Supporting Information

A Fundamental Understanding of Whole Biomass Dissolution in Ionic Liquid for Regeneration of Fiber by Solution-Spinning

Ngoc A. Nguyen,[1]* Keonhee Kim,[2] Christopher C. Bowland,[1] Jong K. Keum,[3] Logan T. Kearney,[1] Nicolas André,[2] Nicole Labbé,[2]* and Amit K. Naskar,[1,2]*

[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Center for Renewable Carbon, University of Tennessee, Knoxville, TN 37996
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

* Correspondence to: nguyenna@ornl.gov (N.A.N.); nlabbe@utk.edu (N.L.); naskarak@ornl.gov (A.K.N.)
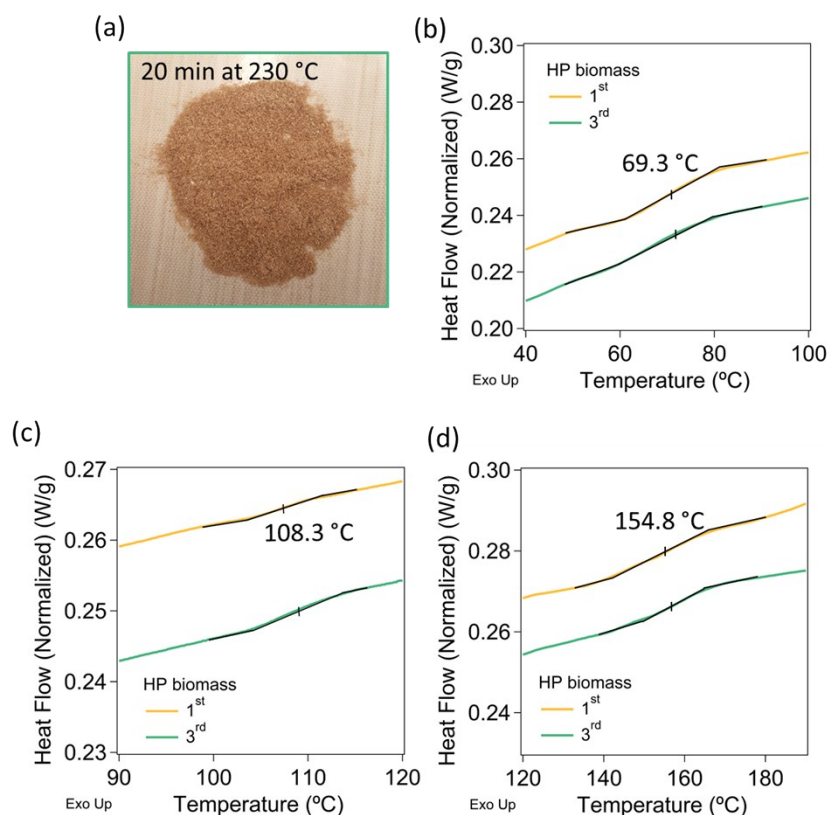
Figure S1. Thermal characteristics of the HP lignocellulosic biomass: (a) Digital image of the HP lignocellulosic biomass after heating at 230 °C for 20 min and (b-d) Glass transition temperatures of the HP biomass.

The digital image in **Figure S1a** shows an example of the HP lignocellulosic biomass after heating on a preheated-hotplate at 230 °C for 20 min indicating no detectable melt and flow characteristics. The material exhibited only a slightly observable color change to dark brown. The glass transition temperatures (T_g) of the HP biomass (**Figures S1b-d**) come from disordered molecular chains of amorphous cellulose, hemicellulose, and lignin. The glass transition temperature of cellulose strongly depends on the moisture content.[1] For example, with a moisture content of *ca.* 5 wt.%, the T_g of cellulose is *ca.* 60 °C.[2] However, the behavior of cellulose amorphous chains is also strongly influenced by the

presence of aromatic and branching hemicellulose and lignin networks due to the steric hindrance effects and the intermolecular interactions, such as hydrogen bonds, that limit the molecular motion and normally result in a higher T_g. Multiple T_gs of wood were reported elsewhere.[1] It was demonstrated that different morphological formation of the wood cells also resulted in various cellulose fibril arrangement and orientation,[3] thus causing different molecular relaxation of the amorphous phase. Here, the HP biomass indicates repeatable and almost identical thermal transitions throughout three different cycles as shown in **Figures S1b-d** (only the first and the third cycles are presented). Three distinguishable thermal relaxations of amorphous structures within the whole HP biomass were detected at ca. 69.3 °C, 108.3 °C, and 154.8 °C (Figures S1b-d) by the DSC scans.
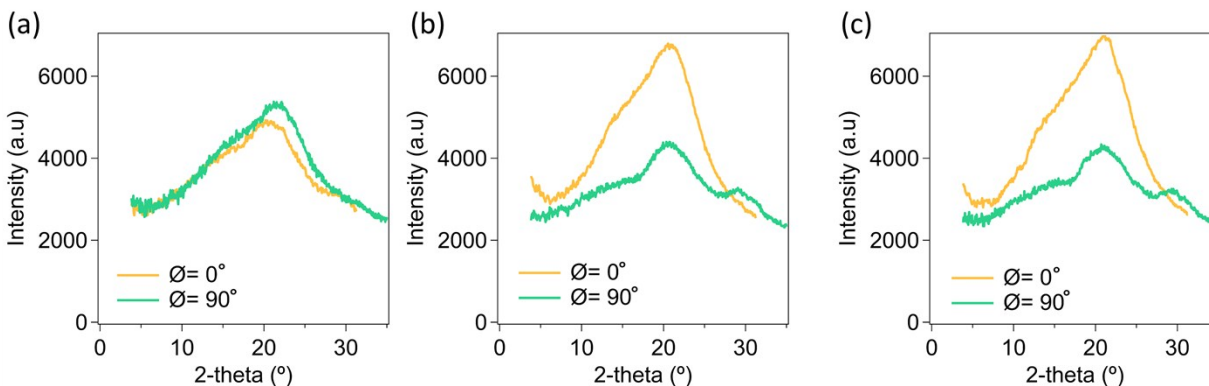
Figure S2. Intensity as a function of 2-theta at Ø = 0° and Ø = 90° of (a) fabricated film from 6.5 wt.% HP biomass- IL solution and spun fibers made from: (b) 5.5 wt.% HP biomass- IL solution and (c) 6.5 wt.% HP biomass- IL solution.

The 6.5 wt.% HP biomass film shows similar scattering profile in Q_{xy} and Q_z (**Figures S2a)**. However, both 5.5 wt.% and 6.5 wt.% HP biomass fibers exhibit considerably high scattering intensity at Ø = 0° indicating higher crystallinity along the fiber axis in comparison to the perpendicular axis (Ø = 90°) (**Figures S2b** and **S2c**). Cellulose normally has broad crystalline peaks, but the main scattering peak at *ca.* 2-theta = 20° can be deconvoluted into four individual peaks.[4] Here, to better evaluate the relative cellulose crystallinity (by volume), the scattering peaks at ~ 20° were deconvoluted into four individual peaks including the contribution of the amorphous area (A_a) and the crystalline area (A_{c1}, A_{c2}, and A_{c3}) as shown in **Figure S3**.
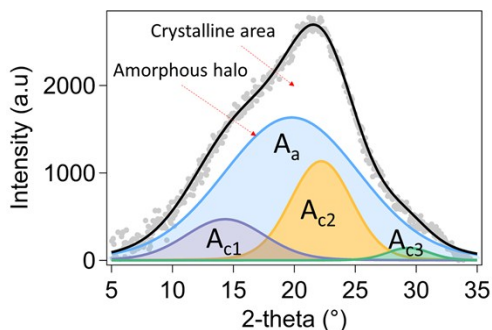
Figure S3. An example of the 2D-WAXS peak deconvolution for evaluating biomass fiber crystallinity.

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The relative crystallinity (C) of the sample can be determined by equation 1.[4]

$$C= (A_{c1} + A_{c2} + A_{c3})/ (A_{c1} + A_{c2} + A_{c3} + A_a) \qquad (1)$$

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