Applications of Enzymatic Saccharification Residues as a Fully Biobased Adhesive

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ABSTRACT

Saccharification of woody biomass often leaves behind solid residues that are rich in lignin. Lignin is a natural phenolic binder for cell walls in woody plants, and therefore the objective of this study was to produce environmentally benign adhesive from such residues. The residues were ground to nano-scale fragments, and then applied to wood with hexamethylenetetramine (HMTA) as a crosslinker. Lap shear results show that the bond strength of nanofiber-containing adhesive was higher if nanofiber was fibrillated from samples pre-saccharified to a higher level (80%) or using a smaller grinding clearance (smaller nanofiber). Addition of HMTA further improved the bond strength to 80% of the value of commercial phenol-formaldehyde adhesive. Infra-red spectroscopy verified corsslinking in nanofiber treated with HMTA. Differential scanning calorimetry revealed 73% degree of curing. Overall results show that a fully biobased adhesive can be prepared from wood saccharification residues without purifying for lignin.

Keywords: adhesion, lignin, saccharification residues, green adhesives, nanofiber

1 INTRODUCTION

When woody biomass is enzymatically treated to release from its polysaccharide components fermentable sugars for bio-alcohols and other chemicals production, it typically leaves behind in the waste stream solid residues that are rich in lignin. Lignin is a natural phenolic binder for cell walls in woody plants, and thus it is not surprising that utilization of lignin as adhesives has long been investigated. Many such studies(1) were directed towards substitution of phenol by lignin at different mass fractions in the synthesis of phenol-formaldehyde resin, as well as mixing lignin with other components such as tannins(2,3). Modification of lignin using aldehydes was also studied as a pre-step before preparing lignin adhesive formulations(4). Adhesive applications of this renewable material are limited by its low reactivity compared to phenols(5). In this study, we attempted to 1) simplify the preparation process by directly utilizing lignin-rich residues of biomass for adhesives without having to pre-purify lignin, and 2) alleviate reactivity issues by pre-converting lignin-rich materials into nano-scale elements for increased surface areas. These two approaches constitute the new aspects of our research contributions.

The research goal of this study was to examine technical feasibility of directly utilizing saccharification residues of woody biomass for adhesive applications.

2 EXPERIMENTAL

Aspen wood flour (10-mesh pass) were pre-treated with NaOH 10% w/v concentration at 100°C for 2 hours. The pre-treated sample was treated with cellulase enzyme to attain 40% and 80% saccharification (glucose removal) levels. Pre-treated and saccharified samples were milled to nano-sized fibers using an ultra-fine friction grinding machine "Supermasscolloider" (Msuko Sangyo Co., Ltd). The grinding disks of the machine were brought into contact with each other to provide the friction for grinding which was performed at 1,500 rpm. The friction can be controlled by adjusting the “closeness” between the two disks, i.e., from 0 µm (slight contact) to -50 µm (more contact) and -125 µm (even more contact). In this paper, the nanofiber (NF) fibrillated from -50 µm clearance is named “NF (medium)”, while those from -125 µm clearance is named “NF (fine)”.

Adhesives were prepared from nanofibers with or without hexamethylenetetramine (HMTA). Birch wood of 40 x 8.5 x 4 mm in dimensions were used as the bonding substrate (Figure 1). The bond area was 6.5 x 8.5 mm^2.

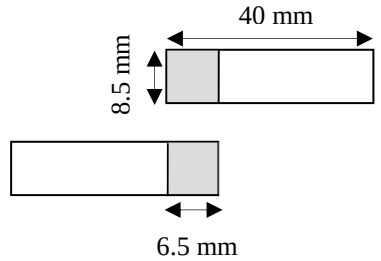

Figure 1: Lap shear specimen for testing strength of adhesive bond on wood

Phenol-formaldehyde resin was used as a control for comparison with nanofiber adhesive. All adhesives were applied at a spread rate of 200 g/m^2. After the required amount of adhesive was applined on the wood, the assembly was hot-pressed at 180 ^{o}C for 5 minutes. After hot press, the glued samples were conditioned at 50% relative

humidity for 1 day. Lap shear tests were conducted using an Instron machine to evaluate bond strength.

FTIR spectroscopy (Nicolet Series II Magna-IR System 750) was used to determine the important functional groups in the cured samples. IR spectra were collected in the wavenumber range of 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1}. DSC measurements were conducted using TA Q2000 instrument. Capsules (270 µL volume) that can withstand pressure up to 300 kPa were used. During the scan, the temperature was increased from 50 to 200 ^{o}C at a heating rate of 10 ^{o}C/min. The area under the exothermic peak indicates the heat of cure. The degree of curing was calculated based on the following equation

$$\alpha = (Q_t - Q_r)/Q_t, \qquad (1)$$

where α is the degree of curing, Q_t the total heat of cure of reference sample (without pre-cure), and Q_r the residual heat of cure for the pre-cured sample.

3 RESULTS AND DISCUSSION

3.1 Saccharification level

Figure 2 shows results of lap shear tests for NF fibrillated from NaOH-pretreated (0% saccharification), 40% saccharified, 80% saccharified samples. The adhesive bond becomes stronger as the level of saccharification increases. When NF was prepared from 80% saccharified sample, the resulted adhesive attained a bond strength of 70% of that of phenol-formaldehyde.

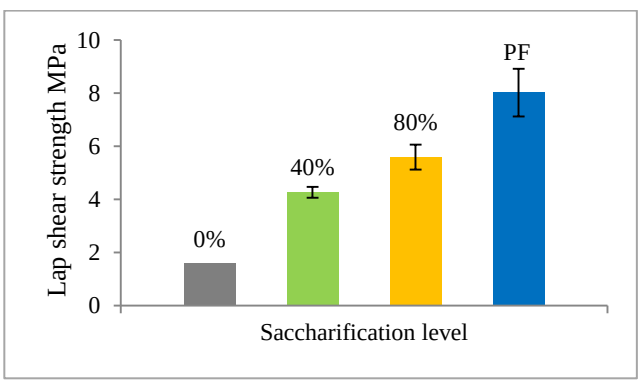

Figure 2: Bond strength of nanofiber adhesive from wood of different saccharification levels. Note: phenol-formaldehyde (PF) as reference

3.2 Fiber size

Based on the bond strength observed earlier (Figure 2), nanofiber adhesive from 80% saccharified sample was selected for further studies. The first of these studies is examining effects of surface area. We used 80% saccharified wood flour (without grinding) as a reference and representative of large-size particle, For nanofiber, the size is expected to be smaller as grinding clearance was decreased from -50 µm (medium-size NF) to -125 µm (fine nanofiber). Figure 3 summarizes results of lap shear strength for different fiber sizes. The results demonstrate the significance of increased surface area (decreased fiber size) on the bond strength of nanofiber adhesive.

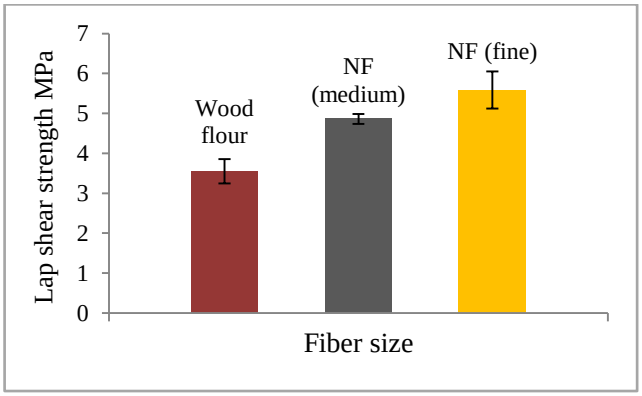

Figure 3: Effect of particle size on bond strength of nanofiber (NF) adhesive from 80% saccharified sample. Note: NF (medium) and NF (fine) were from grinding at clearance of -50 µm and -125 µm, respectively.

3.3 Effect of HMTA treatment

To examine the effects of hexamethylenetetramine (HMTA) crosslinker, fine nanofiber (-125 µm grinding clearance) from 80% saccharified sample were examined. Results show that HMTA treatment resulted in 20% improvement in bond strength (Figure 4). This bond strength value (6.8 MPa) is 80% of the value of phenol-formaldehyde.

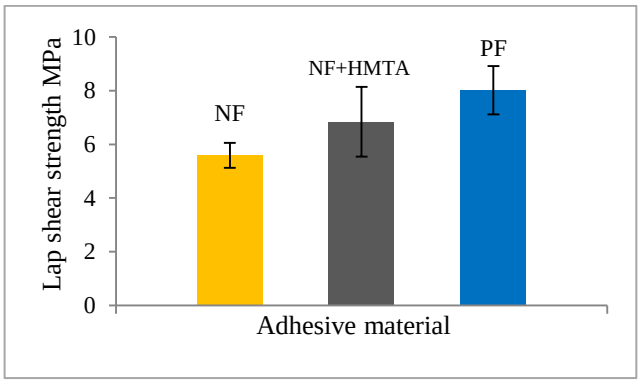

Figure 4: Effect of hexamethylenetetramine (HMTA) on bond strength of nanofiber (NF) adheive from 80% saccharified sample. Note: phenol-formaldehyde (PF) as reference

3.4 Transform Infrared Spectroscopy FTIR

FTIR spectra of the cured NF-S80 adhesive were studied (Figure 5). Peaks at 1594 cm^{-1} and 1498 cm^{-1} correspond to the C=C aromatic ring vibrations. The 1370 cm^{-1} peak corresponds to the phenol O-H group. The peak at 3400 cm^{-1} corresponds to O-H stretching[6]. The pronounced peak at 1050 cm^{-1} indicates the presence of methylene ether groups that bridge lignin phenolic ring [7]. Therefore, it can be concluded that saccharified residues were successfully crosslinked through bridges of methylene ether from the reaction with HMTA.

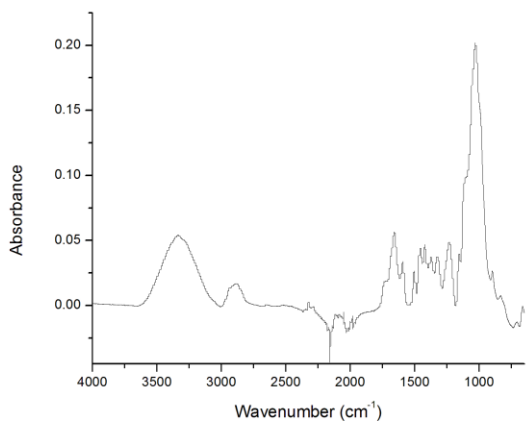

Figure 5: FTIR spectra of PF resin adhesive after curing

3.5 Differential scanning calorimetry (DSC)

Results from DSC scans are presented in Figures 6 and 7. Maximum heat release is observed at 150-160 ^{o}C for uncured sample and 175-185 ^{o}C for pre-cured sample. Areas under these peaks were obtained from integration to calculate heat of curing. The heat of curing for non-cured (reference) sample is 8.655 J/g, while the residual heat of curing for pre-cured sample is 2.345 J/g. By using Equation 1, the degree of cure is calculated as 73%. This curing degree suggests opportunities to further optimize curing conditions for achieving an even higher bond strength.

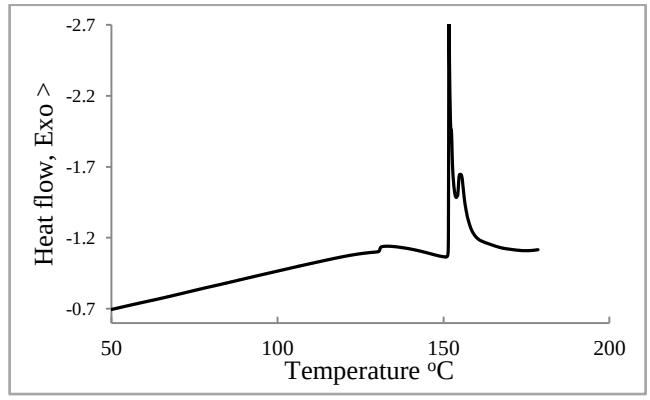

Figure 6: DSC scan for uncured nanofiber adhesive from 80% saccharified sample

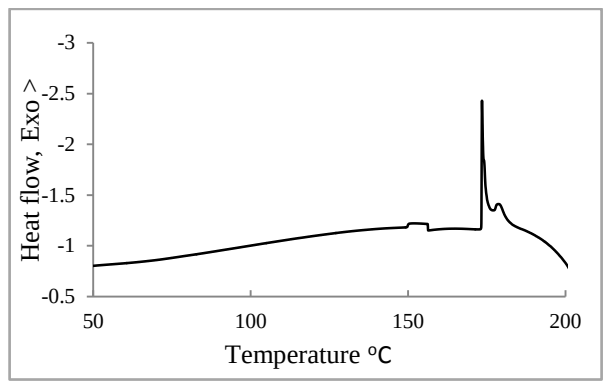

Figure 7: DSC scan for pre-cured nanofiber adhesive from 80% saccharified sample

4 CONCLUSION

Biobased adhesive was successfully prepared from nanofibrillated wood saccharification residues. Lap shear strength of the adhesive attained up to 80% of the commercial phenol-formaldehyde adhesive. FTIR scan confirmed the presence of methylene ether bridges between lignin phenolic groups. More studies are currently conducted to improve the adhesive properties. The improvement is expected to provide competing power against fossil-based adhesives. By transforming, with minimum conversion, saccharification wastes to adhesive products, this study has the impact of increasing the economic viability of bioenergy system.

5 ACKNOWLEDGMENTS

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