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Cellulose-wheat gluten bulk plastic materials produced from processing raw powders by severe shear deformation

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ABSTRACT

Cellulose-based renewable bulk plastics with significantly improved mechanical properties were produced by using a small proportion of wheat gluten (WG) as an additive to enhance the material processing capability. The strong shear-deformation during equal channel angular pressing (ECAP) generated effective chain penetration and strong intermolecular interactions between the amorphous cellulose and WG components. The micro-cracking of the obtained materials was minimized, and the processing temperature was reduced. The crystallinity of the cellulose component was also decreased, whereas the crystalline size and regularity was less modified. The present study has further demonstrated that ECAP is a promising methodology to produce renewable and biodegradable "wood plastics" from cellulose-based agricultural waste.

1. Introduction

Developing suitable methodologies to thermally process natural polymers (especially those derived from agricultural waste streams) into packaging materials is a big challenge. Cellulose, being the most abundant polymer in nature with excellent properties in many aspects, has drawn a great attention of both academic research and industrial applications (Klemm, Heublein, Fink, & Bohn, 2005; Lu, Zhang, Rong, Shi, & Yang, 2003; Nishino, Matsuda, & Hirao, 2004; Ragauskas et al., 2006; Shibata, 2009; Vazquez & Alvarez, 2009; Wang & Zhang, 2009). However, it is difficult to thermally process cellulose into plastic materials without resorting to significant chemical modification due to the complicated structure and high crystallinity. Recently we have reported the success in consolidating cellulose particles into bulk plastic materials through equal channel angular pressing (ECAP) without using any additional plasticizers (Zhang, Wu, Gao, & Xia, 2012). The strong shear deformation during the ECAP process caused an efficient deformation of cellulose granular and crystalline structures, resulting in effective chain penetration and strong intermolecular interactions throughout the whole material. This initial success provides a potential method to manufacture renewable and biodegradable materials from cellulose-based agricultural waste.

However, the rigid cellulose lacks sufficient mobility to cope with the large shear deformation in ECAP, thus some extend of micro-cracking could occur parallel to the shear plane in the bulk samples especially when processing at lower temperatures (Zhang et al., 2012). This could generate a series of problems in material performance especially mechanical properties. In the present research, wheat gluten (WG) was used as an additive in processing cellulose particles. As a by-product in the wheat starch industry with the lowest price among plant proteins, the amorphous WG can be processed into thermal plastics with excellent properties (Belton, 1999; Zhang, Burgar, Do, & Lourbakos, 2005; Zhang, Hoobin, Burgar, & Do, 2006). In addition, WG is partially insoluble and its water resistance can be further improved by crosslinking during thermal processing. Since both cellulose and WG are biodegradable natural polymers, the combined cellulose/WG materials would still retain the renewable and biodegradable characteristics.

The material processing methodologies, morphologies, mechanical properties and glass transition behaviors of the cellulose/WG materials were examined. Molecular motions, phase structures and intermolecular interactions between cellulose and WG components were also studied using high-resolution solid-state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD), and correlated to the material performance.

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2. Experimental

2.1. Materials

The cotton linters microcrystalline cellulose powder (20 μm) was purchased from Sigma–Aldrich (product number 310697, molecular weight Mn around 70,000) with natural moisture content of about 6 wt%. The raw vital wheat gluten (WG) powder was supplied by Manildra Group Australia as food grade products obtained via commercial processing. The WG contained 80% of proteins, 15% of residual starch, 4% lipid, and 1% of fiber plus other impurities on a dry base. The moisture content in the WG was 9–10%. These samples were processed without any pre-treatment.

2.2. ECAP set-up

The ECAP set-up is the same as described previously (Zhang, Gao, Wu, & Xia, 2008; Zhang et al., 2012). The die had a 90° angle between the channels of 9 mm × 9 mm in cross section. The cellulose particles or cellulose/WG mixtures at different proportions were ball-milled for 2 h (a 10 min break in the middle of milling to avoid excessive heating) at a speed of 300 rpm before ECAP. The ratio of powder sample to steel balls was 1:20 (in weight) and both large and small (7 and 4 mm in diameter, respectively) steel balls (1:1 in weight) were used. The powder samples were packed in the entrance channel, and pressed at a speed of 25 mm/min with a constant back pressure of 100 MPa. L-shaped bulk cellulose samples with a length of 40–45 mm passing the shear plane (the longer arm of L) were produced following ECAP. The samples were then conditioned at room temperature under a relative humidity (RH) of 50 ± 2% (achieved by using saturated $Mg(NO_3)_2$ salt solution) for 2 weeks before any testing. The moisture contents of these samples were around 6%, measured as weight loss after heating at 105 °C for 5–6 h to reach a constant weight.

2.3. Material characterization

The details of material characterization methods were described previously (Zhang et al., 2008, 2012). Fracture surfaces of the cellulose/WG samples were produced by bending at a location passing the shear plane in ECAP after frozen in liquid nitrogen, and examined by scanning electron microscopy (SEM) using Philips FEI XL-30 SFEG. Sputter coating with gold of 20 nm thickness was conducted and the electron beam with an accelerating voltage of 5 kV was used to produce high definition images.

For 3-point bending testing, each sample bar was placed on two parallel rollers with a span of 32 mm. The load and displacement were recorded and converted into stress versus strain curves to obtain the flexural strength and elastic modulus.

The X-ray diffraction (XRD) measurements were conducted on a Bruker D8 XRD operating at 40 kV, 40 mA, Cu Kα radiation monochromatized with a graphite sample monochromator using program Topas^{TM} V4.1.

A PerkinElmer PYRIS^{TM} Diamond dynamic mechanical analyzer (DMA) in the single cantilever bending mode was used for DMA experiments at a frequency of 1 Hz. The temperature range was set from −100 °C to 160 °C with a heating rate of 2 °C/min.

High-resolution solid-state NMR experiments were conducted at room temperature either using a Bruker AV500 spectroscopy (125 MHz for ^{13}C and 500 MHz for ^{1}H) or a Varian NMR300 System (75 MHz for ^{13}C and 300 MHz for ^{1}H). ^{13}C NMR spectra were observed under cross polarization (CP), magic angle spinning (MAS) and high power dipolar decoupling (DD) conditions. The 90° pulse for ^{1}H and ^{13}C channels was 2.9 or 5.5 μs for the experiments using Bruker AV500 or Varian NMR300. The spinning rate of MAS was set at 7.5 kHz and a contact time of 1.0 ms was used for measuring all CP/MAS spectra in both spectrometers. The chemical shift of ^{13}C spectra was determined by taking the carbonyl carbon of solid glycine (176.3 ppm) as an external reference standard. Torchia pulse sequence (Torchia, 1978) was used to measure the ^{13}C CP/MAS spectra of the crystalline components with longer ^{13}C spin-lattice relaxation time (^{13}C T_1) on the Bruker AV500 NMR spectrometer. The ^{1}H spin-lattice relaxation time (^{1}H T_1) was measured indirectly through the change of ^{13}C magnetization prepared by CP after inversion-recovery pulse sequence in ^{1}H channel (McBrierty & Packer, 1993) with a long repetition time of 8–12 s on the Varian NMR300 system.

Table 1
3-Point bending strength and modulus of cellulose/WG materials.[a]

Samples	ECAP processing temperature (°C)	Flextural strength (MPa)	Elastic modulus (MPa)
Cellulose, 150 °C	150	7.6	3215
Cellulose/WG = 90/10	125	40.0	4987
Cellulose/WG = 80/20	125	17.9	3244
Cellulose/WG = 70/30	125	39.1	3761

[a] Error bar of 7–15%.

3. Results and discussion

The images of cellulose particles before and after ball milling are shown in Fig. 1. It appears that the particle size were not significantly decrease by the milling (Fig. 1(a) and (b)). Efficient mixing between cellulose and WG was achieved by the ball-milling with WG particles stuck onto the surface of cellulose particles (Fig. 1(c)). Note that continuous structures were obtained for cellulose/WG materials containing 10–30 wt% of WG (shown in Fig. 1(d–f)) after ECAP at 125 °C. Broken structures of the plastic phases were observed on the fracture surfaces at a higher magnification as shown in Fig. 1(d'–f'). Importantly, no observable cracking was found in the materials when using 10–30% of WG as additives. In contrast, the cellulose-alone bulk plastics produced via ECAP at 130 °C displayed cracking along the shear-plane direction (Zhang et al., 2012). The amorphous WG added could act as lubricant or plasticizing agent at 125 °C to enhance the ability of the cellulose materials to sustain the severe shear deformation during ECAP. Processing at higher temperatures (e.g. 150 °C) was also conducted but porous structures were observed possibly due to thermal decomposition of WG under the ECAP conditions (Zhang et al., 2008).

The results of 3-point bending tests for the cellulose/WG materials are shown in Table 1 with comparison to those of milled cellulose processed at 150 °C (Zhang et al., 2012). The flexural strengths of the cellulose/WG materials are all considerably higher than the strength of the cellulose-only material and comparable to those of WG (flexural strength of 28–37 MPa) processed at 120–130 °C using ECAP (Zhang et al., 2008), indicating the mechanical strength of the cellulose materials was significantly improved by using WG as additives in ECAP, probably as a result of minimized micro-cracking in cellulose phase. The elastic moduli, on the other hand, are comparable.

The DMA results of the cellulose/WG samples are shown in Fig. 2 with key data listed in Table 2. Similar to those of plasticized WG and ECAP processed cellulose (Zhang et al., 2005, 2006, 2008, 2012), the storage modulus E' of the cellulose/WG samples experienced a little change as temperature increased in the low range, and then dropped at a critical temperature when the glass transition started while a tan δ (loss modulus E"/storage modulus E') peak was observed corresponding to the transition. Note that the E' values of cellulose/WG samples below T_g (ca, 20 °C) were significantly higher (1.7–2.1 times) than those of the WG-only samples, whereas the pre-milled cellulose-alone sample processed at 150 °C displayed

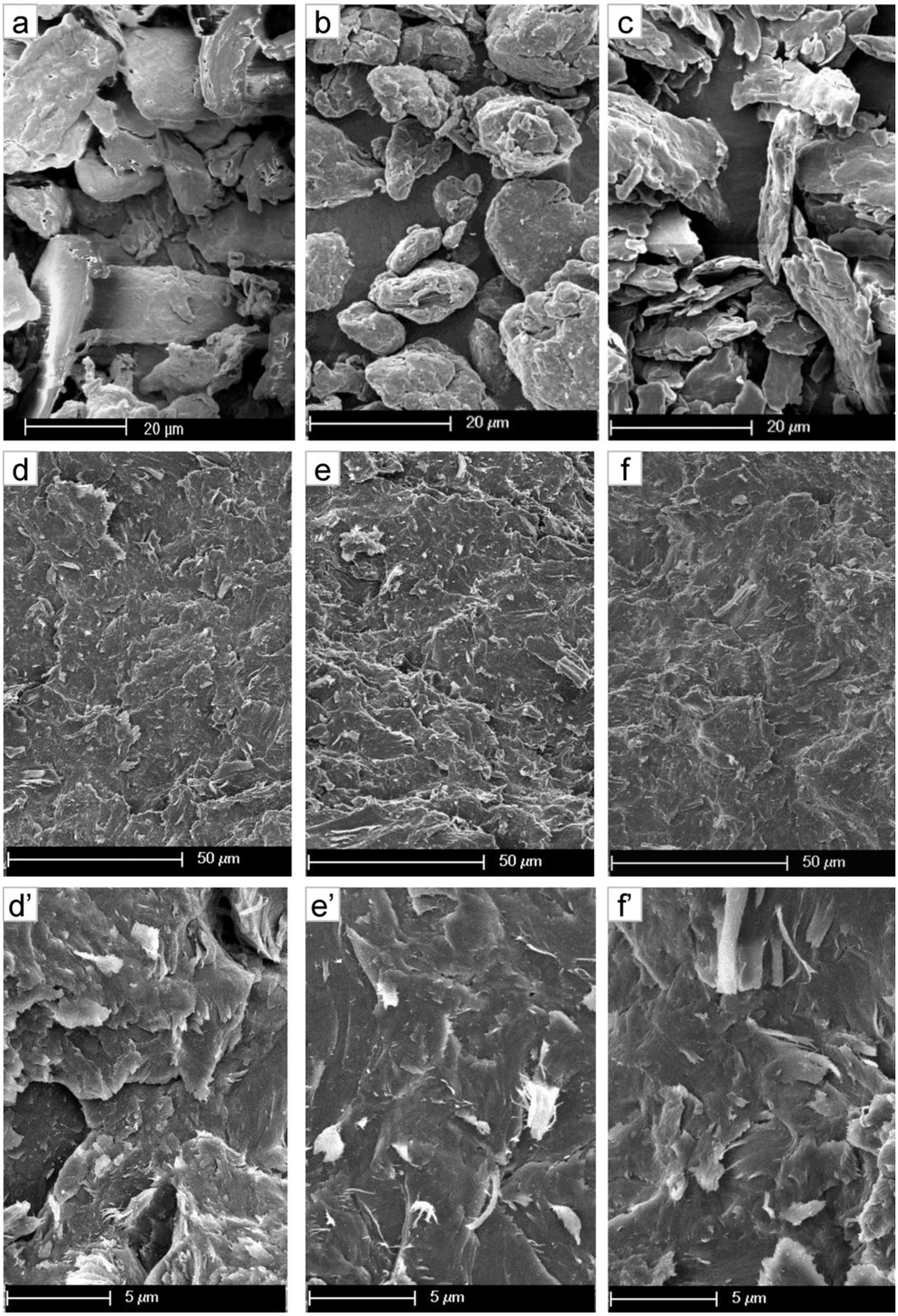

Fig. 1. SEM images of (a) original cellulose particles, (b) ball-milled cellulose powder, (c) ball-milled cellulose/WG = 80/20 mixture, and the fracture surfaces of cellulose/WG bulk plastic samples with WG of 10% (d, d'), 20% (e, e') and 30% (f, f') processed by ECAP at 125 °C.

a lower E' at 20 °C than that of WG. The low E' of the cellulose sample could be attributed to micro-cracking, and such cracking was largely eliminated when using WG as additives. Because the theoretical modulus of the microcrystalline cellulose (Eichhorn & Young, 2001; Tanaka & Iwata, 2006) is much higher than that of WG, the decrease in E' of cellulose/WG systems reflected the amount of WG added: the higher the amount of WG used in the materials, the lower the E' below T_g and the lower the $T_{\text{g-start}}$ value as well. This seems not quite consistent with the 3-piont bending results shown in Table 1, possibly because the WG phase played a different role in DMA and the 3-point bending test.

The tan δ maxima corresponding to the glass transition for the cellulose/WG samples all shifted to higher temperatures while the maximum values all decreased as compared to those in the WG-only sample, suggesting motional restriction of the WG molecules in the matrix of the amorphous cellulose at the glass transition

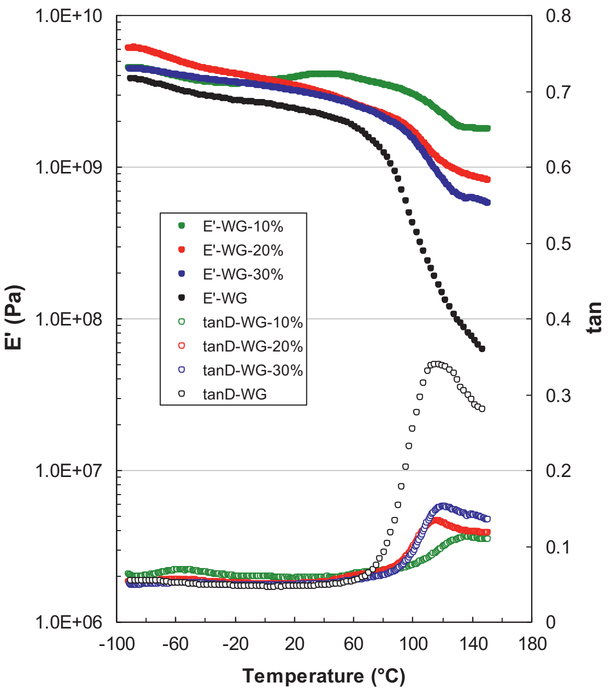

Fig. 2. DMA results (E' and tan δ) of the ECAP processed WG and cellulose/WG bulk plastic samples (WG-10%, -20%, and -30%).

temperature. These results suggest that the WG and amorphous cellulose components were intimately mixed with strong intermolecular interactions possibly through hydrogen-bonding. It is interesting to note that these tan δ maximum values of cellulose/WG systems are also lower than the value of the cellulose-only system produced at a higher temperature (150 °C). For cellulose/WG = 90/10 sample, the T_g was not distinct at all from both E' and tan δ curves, indicating a pronounced motional restriction for WG and cellulose polymer chains and even chemical crosslinking between the two components under ECAP conditions.

Multi-pass (8 passes) ECAP was also applied to the cellulose/WG = 80/20 sample, but it generated a much lower E' below T_g (1.08 GPa at 20 °C). The T_g also shifted to lower temperatures with $T_{g\text{-start}}$ at 67 °C, even lower than that of the ECAP processed WG. It seems such multi-pass processing significantly disrupted the material structures due to repeated severe shear-deformation.

The XRD results of pre-milled and ECAP processed (at 125 °C) cellulose and cellulose/WG samples are shown in Fig. 3, with cellulose I type patterns corresponding to the (1 0 1), (1 0 −1), (0 0 2) and (0 4 0) crystallographic structures of cellulose (Focher et al., 2001; Ishii, Tatsumi, & Matsumoto, 2003; Newman, 1999; VanderHart & Atalla, 1984; Zhao et al., 2007). The intensities of these patterns were decreased and all peaks became broader as compared to the original cellulose powder (Zhang et al., 2012), indicating a decrease in cellulose crystallinity and crystalline regularity after the milling and processing with WG. However, the cellulose/WG materials showed only a minor difference as compared to the ball-milled cellulose, and this needs to be further examined.

Table 2
DMA results of the cellulose and cellulose/WG bulk plastics processed by ECAP.[a]

Samples	E' at 20 °C (GPa)	$T_{g\text{-start}}$ (°C from E')	tan δ peak (°C)	tan δ max.
Cellulose, 150 °C	1.84	106	138	0.181
Cellulose/WG = 90/10	3.91	101	136	0.113
Cellulose/WG = 80/20	3.44	93	118	0.134
Cellulose/WG = 70/30	3.19	84	121	0.152
WG, 130 °C	2.42	74	117	0.340

[a] The cellulose sample was processed at 150 °C after ball-milling and the data were taken from a previous publication (Zhang et al., 2012). The WG sample was processed at 130 °C without prior-milling and the data were taken from a previous publication (Zhang et al., 2008). All cellulose/WG samples were processed at 125 °C.

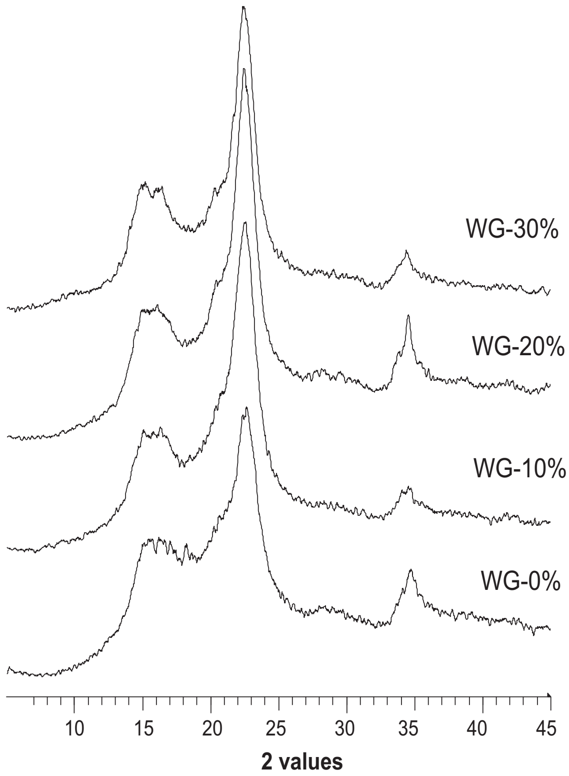

Fig. 3. XRD results of the ball-milled cellulose (WG-0%) and the ECAP processed cellulose/WG bulk plastic samples (WG-10%, -20%, and -30%).

High-resolution solid-state NMR was used to study the crystalline structures of the cellulose/WG systems as leveraging the methodologies from a series of previous publications (Atalla & VanderHart, 1999; Horii, Hirai, & Kitamaru, 1987; Ishii et al., 2003; Newman, 1999; VanderHart & Atalla, 1984). The ^{13}C CP/MAS NMR spectrum of the original cellulose powder (Fig. 4A) has been assigned to C-1 (106 ppm), C-4 (80–95 ppm), C-2,3,5 (70–80 ppm) and C-6 (60–70 ppm) of the glycosyl units respectively. The resonances of WG (Fig. 4) were assigned to proteins with the C=O at 174 ppm, the C-α, C-β and C-γ resonances at 50–60 and 30–15 ppm as the major components (Zhang et al., 2005), while the resonances of residual starch were detected at 103, 83 and 73 ppm (C-1, C-4 and C-2,3,5 of starch), and the C-6 overlapped with those of proteins at 64 ppm (Zhang et al., 2005). After ECAP, the linewidth of most WG resonances in the cellulose/WG samples became broader suggesting the formation of a broad distribution of chemical environment of the component as consistent with its strong intermolecular interactions with the amorphous cellulose component.

As described previously, the separation of C-4 or C-6 resonances of cellulose was due to the crystalline (91 or 67 ppm) and the amorphous (85 or 64 ppm) phases (Horii et al., 1987; Newman, 1999), and the relative intensities could be used to estimate the crystallinity of the cellulose component in the processed materials. The effect of weak resonance of starch (impurity in WG) at 83 and 64 ppm could be ignored especially when the WG content is low (e.g. cellulose/WG = 90/10). However, in the systems containing a high amount of WG, these residue starch signals would overlap with the intensities of amorphous cellulose, leading to underestimated crystallinity. Nevertheless, the crystallinity data (Table 3) indicate that the milling of cellulose/WG mixture did not decrease

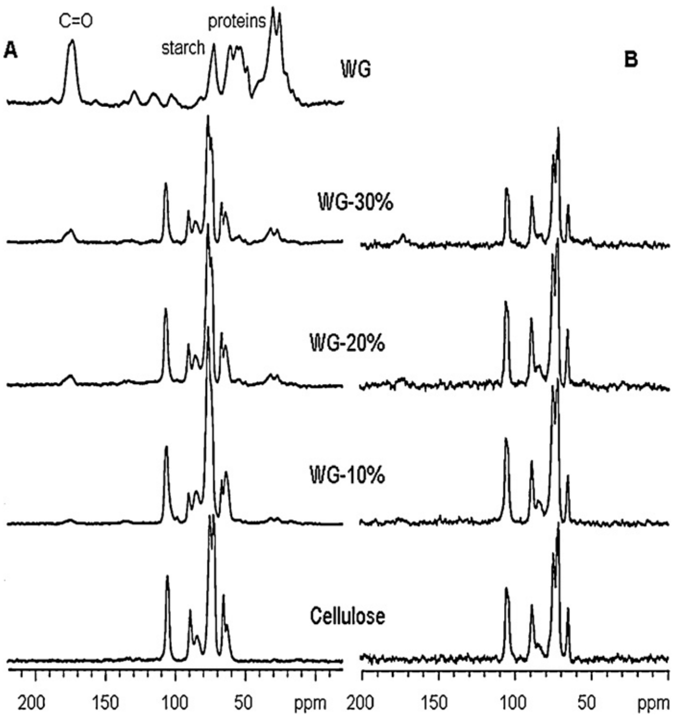

Fig. 4. ^{13}C CP/MAS NMR spectra (500 MHz) of the original cellulose particles (cellulose), raw WG powder (WG) and the ECAP processed cellulose/WG bulk plastic samples (WG-10%, -20% and -30%), observed by (A) the normal CP/MAS sequence and (B), the Torchia pulse sequence with the τ delay time of 50 s (mainly the crystalline phases were detected).

Table 3
The crystallinity of the cellulose/WG samples measure by NMR (500 MHz).

Cellulose samples	Measured at 85–91 ppm	Measured at 64–67 ppm
Cellulose particles, 20 μm	51%	50%
Cellulose, ball-milled[a]	29%	32%
Cellulose/WG = 80/20 ball-milled	44%	40%
Cellulose/WG = 70/30	38%	36%
Cellulose/WG = 80/20	35%	38%
Cellulose/WG = 90/10	25%	28%

[a] Data taken from Zhang et al. (2012).

the cellulose crystallinity as greatly as that in milling cellulose-only powder (Zhang et al., 2012) under the same milling condition. ECAP process conducted thereafter further reduced the crystallinity to some extent, but only the crystallinity of cellulose/WG = 90/10 sample was reduced to 25% after ECAP, a level similar to that reached in the cellulose-only system. When the WG content was higher (the 70/30 and 80/20 systems), a crystallinity within 35–38% for the cellulose component was obtained. These might be attributed to the lubricating or plasticizing effect of WG, which reduced the milling and shear deformation effect on the crystalline cellulose. However, the extent of decrease in the crystallinity of the cellulose component was still larger than that in the cellulose/proteins blends prepared by solution casting (Yang et al., 2009) or mechanical mixing (Zhou, Zheng, Wei, Huang, & Chen, 2008), indicating the disruption of cellulose crystalline structures due to milling and ECAP.

The ^{13}C spin-lattice (T_1) relaxation time is sensitive to molecular motions of different groups in different phases due to the ^{13}C rare unclear system without spin-diffusion interactions. In general longer ^{13}C T_1 values were obtained for carbon resonances in the crystalline phases while the values for those in the amorphous phases would be much shorter. Fig. 4B displays the ^{13}C NMR spectra of the crystalline phases of the cellulose component in the cellulose/WG systems as detected by the Torchia pulse sequence where amorphous components had decayed significantly when a long delay time (τ = 50 s) was used. The similarity of these spectra as compared to that of the original cellulose sample before milling and processing indicates that the cellulose I type character remained in the cellulose components after ECAP with WG and the crystalline size and regularity were similar to those of the original cellulose.

High-resolution solid-state NMR also provides a powerful technique to examine phase structures and intermolecular interactions between different components. The study of ^{1}H spin-lattice (T_1) relaxation time for each component in a multi-component system provides not only the information of molecular motions at MHz range, but also the homo- or heterogeneity of the system on a scale of effective spin-diffusion length during the ^{1}H T_1 times, ca. ~30 nm (McBrierty & Packer, 1993) for rigid polymer systems. Since the resonances of WG at 174 and 25–30 ppm are not overlapping with those of cellulose in the spectra of cellulose/WG samples (Fig. 4), the ^{1}H T_1 values observed from these WG resonances should reflect the behavior of the WG component in the cellulose/WG systems.

^{1}H T_1 data of cellulose, WG and the cellulose/WG samples observed via different ^{13}C resonances are summarized in Table 4. The values of the ECAP processed WG sample was 0.43–0.48 as observed at 174 and 27 ppm, while those at 106 and 74 ppm reflecting the nature of residual starch in WG. When introducing WG as an additive in the cellulose materials, the ^{1}H T_1 data of the WG component (observed at 174 ppm) increased by 100% and 140% in the cellulose/WG = 70/30 and 80/20 samples, respectively. These increases are larger than those observed at 27 ppm of the WG component (45 and 75% in the corresponding systems), suggesting that the C=O groups of the WG may have been involved in the intermolecular interactions with the cellulose matrix possibly through hydrogen bonding. The WG signals became so broad in the 90/10 sample (see Fig. 4) that the T_1 values were detected with a large error bar, but the same trend can still be observed. On the other hand, the ^{1}H T_1 of the cellulose component was also decreased to some extent. These results indicated that strong spin-diffusion interactions occurred between the WG and cellulose components, leading to the ^{1}H T_1 values of both components to average out. However, the crystalline phase in the cellulose component was still present and the cellulose/WG materials did not reach a homogeneous mixing. Therefore, the ^{1}H T_1 data observed for both cellulose

Table 4
^{1}H T_1 (s) values (300 MHz) of the cellulose/WG materials processed by ECAP.

Samples	174 ppm	106 ppm	74 ppm	27 ppm
Cellulose particles, 20 μm		2.5 ± 0.1	2.4 ± 0.1	
Cellulose-milled[a]		2.3 ± 0.1	2.2 ± 0.1	
Cellulose, 150 °C (ECAP)		2.2 ± 0.1	2.1 ± 0.1	
Cellulose/WG = 90/10[a]	1.36 ± 0.43	1.94 ± 0.03	1.99 ± 0.03	1.25 ± 0.53
Cellulose/WG = 80/20[a]	1.04 ± 0.05	1.86 ± 0.01	1.75 ± 0.04	0.82 ± 0.15
Cellulose/WG = 70/30[a]	0.87 ± 0.08	1.82 ± 0.05	1.71 ± 0.02	0.70 ± 0.11
WG, 130 C (ECAP)[a]	0.43 ± 0.02	0.68 ± 0.04	0.75 ± 0.03	0.48 ± 0.04

[a] All of these samples were processed at 125 °C and 25 mm/min after ball mill. WG was processed at 2 mm/min without ball mill.

and WG components did not become identical yet on the ^{1}H T_1 measurement scale, ca. ~30 nm. In addition, the strong interactions only occurred between the WG segments and the amorphous cellulose component and thus, the ^{1}H T_1 increase for the WG component was much greater than the ^{1}H T_1 decrease in the cellulose component.

The results presented in this paper have further demonstrated that the ECAP technique is an effective methodology to process raw cellulose powders into plastic bulk materials and the material performance can be improved by using a small amount of plastic additives such as WG. The ECAP processing of cellulose/WG materials was conducted at 125 °C, and this temperature is relatively low compared to those used in conventional thermal extrusion or molding of many conventional semi-crystalline polymers. Trials on wood particles will be carried out next to produce bulk "wood plastics" where the "impurities" existing in wood (such as hemicellulose and lignin) might act as useful intrinsic "additives". The success of this work could lead to a new paradigm for manufacturing plastic materials from agricultural cellulose-based waste and the methodology should be easily up-scaled for industrial applications.

4. Conclusions

The present study has further demonstrated that ECAP is an effective method to process cellulose powder into bulk plastic materials at relatively low temperatures. When using WG as an additive, the material processing capability was significantly improved. Strong intermolecular interactions between the WG segments and the amorphous cellulose matrix were formed under such a severe shear deformation condition, which minimized the microcracking in the materials, and consequently, significantly improved the mechanical strength of the cellulose/WG samples as compared to that of the cellulose-only samples. The crystallinity of the cellulose component was reduced; however the crystalline structure was less modified. The ECAP process promises to offer a new opportunity to produce renewable and biodegradable "wood plastics" from cellulose-based agricultural waste streams.

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