



## Bulk cellulose plastic materials from processing cellulose powder using back pressure-equal channel angular pressing

Xiaoqing Zhang<sup>a,\*</sup>, Xiaolin Wu<sup>b</sup>, Dachao Gao<sup>a</sup>, Kenong Xia<sup>b,\*\*</sup>

<sup>a</sup> CSIRO Materials Science and Engineering, Private Bag 33, Clayton South MDC, Clayton South, VIC 3169, Australia

<sup>b</sup> Department of Mechanical Engineering, The University of Melbourne, VIC 3010, Australia

### ARTICLE INFO

#### Article history:

Received 8 August 2011

Received in revised form

27 September 2011

Accepted 7 November 2011

Available online 15 November 2011

#### Keywords:

Cellulose

Renewable natural polymers

Crystalline structures

Polymer processing

Equal channel angular pressing

### ABSTRACT

Bulk cellulose plastic materials with a continuous morphology were successfully processed from cellulose powder through back pressure-equal channel angular pressing (BP-ECAP) at 150 °C without using any additives. The strong shear deformation during the process caused an efficient deformation of cellulose granular and crystalline structures, resulting in effective chain penetration and strong intermolecular interactions throughout the whole material. The mechanical behaviour of the cellulose plastics was comparable to those of polymer/cellulose composites. Ball milling the cellulose powder prior to processing disrupted the crystalline structures thus resulting in more significant modifications of the molecular motions of the cellulose. The outcome of this research provides a potential methodology for manufacturing renewable and biodegradable bulk materials from cellulose-based agricultural waste.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

Cellulose is the most abundant raw polymer in nature and can be considered to be an inexhaustible resource. Its renewable, biodegradable and biocompatible nature in conjunction with low density, good strength and high stiffness, has made it one of the most important natural materials (Klemm, Heublein, Fink, & Bohn, 2005; Ragauskas et al., 2006; Wang & Zhang, 2009, chap. 6). However, thermal processing of natural polymers (not only cellulose, but also starch and plant proteins) using conventional thermal methods is difficult due to strong intra- and intermolecular interactions (hydrogen bonding) and even chemical crosslinking in these materials. Addition of a large amount of plasticizers is necessary for thermal processing starch and proteins to enhance their flexibility and extensibility, and therefore to improve the processing capability. But this method cannot overcome the difficulty in thermal processing cellulose. As a highly crystalline material with a relatively low thermal decomposition temperature, cellulose would normally undergo thermal decomposition before melting upon heating, although melting cellulose under special conditions might be achieved (Nordin, Nyren, & Back, 1973, 1974, Schroeter &

Felix, 2005). Currently cellulose is widely used to blend with other polymers or as a reinforcing agent in the production of polymer composites. In many cases, chemical modification or pretreatment of cellulose is needed in the process (Lu, Zhang, Rong, Shi, & Yang, 2003; Nishino, Matsuda, & Hirao, 2004; Shibata, 2009, chap. 12; Vazquez & Alvarez, 2009, chap. 11; Wang & Zhang, 2009, chap. 6). Development of a new material processing technology for cellulose is desirable for extending the application of cellulose-based materials.

Equal channel angular pressing (ECAP) with back pressure (BP) was originally developed as a novel process to consolidate metal particles (Xia & Wu, 2005; Xia, Wu, Honma, & Ringer, 2007; Wu & Xia, 2007). The oxide layer on the metal surface would be disrupted by the severe shear deformation involved in the process to generate an intimate contact among metal particles. Full density metal was produced with excellent mechanical properties. The other advantage of ECAP consolidation is that the processing can be conducted at temperatures far below the melting temperature of metals. Similar technologies have been applied to polymer materials in the last decade, mainly focused on modification of semi-crystalline polymers and production of their nano-composites (Li, Xia, & Sue, 2000; Phillips, Zhu, & Edward, 2006; Sue & Li, 1998; Sue, Dian, & Li, 1999; Woen & Sue, 2005; Woen, Xia, & Sue, 2005; Xia, Sue, Hsieh, & Huang, 2001; Xia, Sue, & Rieker, 2000). The strong shear deformation during the process (as compared to thermal extrusion in the molten state) could effectively modify polymer morphologies and chain orientation at a temperature below the glass transition

\* Corresponding author. Tel.: +61 3 95452653; fax: +61 3 95441128.

\*\* Corresponding author. Tel.: +61 3 83446664; fax: +61 3 93478784.

E-mail addresses: [Xiaoqing.Zhang@csiro.au](mailto:Xiaoqing.Zhang@csiro.au) (X. Zhang), [K.Xia@unimelb.edu.au](mailto:K.Xia@unimelb.edu.au) (K. Xia).

temperature ( $T_g$ ) for amorphous polymers or the melting temperature ( $T_m$ ) for semi-crystalline polymers, resulting in significant modification of structures and mechanical properties. The advantages of the BP-ECAP technology, especially the low temperature processing capability, are desirable for processing natural polymers into plastic bulk materials. Due to the high shear strain (to 2.0 with a ECAP die of  $90^\circ$ ) achieved in the process (Phillips et al., 2006; Sue & Li, 1998; Sue et al., 1999; Xia et al., 2000), it is expected that the granular structures and crystalline phases of cellulose would be disrupted to some extent and this would be beneficial to the formation of a continuous morphology throughout the material, resulting in the production of cellulose-based biomaterials.

Bulk plastics from raw wheat starch (WS) and wheat gluten (WG) powders were produced by this methodology, and the mechanical strengths of these materials were comparable to those of conventional polymers but stronger than those of thermoplastic WS or plasticized WG (Zhang, Gao, Wu, & Xia, 2008). In the present research, we attempt to use this BP-ECAP methodology to produce bulk plastic materials from cellulose particles which is difficult to be thermally processed by any conventional polymer processing methodologies. A series of advanced material analytical techniques including high-resolution solid-state nuclear magnetic resonance (NMR) and dynamic mechanical analysis (DMA) and X-ray diffraction (XRD) were used to characterize the obtained cellulose plastics. The material morphology, phase structures and molecular motions were examined and correlated to the material performance. The potential in manufacturing bulk cellulose-based natural polymer materials was also discussed.

## 2. Materials and methods

### 2.1. Materials

The cotton linters microcrystalline cellulose powder (20  $\mu\text{m}$ ) was purchased from Sigma–Aldrich (product number 310697), and processed without any pre-treatment or additives. Natural moisture content of the cellulose powder was about 6 wt%.

### 2.2. BP-ECAP processing method

The BP-ECAP set-up is shown in Fig. 1, the same as that reported previously (Zhang et al., 2008). The die had a  $90^\circ$  angle with a sharp corner and the channel dimensions were 9 mm  $\times$  9 mm in cross section. In addition to the forward plunger in the entrance channel, a back plunger was placed in the exit channel to provide a constant BP during ECAP. The die was heated to and kept at a processing temperature using a heating device controlled within  $\pm 1^\circ\text{C}$  with a K-type thermal couple placed close to the sample. The powder was packed in the entrance channel. Once the temperature reached a target value and stabilized, pressing started at a certain speed with a constant back pressure of 100 MPa. The shear strain was 2 for using this  $90^\circ$  die and the stress for pressing the sample through the shear zone varied over a broad range (up to 1200 MPa) for different samples at different processing temperatures.

Ball milling was also conducted in some cases with a ratio of sample/steel balls = 1/20 (in weight) for 2 h (10 min break in the middle of milling to avoid excessive heating) at a speed of 300 rpm using both large and small (1:1 in weight) steel balls (7 and 4 mm in diameter, respectively). ECAP was conducted immediately after the milling following the same procedures.

L-shaped bulk cellulose samples with a cross section of  $\sim 9\text{ mm} \times 9\text{ mm}$  and a length of 40–45 mm passing the shear plane (the longer arm of L) were produced by the BP-ECAP method under varied conditions. The sample density was determined by carefully measuring the dimensions and weight. All samples were

conditioned at room temperature (20–22  $^\circ\text{C}$ ) under relative humidity (RH) of  $50 \pm 2\%$  (achieved by using saturated  $\text{Mg}(\text{NO}_3)_2$  salt solution) for 2 weeks before testing. The moisture contents of the processed samples were around 5–6% after the conditioning, measured as weight loss after heating at 105  $^\circ\text{C}$  for 5–6 h to reach a constant weight.

### 2.3. SEM analysis

Fracture surfaces of the samples were produced by bending at specific locations of the ECAP processed sample either before or after passing the shear plane, and examined by scanning electron microscopy (SEM) using Philips FEI XL-30 SFEG. The samples were mounted with double-sided conductive tape and then sputter coated with gold of 20 nm thickness in argon atmosphere. The electron beam with an accelerating voltage of 3–5 kV was used to produce high definition images.

### 2.4. XRD analysis

The X-ray diffraction (XRD) measurements were conducted on a Bruker D8 XRD operating at 40 kV, 40 mA, Cu K $\alpha$  radiation monochromatized with a graphite sample monochromator using program Topas<sup>TM</sup> V4.1. The diffractogram was recorded between  $2\theta$  angles of  $2^\circ$  and  $45^\circ$ .

### 2.5. DMA analysis

A PerkinElmer PYRIS<sup>TM</sup> Diamond DMA was used for DMA experiments in dual cantilever bending mode at a frequency of 1 Hz. The temperature range was set from  $-100$  to  $230^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}/\text{min}$ . The storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan \delta$  ( $E'/E''$ ) were recorded as a function of temperature throughout the experiment.

### 2.6. NMR spectroscopy

High-resolution solid-state NMR experiments were conducted at room temperature using a Bruker AV500 spectrometer at resonance frequencies of 125 MHz for  $^{13}\text{C}$  and 500 MHz for  $^1\text{H}$ .  $^{13}\text{C}$  NMR spectra were observed under cross polarization (CP), magic angle spinning (MAS) and high power dipolar decoupling (DD) technique. The  $90^\circ$  pulse was 2.9  $\mu\text{s}$  for  $^1\text{H}$  and  $^{13}\text{C}$ , while the spinning rate of MAS was set at 7.5 kHz. A contact time of 1.0 ms was used for measuring all CP/MAS spectra with a repetition time of 3 s. The  $^{13}\text{C}$  spin-lattice relaxation time ( $T_1$ ) was measured through Torchia pulse sequence (Torchia, 1978). The chemical shift of  $^{13}\text{C}$  spectra was determined by taking the carbonyl carbon of solid glycine (176.3 ppm) as an external reference standard.

## 3. Results and discussion

Bulk cellulose samples were successfully produced by the BP-ECAP method at 130  $^\circ\text{C}$  or 150  $^\circ\text{C}$ . The density of the proportion after passing the shear plane was 1.42–1.52  $\text{g}/\text{cm}^3$ , which is within the range of “true density” of microcrystalline cellulose with 4 wt% of moisture ( $\sim 1.46\text{ g}/\text{cm}^3$ , Sun, 2005). Fig. 1 shows the changes of the original cellulose powder (Fig. 1A) after being processed by BP-ECAP at 150  $^\circ\text{C}$  at a pressing speed of 25 mm/min. Before passing the shear plane, the fracture surface of the sample showed the compression of the packed cellulose particles under high pressure (Fig. 1B), while no such packed particle shapes were observed but a continuous morphology was obtained for the sample after passing the shear plane (Fig. 1C and D). Materials with similar densities were obtained by varying the pressing speed between 0.5 and to 25 mm/min at both 130 and 150  $^\circ\text{C}$ . The color of the samples

Download English Version:

<https://daneshyari.com/en/article/10597824>

Download Persian Version:

<https://daneshyari.com/article/10597824>

[Daneshyari.com](https://daneshyari.com)