

Direct Dissolution and Spinning of the Agricultural Waste of Corn Straw Pulp

Xin Gao, Yongqi Yu, Zeming Jiang, Yang Liu, Wentao Zhang, and Liping Zhang *

Agricultural waste of corn straw pulp was successfully prepared into fibers using a tetrabutylammonium acetate (TBAA) and dimethyl sulfoxide (DMSO) solvent system *via* a dry-jet wet spinning process at 35 °C. The dissolving process of cellulose in TBAA/DMSO was observed through a polarization microscope, and the rheological behavior of the cellulose/ TBAA/DMSO solution was also studied. The crystalline and microstructure of the regenerated cellulose fibers prepared from corn straw were investigated by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). In addition, the morphology was characterized with a scanning electron microscope (SEM). The thermal stability of corn straw pulp and the regenerated cellulose was also explored. Due to the presence of residual lignin, a longer time was needed for the complete dissolution of corn straw compared with pure wood pulp. In addition, the degree of polymerization and the elongation-at-break of the regenerated fiber had a small amount of attenuation. Despite the deficiencies, a good spinnability of corn straw cellulose solution could still be achieved. Fibers with a round and compact structure as well as a smooth surface were obtained.

Keywords: Corn straw; Tetrabutylammonium acetate; Dimethyl sulfoxide; Dry-jet wet spinning; Regenerated fiber

Contact information: Ministry of Education Key Laboratory of Wooden Material Science and Application, College of Materials Science and Technology, Beijing Forestry University, No. 35 Tsinghua East Road, Haidian District, Beijing 100083, China; *Corresponding author: zhanglp418@163.com

INTRODUCTION

Synthetic polymers permeate every aspect of society, so much that they have not only simplified daily living and but have also predominantly influenced modern civilization (Gao *et al.* 2012). Research studies are now focusing on renewable raw materials and more environmentally friendly resources, such as biodegradable, renewable, and abundant cellulosic fibers due to health concerns (Yao *et al.* 2013), exhausting fossil resources, and environmental pollution caused by petroleum fuels (Ma *et al.* 2015). The utilization of biopolymer-based materials in many applications has increased so rapidly that a dramatic shift in the development of novel materials derived from those resources has emerged (Faruk *et al.* 2012; Thakur *et al.* 2014).

Cellulose, as the most common abundant renewable organic polymer, has a wide range of applications in fibers, films, and plastics. Moreover, numerous new functional materials containing cellulose are being developed. As is well known, wood pulp remains the most important raw material source for the processing of cellulose. However, most of it is used for paper making, while only very small amounts are used for the production of fibers as well as for the synthesis of cellulosic esters and ethers (Li *et al.* 2012). Though the vast majority of garments and textile products with non-synthetic components are

made of cotton, its limited production can no longer keep pace with the steadily increasing demand driven by the global population growth.

Agriculture is facing unpredicted challenges and risks with the increase of global population, which will require a rapid increase of global food demand from existing agricultural land that is unlikely to further increase (Tilman *et al.* 2011; Bouwman *et al.* 2013; Zhang *et al.* 2017). Fortunately, the relatively high yield and easy planting make corn a better choice. In addition to food, the utilization of abundant, inexpensive, and readily available corn straw has received increasing attention during the past few decades. The on-site incineration of corn straw in the large rural area of China has raised serious problems of air pollution and wasting resources (Song *et al.* 2017). Given the need to ensure the demand for food in combination with sustainable land management, environmental protection, and other sustainability requirements, new and efficient methods and processes are needed to help unlock the promise of this crop straw. Therefore, man-made cellulosic fibers are needed to fill this so-called cellulose gap. Hence, making full use of crop straw to produce regenerated fibers for textile has become a promising trend.

However, a significant portion of the lignin, hemicellulose, and cellulose in the plant and unbleached pulp are chemically bonded and present in the cell wall of the plant fiber in the form of a lignin-carbohydrate complex (LCC). The LCC structure (especially the benzo-ether bond type) hinders the removal of lignin. Approximately 92% of the LCC linkages are lignin and xylan, glucomannan, and only approximately 8% of this comprises the link of lignin and cellulose (Lawoko *et al.* 2003). Therefore, the processing of lignocellulosic materials involves energy-consuming separation of the components that makes it difficult to utilize biomass. Currently, the extraction of cellulose from raw materials still mainly relies on pulp and paper technology. Due to the high energy consumption in the pulping process, most of the required energy is generated by combustion, which aggravates environmental pollution. (Nurmesniemi *et al.* 2008). The byproducts formed during the classic pulping process based on hydrogen peroxide, chlorinated compounds, *etc.*, are toxic, mutagenic, persistent, and bioaccumulating, which can cause numerous harmful disturbances in biological systems (Techapun *et al.* 2003). Undoubtedly, environmental pollution has become the most serious problem that the pulping industry faces. Furthermore, in the pulp and paper industry a huge amount of water is needed in different stages during the manufacturing process, which means an increased production of sewage (Mänttari *et al.* 2004).

Since imidazolium-based ionic liquids (ILs) have been reported to be used to dissolve cellulose directly and the dissolved cellulose can be easily regenerated by precipitation upon addition of water or other common solvents, a variety of ILs are beginning to be studied, such as 1-butyl-3-methylimidazoliumchloride ([BMIM][Cl]), 1-ethyl-3-methylimidazoliumacetate ([EMIM][Ac]), and 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) (Swatloski *et al.* 2002; Wu *et al.* 2004; Liu *et al.* 2010; Tan *et al.* 2011; Zhao *et al.* 2012). ILs are viewed as promising cellulose solvents for properties such as chemical and thermal stability, recyclability, immeasurably low vapor pressure, and excellent dissolving capability. On the other hand, there are some disadvantages, such as slow dissolution rate, high dissolution temperature, and high viscosity of these dissolution systems that still obstruct the effective use of cellulose.

Recently, a new solvent system, tetrabutylammonium acetate/dimethyl sulfoxide solution, has been used to dissolve cellulose in our laboratory (Miao *et al.* 2014). Compared with ILs has been reported before, the dissolution temperature is lower

(≤ 60 °C) and the dissolution rate is more rapid (≤ 1 h). Furthermore, both TBAA and DMSO can be recycled. After that, the dissolving power and dissolution mechanism of TBAA/ DMSO were further studied. Carboxylate anions of TBAA and the cellulose, forming strong hydrogen bonds was found to be the key factor for the dissolving behavior of cellulose in the mixed solvent. Meanwhile, DMSO not only reduced the viscosity of the mixed solvent but also interacted with cellulose to stabilize the dissolved cellulose molecule from reforming inter- and intramolecular hydrogen bonds (Huang *et al.* 2016).

So far, the dissolution and regeneration of soft wood pulp (WP), bamboo pulp, and degreased cotton in tetrabutylammonium acetate/dimethyl sulfoxide solution has been studied (Jiang *et al.* 2016), while the application in corn straw pulp (CP) has not been reported previously. Especially, the corn straw pulp obtained from Jilin Chemical Fiber Co., Ltd which was produced using a new clean, low-energy process. So, the aim of this study is to offer an alternative, economical, and environmentally friendly way for the value-added conversion of agricultural waste, *viz.*, corn straw pulp. New and efficient solvent TBAA/DMSO was used to help unlock the promise of agricultural waste corn straw, and the corn straw pulp was successfully spun into corn straw regenerated fibers (CRF). What's more, wood pulp regenerated fibers (WRF) were used for comparison.

EXPERIMENTAL

Materials

The corn straw pulp containing 82% α -cellulose, and 2.04% lignin was obtained from Jilin Chemical Fiber Co., Ltd. (Jilin, China), and softwood pulp with α -cellulose content of more than 92% was provided by the Shandong Rizhao Senbo Pulp Paper Co., Ltd., China. These were used as the cellulose material. The viscosity-average degree of polymerization (DP) of the corn straw pulp and softwood pulp were estimated to be 750 to 800 and 950 to 1000 based on measurements using an Ubbelohde viscometer (Qihang Glass Instrument Factory, Shanghai, China) in cupric ethylenediamine hydroxide solution (CUEN). The solvent tetrabutylammonium acetate (TBAA) was purchased from Tokyo Chemical Industry Shanghai, China. The dimethyl sulfoxide (DMSO), NaOH, ethanol, ethylenediamine, and all other chemicals used were analytical grade and used without further purification (Beijing Chemical Works, Beijing, China).

Preparation of cellulose solution and regenerated fibers

A two-component solvent system containing a homogeneous mixture of 6 g TBAA and 24 g DMSO was placed in a 100 mL bottle, and then 2.4 g dried cellulose materials were added to the mixture. The mixture were stirred at 300 r/min for approximately 10 h at 60 °C until a homogeneous cellulose solution was obtained at last, and then dried in a vacuum oven at 60 °C for 48 h to remove bubbles generated after the dissolution process. An oil bath was used to control the dissolution temperature. A custom made dry-jet wet spinning equipment that consisted of a micro-syringe pump system, a glass syringe (inner diameter, $\Phi=10$ mm with a needle (length of 35 mm; inner diameter, $\Phi=0.355$ mm) as a spinneret, a spinning bath, and a take-up device but also draft equipment, was used for the spinning trials. The cellulose solution obtained earlier was introduced into the glass syringe with a precise drive. The extrusion speed was 0.4 mL/min. Air gap length was fixed at 35 mm. The winding speed was controlled at 12

m/min. Clear water was used as the coagulation, and the solution temperature was changed by the heating cylinder. The temperature of the cellulose solutions was kept at 35 °C.

Methods

Dissolution of cellulose in TBAA/DMSO

The dissolving process of corn straw pulp cellulose in TBAA/DMSO at room temperature was real time monitored using a polarization microscope (Pudan, Shanghai, China) that was equipped with a hot stage and a digital camera. A small quantity of corn straw pulp and TBAA/DMSO solvent was sandwiched between slides and coverslips and put on the hot stage at 25 °C. Record the dissolution process using the digital camera and select images for some certain moments.

Characterization of cellulose solution

The dynamic rheology experiment was conducted on an ARES-RFS III rheometer (TA Instruments, New Castle, DE, USA) equipped with a PP20 plate-plate geometry and a temperature control system. Shear rates varied from 0.001 to 150 s⁻¹. Changes in viscosity with shear rate were measured every 5 °C from 25 °C to 60 °C.

Characterization of regenerated fibers: Morphology of regenerated fibers

The morphology of surface and cross-sections of fibers spun from the cellulose material were observed by means of a scanning electron microscope (Hitachi, Tokyo, Japan). The fibers were frozen in liquid nitrogen, immediately snapped, and then vacuum-dried. The samples were sputtered with gold with a high resolution sputter coater (Cressington, Watford, UK) before being observed and photographed.

Characterization of molecular structure

The Fourier transform infrared (FT-IR) spectra of the cellulose material and regenerated fibers were the result of averaging 32 scans in wavelengths that ranged from 4000 cm⁻¹ to 500 cm⁻¹ at a resolution of 2 cm⁻¹ by using pellet type samples on an infrared spectrometer (Tensor 27, Bruker, Karlsruhe, Germany). The pellets were prepared by combining the samples with KBr.

Characterization of crystal structure

X-ray diffraction (XRD) measurements of the cellulose material and regenerated fibers were performed on a XRD diffractometer (Shimadzu XRD-6000, Kyoto, Japan). Samples were vacuum-dried for 24 h before their measurement and ground into powders to erase the influence from the crystalline orientation of each fiber sample. The patterns were measured with Cu Ka radiation ($k = 0.154$ nm) at 40 kV and 30 mA. The powder samples were scanned from 5° to 40° at a scanning rate of 2 °/min. The crystallinity value was calculated using a software named MDI jad 5.0.

Thermal stability

Thermogravimetric analysis (TGA) was performed with a STA 449F3 instrument (NETZSCH Group, Bavaria, Germany). The samples were evenly and loosely distributed in an open sample pan 6.4 mm in diameter and 3.2 mm deep with an initial sample amount of 8 to 10 mg. Each sample was heated from 25 °C to 450 °C at a rate of 10 °C·min⁻¹ under argon.

Mechanical properties

A micrometer was used to measure the diameter of the regenerated fibers. The tensile strength and elongation-at-break of the dried fibers were measured on an electronic tensile tester (Instron, Canton, USA). Every sample length was 10 cm. Each specimen was tested for 15 times and the average value was taken.

RESULTS AND DISCUSSION

The Dissolution of Cellulose in TBAA/DMSO

The dissolving process of corn straw pulp in TBAA/DMSO at room temperature was real time monitored using a polarization microscope. The corn straw pulp with DP values as high as 750 to 800 and a lignin content of approximately 2% could be dissolved in the TBAA/DMSO solvent system within 55 min at 25 °C. At room temperature, the dissolution rate of corn straw pulp in the solvent was quite fast. In pure wood pulps, the cellulose molecule will swell, such that the molecular chains move apart in the cellulose solvent system. Moreover, it was remarkable that the corn straw pulp cellulose with a larger amount of lignin dissolved in TBAA/DMSO rapidly without any pretreatment or activation at 25 °C. Compared with the speed of pure wood pulp cellulose dissolved in the solvent TBAA/DMSO, the corn straw pulp cellulose containing lignin became completely dissolved over a longer period of time (Miao *et al.* 2014). As previously reported, any carbohydrates not bonded to lignin or with fewer lignin bonds will be preferentially dissolved (Sun *et al.* 2009). At least 90% of the residual lignin in corn straw pulp is proposed to be covalently linked to carbohydrates, 92% of which is bound to xylan and glucomannan and 8% is bound to cellulose (Lawoko *et al.* 2003). Thus, as shown in Fig. 1, in the first 10 min the cellulose dissolved quickly, after which the dissolution rate of the cellulose was slowed down and it was completely dissolved until 55 min.

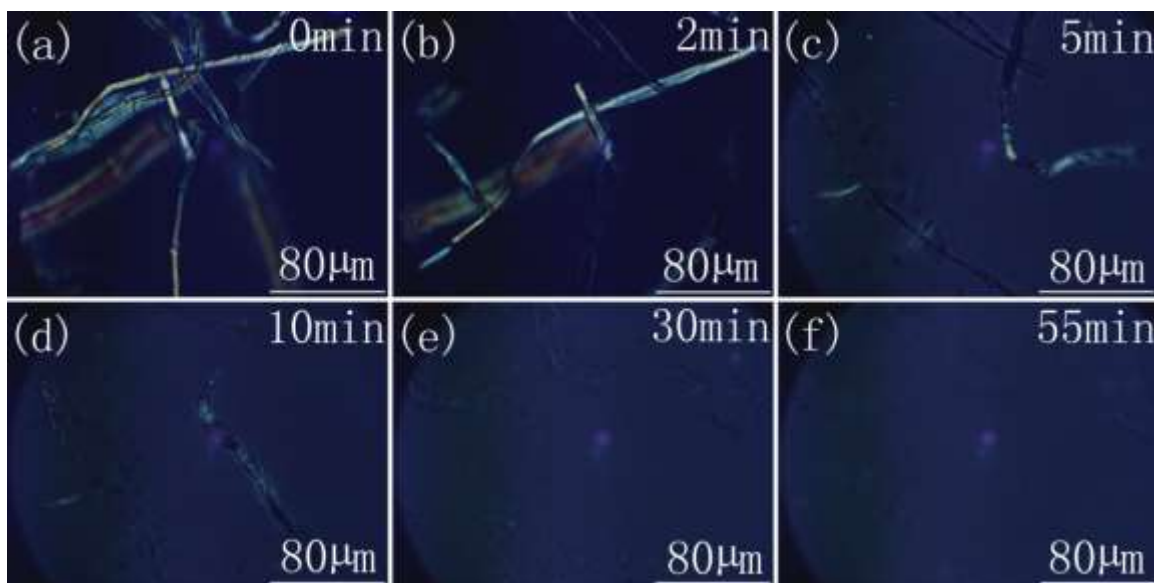


Fig. 1. Images of corn straw pulp dissolved in TBAA/DMSO at 25 °C at various time intervals: a) 0 min, b) 2 min, c) 5 min, d) 10 min, e) 30 min, and f) 55 min

Rheological Properties of Cellulose Solution

Steady shear rheological behaviors of cellulose-TBAA/DMSO solutions

The rheological properties of spinning solution were tested at various test temperatures (25 °C, 35 °C, 45 °C, and 55 °C). Figure 2 shows that the initial apparent viscosity of the spinning solution at 25 °C was largest and the initial apparent viscosity of the spinning solution at 35 °C, 45 °C, and 55 °C were considerably reduced, which indicated that the temperature had an effect on the apparent viscosity of the solution and the apparent viscosity decreased with the increasing temperature. When the shear rate was increased, the apparent viscosity of the spinning solution decreased sharply at the four temperature conditions at the shear rate of 10 s⁻¹ quickly approaching zero, which proved that the shear rate was still an important reason for the apparent viscosity of the spinning solution.

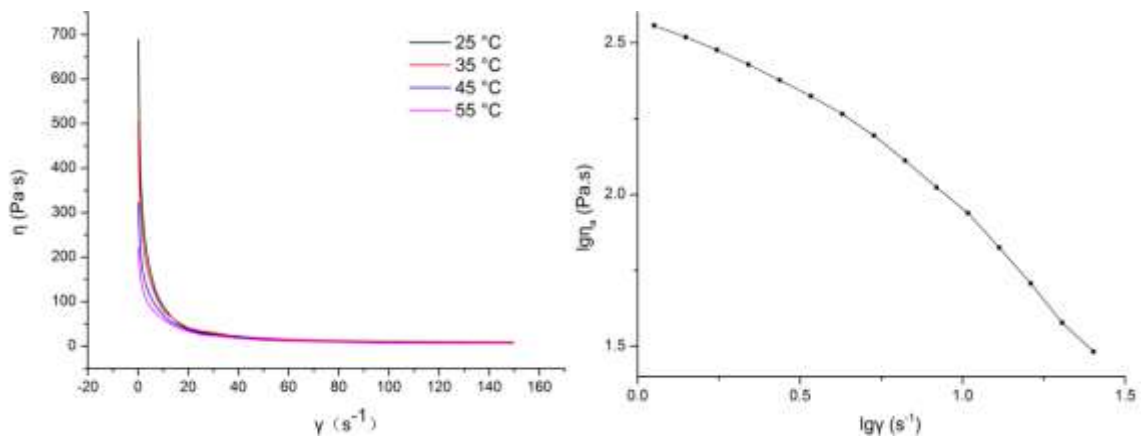


Fig. 2. The flow curve of cellulose of corn straw in TBAA/DMSO

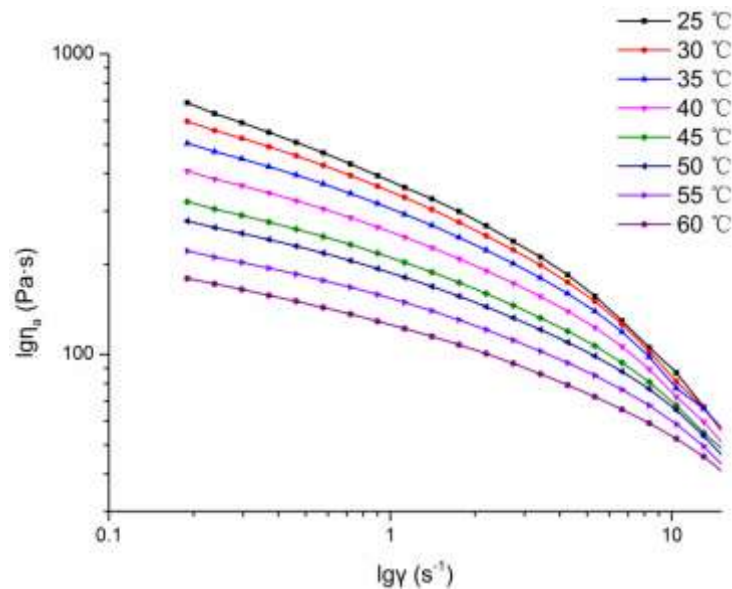


Fig. 3. Steady shear rheological curves for the cellulose of corn straw in TBAA/DMSO solutions at different temperatures

The viscosity of the cellulose solutions exhibited shear-thinning behavior, and the increasing concentration of cellulose solution led to an increase in chain entanglement resulting in an increase in solution viscosity. Clearly, as the temperature increased, the viscosity of the solution decreased, and the values of viscosity of 8% cellulose solution in the new solvent at 25 °C to 60 °C were approximately 180 Pa·s and 700 Pa·s, which was almost the same as that of pure wood pulp cellulose in TBAA/DMSO (Miao *et al.* 2014). Due to its low viscosity and good formability in H₂O at room temperature, the regenerated cellulose fibers prepared from TBAA/DMSO were easily produced under mild conditions by dry-jet wet spinning.

Non-Newtonian index

The non-Newtonian index represents the degree of deviation from the Newtonian flow, which is a measure of the shear viscosity change sensitive to the shear rate. At the same time, it is also dependent on the parameters such as temperature and molecular mass. The non-Newtonian index is a sign that the polymer fluid deviates from the Newtonian fluid. Increasing the value allows the flow characteristics of the spinning liquid to be closer to the Newtonian fluid, which facilitates the control of the spinning process. The study of the non-Newtonian index of the spinning solution is one of great importance to the control of the spinning process.

As shown in Fig. 4(a), due to the increase of solution temperature, the macromolecule chain motion of the solution increased and the intermolecular force weakened. Consequently, with an increased temperature of the spinning solution, the non-Newtonian index showed an upward trend. Finally, the non-Newtonian index value approached 0.81.

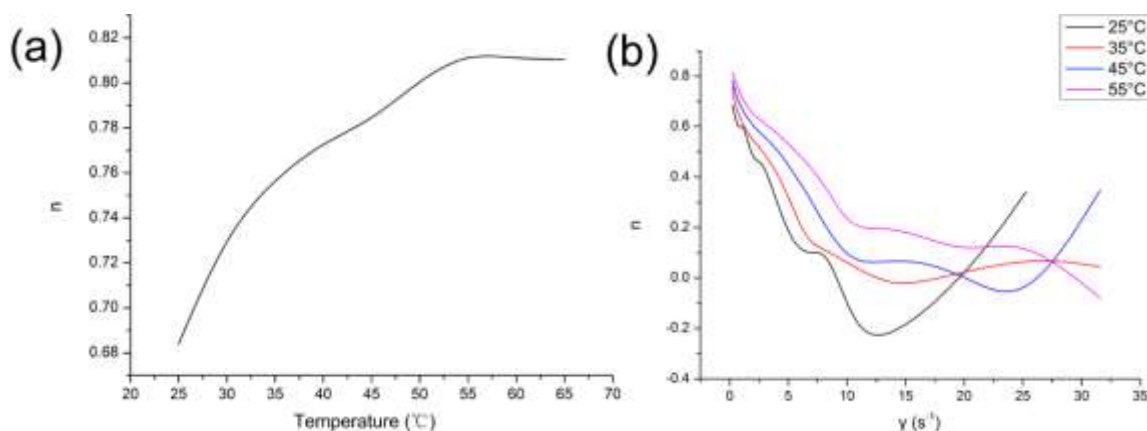


Fig. 4. (a) The temperature dependence of non-Newtonian index of corn straw pulp solution in TBAA/DMSO; (b) The dependence of non-Newtonian index of corn straw pulp solution in TBAA/DMSO on shear rate

The effects of shear rate on non-Newtonian index of cellulose solution are shown in Fig. 4(b). To maintain the stability of the solution during the spinning process, 35 °C was chosen as the spinning temperature not only for its wide stability zone but also because low-spinning temperatures could avoid considerable cellulose degradation (Wang *et al.* 2015). The shear rate range of the spinning can be selected between 15 s⁻¹ and 25 s⁻¹ at the spinning temperature.

Molecular Structure Analysis

The FT-IR spectra of cellulose materials (WP and CP) and regenerated cellulose fibers (WRFs and CRFs) are shown in Fig. 5. No new peaks appeared in the regenerated cellulose fibers. The spectra of the original straw cellulose and regenerated cellulose fibers were similar, and all the expected bond vibrations, including O-H, C-H, and C-O, were observed. The strong, broad absorption band between 3500 cm^{-1} and 3200 cm^{-1} is assigned to the O-H group vibration of hydrogen bonding, which takes place between repeating units within the cellulose matrix (Zhou *et al.* 2001). After dissolution and regeneration, the O-H bond vibration shifted to a higher frequency and became sharper and narrower, indicating the break of hydrogen bonds to some extent (Zhang *et al.* 2005). The C-O vibration band that appeared as a strong absorption between 1150 cm^{-1} and 1000 cm^{-1} was also the characteristic peak of cellulose. The C-H vibration was also evident at 2920 cm^{-1} .

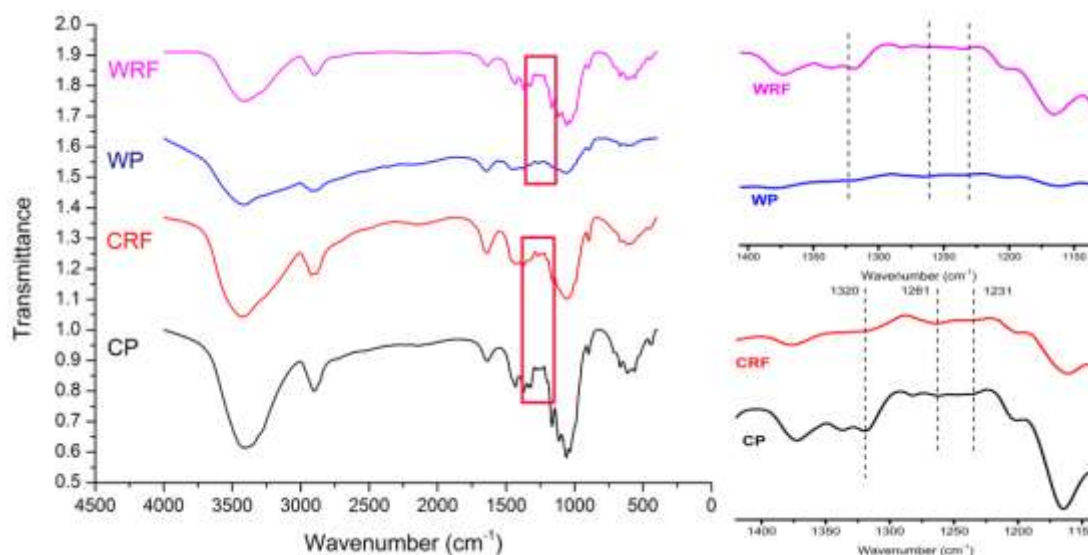


Fig. 5. FT-IR spectra of cellulose material (CP and WP) and regenerated fibers (CRF and WRF)

The typical lignin peaks, at 1261 cm^{-1} to 1231 cm^{-1} , and C-O stretching located at 1320 cm^{-1} were also present in the spectrum of the corn straw pulp cellulose and the regenerated fiber (Labbe *et al.* 2005). These results indicated that the lignin remained. However, these three characteristic peaks were small or almost absent in the spectra of soft wood pulp cellulose. The difference between CP and WP could be established. In the pulping process, impurities in WP were more thoroughly removed. The strong absorption peak at 1050 cm^{-1} belonged to the frame vibration of the glycosidic bond of cellulose (C-O-C). Compared with the cellulose material, the C-O-C vibration of the regenerated fibers became gentler and broader. This indicated that a part of the C-O-C bonds of cellulose are broken down in the process of dissolution (Sun *et al.* 2015).

Crystallinity Analysis

The XRD patterns of cellulose material (CP and WP) and regenerated fibers (CRF and WRF) are shown in Fig. 6. It was reported that the diffraction peaks or peak clusters found at 2θ values of 14.7° , 16.4° , 22.5° , and 34.4° (2θ) from cellulose I oriented with the crystal planes (101), (002), and (040), and 2θ values of 12.1° , 20.0° , and 21.7° from

cellulose II oriented with the crystal planes (110) and (020) (Mansikkamäki *et al.* 2005; Sun *et al.* 2008). The cellulose fibers studied were obtained from corn straw cellulose and soft wood cellulose prior to dissolution and the regenerated cellulose. Before the cellulose dissolved, it was present in its native form, and thus produced a cellulose I pattern with characteristic diffraction maxima at $2\theta = 14.8^\circ$, 16.5° , 22.3° , and 34.6° , associated with the (101), (002), and (040) planes, respectively. However, in the regenerated fibers curve, two crystal peaks appeared at 2θ values of 12.3° and 21.6° , where were assigned to the crystal planes (110) and (020) of cellulose II, respectively (Cheng *et al.* 2011). For the pure cellulose, the cellulose I structure was swollen and the cellulose molecular chain was movable in the cellulose solvent. In this process, when the solvent was removed, the polar opposite molecular chains were cross-linked to form a cellulose II crystal. The presence of lignin prevented the interdigitation of cellulose microfibrils during the recovery process (Revol and Goring 1981). This could be one of the reasons that the crystallinity index values (χ_c) of the CP and CRFs were 54% and 29%, respectively. Moreover, after regeneration, cellulose II was recovered, which was evidence that the corn straw pulp cellulose containing lignin was completely dissolved in the TBAA/DMSO solvent system. Therefore, the XRD result was consistent with the phenomenon observed *via* the polarizing microscope. In addition, the crystallinity index value (χ_c) of the WP was 59%, and it was reduced to 40% after dissolution and regeneration. It could be found that χ_c values of WP and WRFs were greater than CP and CRFs. More interesting was that the decrease in χ_c of CRFs after dissolution and regeneration from CP was more than WRFs. The prevention of the residue to the interdigitation of cellulose microfibrils was considered to be the cause of this phenomenon.

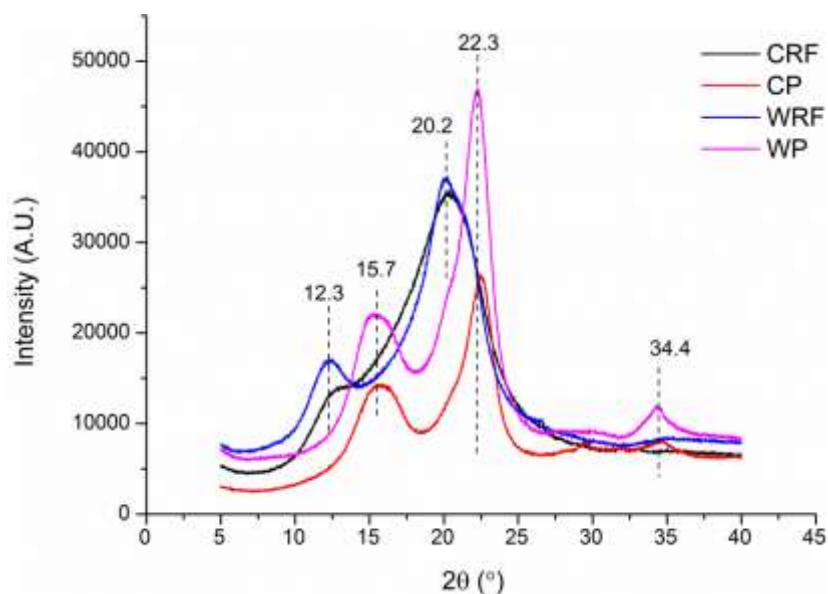


Fig. 6. XRD patterns of cellulose material (CP and WP) and regenerated fibers (CRF and WRF)

Thermal Stability Analysis

The thermo-gravimetric and differential thermo-gravimetric analyses (TGA/DTG) of the cellulose material and regenerated fibers are shown in Fig. 7. It should be noted that maximum decomposition temperature (T_{dmax}) at the first stage of TG scan of

regenerated fibers were approximately 70 °C due to the presence of residual DMSO. Preferably, the dissolution temperature of the cellulose in the TBAA/DMSO solvent was controlled to ≤ 70 °C to avoid destroying the stability of the two-component solvent due to the loss of DMSO. The main weight-loss for the cellulose fiber samples at the second stage (250 to 390 °C) indicated primary decomposition and charring of cellulose (Alongi *et al.* 2013). Compared with WP, the CP was not completely processed and there was lignin and ash content residue; this was the reason that the residual mass of the CP was more than WP.

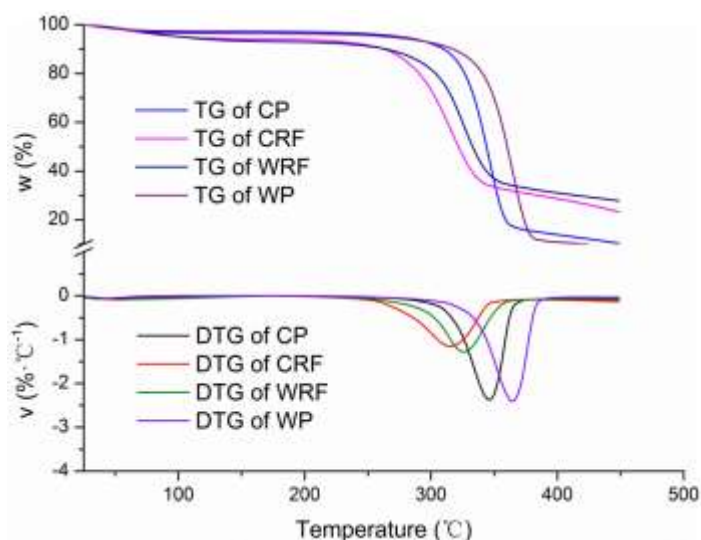


Fig. 7. TGA scans of cellulose material (CP and WP) and regenerated fibers (CRF and WRF); and DTG scans of cellulose material (CP and WP) and regenerated fibers (CRF and WRF)

The DTG scans verified that the T_{dmax} values of corn straw regenerated fibers after dissolution and regeneration and the corn straw pulp were 315 °C and 345 °C, respectively. Meanwhile, the temperature for the maximum weight-loss rate for soft wood pulp and wood regenerated fibers were about 326 °C and 365 °C, respectively. These findings indicated that the thermal stability of regenerated fibers was slightly decreased after dissolution and regeneration. The regenerated fibers showed relatively poor thermal stability due to the decrease in the degree of crystallinity, as measured by XRD (Carrillo *et al.* 2004). It can be also speculated that the reason for the lower maximum weight-loss temperature of CP and CRFs compared with WP and WRFs is relatively low crystallinity.

Morphology Analysis

The SEM images of the surface and cross-section of the CRFs and WRFs prepared from CP and WP dissolved respectively in the TBAA/DMSO are shown in Fig. 8. It was observed that the regenerated fibers were homogeneous with smooth surfaces and circular cross-sections, whose diameters were approximately 40 μm . This situation can be explained by the fact that the cellulose materials were completely dissolved in the solvent and the solution was very homogeneous. This is evidence that CP can be completely dissolved in the solvent. During the process of shaping, the homogeneity of the solution was retained and the regenerated fibers acquired a dense and homogenous structure. In addition, CRF had a circular cross-section that was similar to that of Lyocell fibers (Cai *et al.* 2010) and fibers obtained from softwood pulp and bamboo cellulose

with TBAA/DMSO (Miao *et al.* 2014; Jiang *et al.* 2016). Of course, it could be seen that the surface of A is smoother. From the cross section, WRF is more even and dense than CRF. It was considered that the remains played a harmful role. Actually, these bad influences were not very obvious. A crack was seen in the cross-section of the novel fibers, and this phenomenon was attributed to brittle fracture.

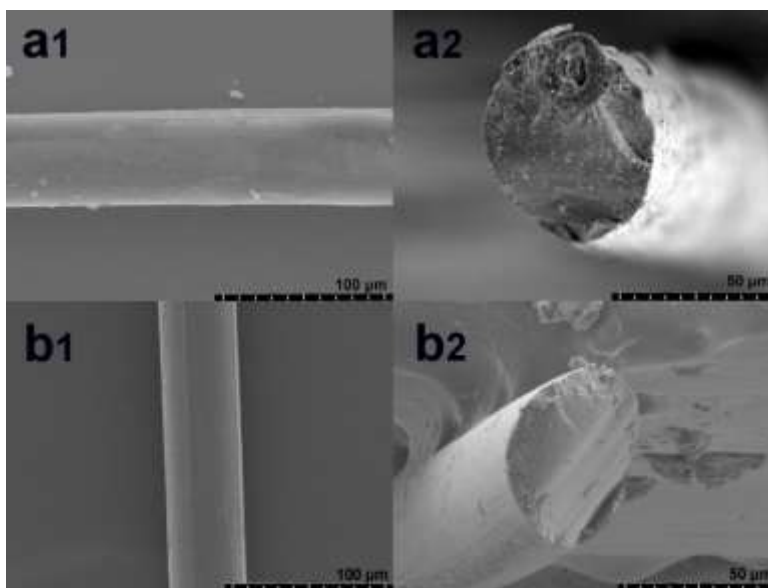


Fig. 8. SEM images of surfaces (a1: surface of CRF; b1: surface of WRF) and cross-sections (a2: cross of CRF; b1: cross of WRF) of the regenerated fibers

Mechanical Properties

Table 1. Mechanical Properties of the Novel Fibers

Sample	Elongation-at-break (%)	Diameter (μm)	Tensile Strength (cN/dtex)
Viscose fiber	18-24	---	2.2-2.6
CRFs	5.07 ± 0.32	36 ± 3	2.07 ± 0.17
WRFs	12.91 ± 0.95	38 ± 3	2.76 ± 0.14

The tensile strength and elongation-at-break of the regenerated fibers (CRFs and WRFs) are summarized in Table 1. The results indicated that the tensile strength of the CRFs reached 2.07 cN/dtex. The tensile strength of the CRFs was close to that of viscose fiber (2.2 cN/dtex to 2.6 cN/dtex). The tensile strength of WRFs regenerated from WP (almost no lignin and ash residues) was 2.76 cN/dtex, and the elongation-at-break was 2.5 times that of CRFs. Compared with WRFs, the elongation at break and tensile strength were reduced because of the presence of lignin and smaller content of α -cellulose. Actually, the mechanical properties of the regenerated cellulosic fibers could be enhanced with improved spinning technology. In this work, for purposes of gaining an understanding, the dissolution and spinning of wood pulp were carried out in the same solvent system. It was found that the regenerated fibers obtained from the more mature production line was better than the regenerated fiber obtained from the laboratory-made spinning machine. Therefore, it is speculated that the mechanical properties of straw cellulose regenerated fiber produced by the production line will be improved. As the

conditions were limited, the production line could not be used for spinning straw cellulose regenerated fiber.

CONCLUSIONS

1. A two-component solvent system containing TBAA and DMSO was successfully used to dissolve corn straw pulp containing small amount lignin under mild conditions, and homogeneous solution exhibited typical shear thinning behavior with varying shear rates could be obtained at last.
2. The regenerated fibers were cellulose II, and they had smooth surfaces and circular cross-sections. Despite the presence of residual lignin, nice mechanical properties were also maintained. Although the tensile strength of CRFs was not as large as WRFs, it reached the level of ordinary viscose fiber.
3. This study provides a new environmentally friendly way for the higher value application of corn straw.

ACKNOWLEDGMENTS

The authors are grateful for the support from the Specialized Research Fund for the Forestry Public Welfare Industry (201504602-2).

REFERENCES CITED

- Alongi, J., Camino, G., and Malucelli, G. (2013). "Heating rate effect on char yield from cotton, poly (ethylene terephthalate) and blend fabrics," *Carbohydrate Polymers* 92(2), 1327-1334. DOI:10.1016/j.carbpol.2012.10.029
- Bouwman, L., Goldewijk, K. K., Van Der Hoek, K. W., Beusen, A. H. W., Van Vuuren, D. P., Willems, J., Rufino, M. C., and Stehfest, E. (2013). "Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900–2050 period," *Proceedings of the National Academy of Sciences* 110(52), 20882-20887. DOI: 10.1073/pnas.1012878108
- Cai, T., Zhang, H., Guo, Q., Shao, H., and Hu, X. (2010). "Structure and properties of cellulose fibers from ionic liquids," *Journal of Applied Polymer Science* 115(2), 1047-1053. DOI: 10.1002/app.31081
- Carrillo, F., Colom, X., Sunol, J. J., and Saurina, J. (2004). "Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres," *Eur. Polym. J.* 40(9), 2229-2234. DOI: 10.1016/j.eurpolymj.2004.05.003
- Cheng, G., Varanasi, P., Li, C. L., Liu, H. B., Menichenko, Y. B., Simmons, B. A., Kent, M. S., and Singh, S. (2011). "Transition of cellulose crystalline structure and surface morphology of biomass as a function of ionic liquid pretreatment and its relation to enzymatic hydrolysis," *Biomacromolecules* 12(4), 933-941. DOI: 10.1021/bm101240z

- Faruk, O., Bledzki, A. K., Fink, H.-P., and Sain, M. (2012). "Biocomposites reinforced with natural fibers: 2000–2010," *Progress in Polymer Science* 37(11), 1552-1596. DOI: 10.1016/j.progpolymsci.2012.04.003
- Gao, C., Yu, L., Liu, H., and Chen, L. (2012). "Development of self-reinforced polymer composites," *Progress in Polymer Science* 37(6), 767-780. DOI: 10.1016/j.progpolymsci.2011.09.005
- Huang, Y., Xin, P., Li, J., Shao, Y., Huang, C., and Pan, H. (2016). "Room-temperature dissolution and mechanistic investigation of cellulose in a tetra-butylammonium acetate/dimethyl sulfoxide system," *ACS Sustainable Chemistry & Engineering* 4(4), 2286-2294. DOI:10.1021/acssuschemeng.5b01749.
- Jiang, Z., Miao, J., Yu, Y., and Zhang, L. (2016). "Effective preparation of bamboo cellulose fibers in quaternary ammonium/DMSO solvent," *BioResources* 11(2), 4536-4549. DOI: 10.15376/biores.11.2.4536-4549
- Labbe, N., Rials, T. G., Kelley, S. S., Cheng, Z.-M., Kim, J.-Y., and Li, Y. (2005). "FT-IR imaging and pyrolysis-molecular beam mass spectrometry: New tools to investigate wood tissues," *Wood Science and Technology* 39(1), 61-76. DOI: 10.1007/s00226-004-0274-0
- Lawoko, M., Henriksson, G., and Gellerstedt, G. (2003). "New method for quantitative preparation of lignin-carbohydrate complex from unbleached softwood kraft pulp: Lignin-polysaccharide networks I," *Holzforschung* 57(1), 69-74. DOI: 10.1515/HF.2003.011
- Li, Q., Zhou, J., and Zhang, L. (2012). "Rheological behavior of cyanoethyl celluloses in aqueous solutions," *Cellulose* 19(5), 1547-1555. DOI: 10.1007/s10570-012-9739-8
- Liu, D., Zhong, T., Chang, P. R., Li, K., and Wu, Q. (2010). "Starch composites reinforced by bamboo cellulosic crystals," *Bioresour. Technol.* 101(7), 2529-2536. DOI: 10.1016/j.biortech.2009.11.058
- Mänttari, M., Pekuri, T., and Nyström, M. (2004). "NF270, a new membrane having promising characteristics and being suitable for treatment of dilute effluents from the paper industry," *Journal of Membrane Science* 242(1-2), 107-116. DOI:10.1016/j.memsci.2003.08.032
- Ma, Y. B., Asaadi, S., Johansson, L. S., Ahvenainen, P., Reza, M., Alekhina, M., Rautkari, L., Michud, A., Hauru, L., Hummel, M., and Sixta, H. (2015). "High-strength composite fibers from cellulose-lignin blends regenerated from ionic liquid solution," *ChemSusChem* 8(23), 4030-4039. DOI:10.1002/cssc.201501094
- Mansikkamäki, P., Lahtinen, M., and Rissanen, K. (2005). "Structural changes of cellulose crystallites induced by mercerisation in different solvent systems; determined by powder X-ray," *Diffraction Method Cellulose* 12(3), 233-242. DOI:10.1007/s10570-004-3132-1
- Miao, J., Sun, H., Yu, Y., Song, X., and Zhang, L. (2014). "Quaternary ammonium acetate: an efficient ionic liquid for the dissolution and regeneration of cellulose," *RSC Advances* 4(69), 36721. DOI:10.1039/c4ra06258b
- Nurmesniemi, H., Poykio, R., Kuokkanen, T., and Ramo, J. (2008). "Chemical sequential extraction of heavy metals and sulphur in bottom ash and in fly ash from a pulp and paper mill complex waste management and research," *Journal of the International Solid Wastes and Public Cleansing Association, ISWA* 26(4), 389-399. DOI:10.1177/0734242X07079051

- Revol, J. F., and Goring, D. (1981). "On the mechanism of the mercerization of cellulose in wood," *Journal of Applied Polymer Science* 26(4), 1275-1282.
DOI:10.1002/app.1981.070260419
- Song, S., Liu, P., Xu, J., Chong, C., Huang, X., Ma, L., and Ni, W. (2017). "Life cycle assessment and economic evaluation of pellet fuel from corn straw in China: A case study in Jilin Province," *Energy* 130, 373-381. DOI: 10.1016/j.energy.2017.04.068
- Sun, H., Miao, J., Yu, Y., and Zhang, L. (2015). "Dissolution of cellulose with a novel solvent and formation of regenerated cellulose fiber," *Applied Physics A* 119, 539-546.
DOI:10.1007/s00339-015-8986-6
- 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 Chemistry* 11(5), 646. DOI:10.1039/b822702k
- Sun, N., Swatloski, R. P., Maxim, M. L., Rahman, M., Harland, A. G., Haque, A., Spear, S. K., Daly, D. T., and Rogers, R. D. (2008). "Magnetite-embedded cellulose fibers prepared from ionic liquid," *Journal of Material Chemistry* 18(3), 283-290.
DOI:10.1039/b713194a
- Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. (2002). "Dissolution of cellulose with ionic liquids," *J. Am. Chem. Soc.* 124(18), 4974-4975. DOI: 10.1021/ja025790m
- Tan, M., Zhao, L., and Zhang, Y. (2011). "Production of 5-hydroxymethyl furfural from cellulose in CrCl₂/zeolite/BMIMCl system," *Biomass Bioenerg.* 35(3), 1367-1370.
DOI: 10.1016/j.biombioe.2010.12.006
- Techapun, C., Poosaran, N., Watanabe, M., and Sasaki, K. (2003). "Thermostable and alkaline-tolerant microbial cellulase-free xylanases produced from agricultural wastes and the properties required for use in pulp bleaching bioprocesses: A review," *Process Biochemistry* 38(9), 1327-1340. DOI:10.1016/s0032-9592(02)00331-x
- Thakur, V. K., Thakur, M. K., Raghavan, P., and Kessler, M. R. (2014). "Progress in green polymer composites from lignin for multifunctional applications: A review," *ACS Sustainable Chemistry and Engineering* 2(5), 1072-1092.
DOI:10.1021/sc500087z
- Tilman, D., Balzer, C., Hill, J., and Befort, B. L. (2011). "Global food demand and the sustainable intensification of agriculture," *Proceedings of the National Academy of Sciences* 108(50), 20260-20264. DOI: 10.1073/pnas.1116437108
- Wang, Y., Sun, M., Yin, L., and Shi, F. (2015). "Inside Back Cover: Catalytic enantioselective arylative dearomatization of 3 - methyl - 2 - vinylindoles enabled by reactivity switch," *Advanced Synthesis and Catalysis* 357(18), 4103-4103.
DOI: 10.1002/adsc.201500901
- Yao, Y., Mukuze, K. S., Zhang, Y., and Wang, H. (2013). "Rheological behavior of cellulose/silk fibroin blend solutions with ionic liquid as solvent," *Cellulose* 21(1), 675-684. DOI: 10.1007/s10570-013-0117-y
- Zhang, H., Wu, J., Zhang, J., and He, J. (2005). "1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose," *Macromolecules* 38(20), 8272-8277. DOI: 10.1021/ma0505676
- Zhang, X., Bol, R., Rahn, C., Xiao, G., Meng, F., and Wu, W. (2017). "Agricultural sustainable intensification improved nitrogen use efficiency and maintained high crop yield during 1980–2014 in Northern China," *Science of the Total Environment* 596, 61-68. DOI: 10.1016/j.scitotenv.2017.04.064
- Zhao, Y., Liu, X., Wang, J., and Zhang, S. (2012). "Effects of cationic structure on

cellulose dissolution in ionic liquids: A molecular dynamics study,” *ChemPhysChem* 13(13), 3126-3133. DOI: 10.1002/cphc.201200286

Zhou, S., Tashiro, K., Hongo, T., Shirataki, H., Yamane, C., and Li, T. (2001). “Influence of water on structure and mechanical properties of regenerated cellulose studied by an organized combination of infrared spectra, X-ray diffraction, and dynamic viscoelastic data measured as functions of temperature and humidity,” *Macromolecules* 34(5), 1274-1280. DOI: 10.1073/pnas.1012878108

Article submitted: November 1, 2017; Peer review completed: February 25, 2018;
Revised version received: May 3, 2018; Accepted: May 5, 2018; Published: May 14, 2018.

DOI: 10.15376/biores.13.3.4916-4930