environmental sound end-of-life option," *Resour. Conserv. Recy.* 117(Part B), 235-248. DOI: 10.1016/j.resconrec.2016.10.012

Soykeabkaew, N., Nishino, T., and Peijs, T. (2009). "All-cellulose composites of regenerated cellulose fibres by surface selective dissolution," *Compos. Part A-Appl. S.* 40(4), 321-328. DOI: 10.1016/j.compositesa.2008.10.021

Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodríguez, H., and Rogers, R. D. (2009). "Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate," *Green Chem.* 11(5), 646-655. DOI: 10.1039/B822702K

Tisserat, B., Larson, E., Gray, D., Dexter, N., Meunier, C., Moore, L., and Haverhals, L. (2015). "Ionic liquid-facilitated preparation of lignocellulosic composites," *Int. J. Polym. Sci.* 2015. DOI: 10.1155/2015/181097

Üner, B., Köse, G., Yürümez, Y., Yalçın, Ö. Ü., and Akgül, M. (2016). "Wood waste turned into value added products: Thermal plasticization by benzylation process," *Drvna Ind.* 67(4), 315-322. DOI: 10.5552/drind.2016.1534

Wang, X., Zhang, Y., Yu, Z., and Qi, C. (2017). "Properties of fast-growing poplar wood simultaneously treated with dye and flame retardant," *Eur. J. Wood Wood Prod.* 75(3), 325-333. DOI: 10.1007/s00107-016-1142-y

Zhao, Q., Yam, R. C. M., Zhang, B., Yang, Y., Cheng, X., and Li, R. K. Y. (2009). "Novel all-cellulose ecocomposites prepared in ionic liquids," *Cellulose* 16(2), 217-226. DOI: 10.1007/s10570-008-9251-3

Article submitted: April 14, 2018; Peer review completed: July 28, 2018; Revised version received: July 30, 2018; Accepted: August 19, 2018; Published: September 4, 2018.
DOI: 10.15376/biores.13.4.7935-7943