Solvent-free modification of lignocellulosic wood pulp into a melt-flowable thermoplastic

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17   **Abstract**   This paper reports on a flowable lignocellulosic thermoplastic prepared from forestry

18   biomass by solvent-free acetylation. The non-solvent approach relies upon a functionalizing agent

19   derived from benzethonium chloride (hyamine) and sulfuric acid, which was chosen for its similar

20   wetting attributes to an ionic liquid for the lignocellulose but was much less inexpensive to use.

21   Besides acetylation, this functionalizing agent became chemically bonded to the lignocellulose by

22   the sulfate group formed *in situ*, as demonstrated by ^{13}C NMR, infrared and elemental analysis.

23   This attached species appeared to contribute strongly to the flowable nature of the product. The

24   modified material showed good melt flowability by compression molding, as demonstrated in this

25   study by the production of semi-transparent films and was characterized by differential scanning

26   calorimetry and dynamic mechanical analysis. An experimental investigation of reaction

27   parameters was included in the study, exploring the mechanism by which the cationic

28   functionalizing agent modified the structure of lignocellulose.

29

30 **Graphic abstract** A solvent-free chemical modification is described to convert sustainable

31 lignocellulosic wood pulp into a value-added bio-thermoplastic.
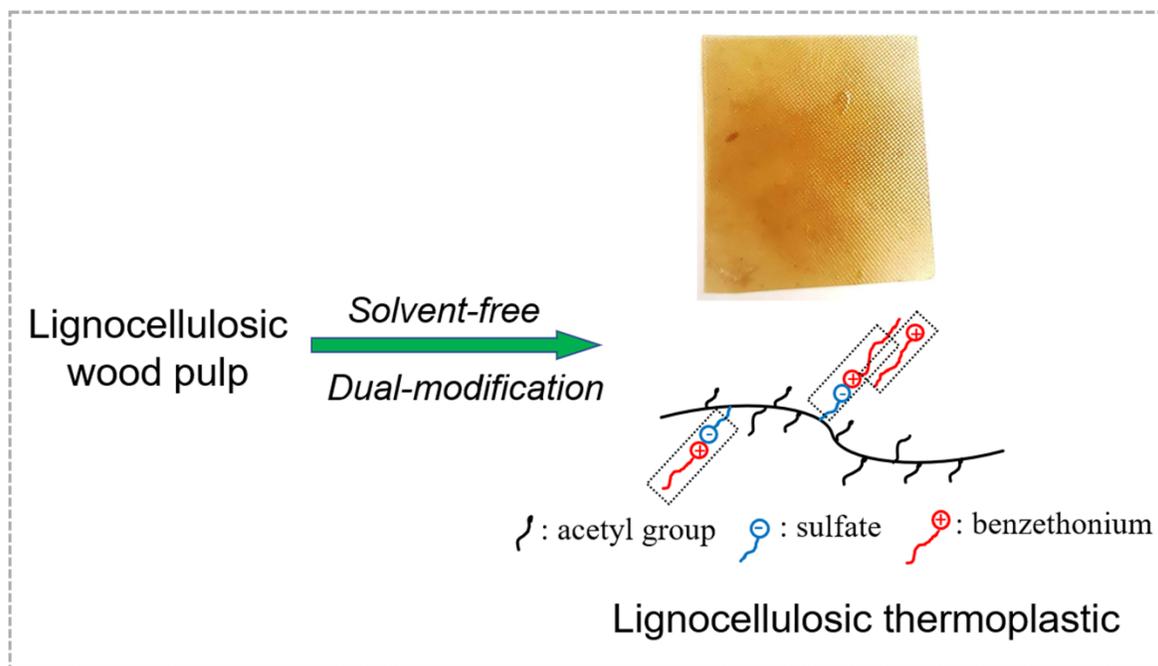
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33 **Keywords** Biomass · Lignocellulose · Solvent-free · Chemical modification · Thermoplastic

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Introduction

The decline in fossil fuel reserves will soon impact the supply chain of the polymer industry. Cellulosic thermoplastics constitute one group of many promising replacements to synthetic plastics. Cellulose is a macromolecule that is insoluble in most solvents and has no innate thermoplasticity, which is attributed to its crystallinity and intra- and inter hydrogen bonds. Chemical modifications can interfere with these hydrogen bonds and simultaneously introduce side groups along the cellulose backbones, which improve chain flexibility and thus afford thermoplasticity (Yan et al. 2009; Toyama et al. 2015; Larsson and Wågberg 2016; Huang et al. 2016a; Chen et al. 2018). However, the manufacturing of current cellulose thermoplastics like cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate is costly, especially as compared with competitive petroleum-based thermoplastics (Edgar et al. 2001).

The production of cellulose thermoplastics currently relies on using a large excess of acetic acid to swell and disperse the insoluble fibrillar mass for chemical modifications (Hummel 2004). Using such a high amount of reactants leads to high costs in the manufacturing of cellulose thermoplastics even though this process recycles much of the residual acetic acid after the modification. Although cellulose obtains better thermoplasticity when longer side-chain substituents are incorporated (Teramoto 2015; Boulven et al. 2019), their incorporation generally requires harsher reaction conditions, which means higher manufacturing costs. Over the past decades, some new solvents, *e.g.,* dimethylacetamide/LiCl (Tanaka et al. 2017), dimethyl sulfoxide/tetrabutylammonium fluoride (Ass et al. 2004) and imidazolium-ionic liquids (Wen et al. 2017; Chen et al. 2018; Hirose et al. 2019), have been used to dissolve cellulose for chemical modifications. Dissolving improves reactant accessibility to cellulose compared to swelling, making it easier to add long-chain substituents and giving greater access to all reaction sites along

58   the chain backbone (Tanaka et al. 2017; Wen et al. 2017; Chen et al. 2018; Hirose et al. 2019).

59   But, chemical modification with these new solvents is still questionable from an industrial

60   standpoint because these solvents are significantly more costly for industrial use than the

61   alternative of using excess acetic acid. Some researchers have tried to improve the economics by

62   partially derivatizing cellulose as the first step of modification to making cellulose soluble in less

63   expensive organic solvents, then carrying out the incorporation of long-chain substituents in the

64   second stage as solutions (Teramoto and Nishio 2003; Tedeschi et al. 2018; Boulven et al. 2019).

65   The reactivity of the cellulose is reportedly low in these organic solvents after the first step of

66   derivation.

67   The purpose of the current study is to develop a thermoplastic cellulosic material from

68   lignocellulose with suitable flow properties for conventional thermal processing equipment.

69   Working with lignocellulose rather than highly purified cellulose eliminates costly pre-processing

70   steps and makes use of lignin, which is increasingly being considered for thermoplastics itself

71   (Nge et al. 2016). There are reported preparations of thermoplastics directly from lignocellulose

72   (Zhen et al. 2016; Chen et al. 2017a, b) using similar heterogeneous or homogenous processes as

73   used for cellulose and in those cases, lignocellulose has displayed similar or even a lower solubility

74   than cellulose (Kotelnikova et al. 2014; Wang et al. 2017). The poor dispersive nature of cellulosic

75   materials makes our investigation of an alternative wetting agent more critical, especially if solvent

76   recovery is viewed as undesirable, and we ultimately seek to develop a bulk reactive extrusion

77   process from the studied chemistry. A novel functionalizing agent based on cationic

78   surfactant/sulfuric acid is introduced in this work for the acetylation of lignocellulose in order to

79   prepare a bio-thermoplastic without need of plasticizer addition. The influence of this

80   functionalizing agent is studied in detail for its participation in the modification of lignocellulose.

81 **Materials and methods**

82 Materials

83   Lignocellulosic wood pulp containing 8.2 wt% Klason lignin (determined by TAPPI-T method

84   222 om-02) was received from Tembec (Montreal, Canada). The received pulp was mechanically

85   wet pulverized in a 27 mm 40 L/D corotating twin-screw extruder (Leistritz, USA) according to

86   a previously published method (Li et al. 2019). The previous study where the method was

87   published, showed the twin-screw extrusion pre-treatment improves the degree of fibrillation of

88   the received lignocellulose, thus improves chemical accessibility to the fibers. An α-cellulose

89   (Sigma Aldrich; Oakville, Canada) of similar particle size to the pretreated lignocellulose, was

90   studied to gain some insights into the contributions of lignin in the modification. Benzethonium

91   chloride (hyamine, HPLC grade), dimethyl sulfoxide (DMSO) (reagent grade) and sodium

92   bicarbonate (ACS grade) were also purchased from Sigma Aldrich (Oakville, Canada), while

93   acetic anhydride (reagent grade), sulfuric acid (trace metal grade) and anhydrous ethanol (reagent

94   grade) were obtained from Caledon Laboratory Ltd. (Georgetown, Canada).

95 Chemical modification of lignocellulosic wood pulp

96 *Dissolution of sulfuric acid/hyamine in acetic anhydride*

97   Different concentrations of hyamine were dissolved in 6 mL acetic anhydride at 120 °C under

98   constant agitation to form a solution. Similarly, different amounts of sulfuric acid were added to

99   the acetic anhydride solution and then stirred for 10 mins. As shown in Table 1, two series of

100   solutions were prepared to investigate the influence of the ratio between sulfuric acid/hyamine,

101   and the total amount of sulfuric acid/hyamine added to acetic anhydride, on the modification of

102   the lignocellulosic pulp. In the first set of trials, sulfuric acid was kept constant at 13.4% (w/w)

103   relative to the pulp, while the amounts of hyamine were varied as 0.32, 0.63, 1.25, or 2.50 g in the

104   solution. The molar ratio of sulfuric acid/hyamine as a functionalizing agent in these trials was

105   1.96, 0.98, 0.49 or 0.25, respectively. The second set of trials involved a fixed sulfuric

106   acid/hyamine ratio at 0.49 while varying the total amount of sulfuric acid (13.4, 26.8 and 40.2%

107   (w/w) relative to the pulp) added to the solution.

108   **Table 1** Reaction formulations for chemical modification of lignocellulose into thermoplastics

Pulp (g)	Sulfuric acid (g)	Sulfuric acid/pulp (w/w, %)	Hyamine (g)	Sulfuric acid/hyamine (molar/molar)
Series I				
1	0.134	13.4	2.5	0.25
1	0.134	13.4	1.25	0.49
1	0.134	13.4	0.63	0.98
1	0.134	13.4	0.32	1.96
Series II				
1	0.134	13.4	1.25	0.49
1	0.268	26.8	2.5	0.49
1	0.402	40.2	5.0	0.49

109
110   The nature of the functionalizing agent formed in the acetic anhydride solution was investigated

111   by regenerating the anticipated salt from the acetic anhydride solution. The solution (without pulp)

112   was heated at an elevated temperature of 165 °C to evaporate the acetic anhydride. After cooling

113   down to room temperature, the obtained salt was vacuum dried to a constant weight. The dried salt

114   was then rinsed with water and finally purified by recrystallization from ethanol solution.

115   *Modification of lignocellulose in sulfuric acid/hyamine solution*

116   In this study, the purpose of the experiments was to maximize conversion and better understand

117   the functionalizing agent, whereas the excessive amounts of reactants will be reduced in future

118   studies using a recycle stream strategy for bulk processing by reactive extrusion. A slurry was

119   created by adding 1 g of the extrusion pre-treated lignocellulosic pulp into the acetic anhydride

120   solution mentioned above. The modification was allowed to proceed at 120 °C for 30 minutes

121   under vigorous stirring. At the end of these reactions, the modified pulp slurry or paste was

122   precipitated in ethanol. After stirring overnight, the modified pulp was filtered, re-dispersed in

123   deionized water, neutralized to a pH of 7 by dropwise addition of a 1 M sodium bicarbonate and

124   then washed repeatedly by distilled water until the conductivity of the washing filtrate was close

125   to the distilled water. Finally, the modified pulps were filtered and vacuum-oven dried at 75 °C

126   for 24 hours before characterizations. Modified α-cellulose was prepared following the same

127   reaction procedure.

128   *Modification of lignocellulose by acetic-acid process*

129   For comparison, lignocellulose acetate was prepared by the conventional acetic acid method

130   (Hummel 2004). Briefly, 1g of extrusion pre-treated wood pulp was first activated by 1 mL of

131   acetic anhydride at 40 °C for 30 mins, then added to a solution containing 2.8 mL of acetic

132   anhydride, 5 mL of acetic acid and 4% (w/w) sulfuric acid catalyst relative to the weight of the

133   pulp. The reaction temperature was gradually increased to 77 °C from 25 °C within 10 minutes,

134   then kept at 77 °C for 20 minutes. The high reaction temperature of 120 °C used in the method

135   with the functionalizing agent was not suitable for the acetic acid method because of the substantial

136   degradation of the wood pulp that would result. At the end of modification, the modified

137   lignocellulose was purified by the same procedure used for the sulfuric acid/hyamine system.

138 *Compression molding of the modified pulps*

139 Modified lignocellulose was placed between two Teflon sheets and sandwiched between two

140 stainless plates. The sandwich was hot-pressed at 190 °C under 2.5 MPa for 2 mins in a Carver

141 4389 benchtop hydraulic press, then hot-pressed under 6.1 MPa for another 10 mins to form a film.

142 Characterizations of modified lignocellulosic wood pulp

143 *Morphology analysis*

144 Morphology of modified lignocellulosic pulp at the end of the reaction was determined by a light

145 microscope (Axioplan 2, Carl Zeiss, German). Modified wood pulp slurry or paste was dropped

146 on a pre-cleaned glass slide, immediately covered with a glass clip, and then observed and imaged

147 under the microscope.

148 *Structural characterizations*

149 Infrared spectra (FTIR) were collected on a Nicolet 6700 spectrometer with a Smart iTRT^M

150 attenuated total reflectance (ATR) sampling accessory. The data was generated from 32 scans in

151 the range of 4000-500 cm^{-1} with a 4 cm^{-1} resolution. Solution state ^{1}H and ^{13}C Nuclear Magnetic

152 Resonance (NMR) spectroscopy were performed in the DMSO-d6 solvent by using a Bruker AVIII

153 700 MHz spectrometer at ambient temperature. Elemental nitrogen and sulfur contents were

154 determined with a UNICUBE elemental analyzer (Elementar).

155 Acetyl content of the modified pulp was determined by colorimetric titration. Dried modified

156 pulp, 0.05 g, was put into a 25-mL glass vial, to which was added 5 mL of 0.25 M NaOH and 5

157 mL of anhydrous ethanol. The mixture was left to stand for 24 h before 10 mL of 0.25 M HCl was

158 added to the system. After 30 mins, the mixture was titrated using 0.25 M NaOH with

159 phenolphthalein indicator. The grafted ester group content was calculated by:

160     $Acetyl \left(\dfrac{mmol}{g} \right) = \dfrac{(V_1 + V_2)C_1 - V_3 C_2}{m}$ (1)

161   where V_1 (mL) is the volume of NaOH added to the system before the titration, V_2 (mL) is the

162   volume of NaOH consumed in the titration, C_1 (M) is the NaOH concentration, V_3 (mL) is the

163   volume of HCl added to the system before the titration, C_2 (M) is the concentration of HCl, and m

164   is the weight of the sample.

165   Intrinsic viscosity was used to assess the degradation of the modified pulp samples with a

166   Cannon Fenske viscometer (25-tube size). Dried sample was added to DMSO solvent and stirring

167   overnight to dissolve the pulp; the insoluble part was separated by filtering and dried for

168   determination of the concentration (c) of the solution. The solvent or pulp solution flowed through

169   the viscometer held at 25 °C, and flow times through the graduated region were recorded. The

170   intrinsic viscosity was estimated as the intercept of the plot of inherent viscosity versus

171   concentrations. Inherent viscosity (η_{inh}) was determined from the flow times of the DMSO solvent

172   (t_0) and pulp solution (t), according to:

173     $\eta_{inh} = \text{In} \left(\dfrac{t}{t_0} / c \right)$ (2)

174   *Thermal properties*

175   Thermal transitions were analyzed using a Q200 differential scanning calorimeter (DSC; TA

176   Instruments, USA) operating in modulated mode. Modified pulp, 9 mg, was loaded and sealed in

177   a Tzero aluminum pan. A hole was punched on the lid to allow the release of water vapour during

178   the test. Samples were equilibrated at -40 °C, then heated to 240 °C at a ramp rate of 5 °C /min,

179   with an oscillation of 1.00 °C every 60 seconds.

180   The thermoplasticity was evaluated by a dynamic mechanical analyzer 850 (DMA; TA

181   Instruments, USA) with tensioning cantilever geometry. DMA measurements were performed on

182   strips with a dimension of 17 mm × 5 mm × 0.2 mm cut from the hot-pressed films at a frequency

183   of 1 Hz and a strain of 0.01%. The temperature was ramped from 20 to 240 °C with a heating rate

184   of 3 °C/min.

185   *Mechanical properties*

186   The tensile properties of compression-molded films were determined with an Instron universal

187   mechanical testing system (Model 3366). Rectangular strips with a dimension of 40 mm × 10 mm

188   × 0.2 mm were cut from the film. Tensile testing was performed at a crosshead speed of 0.083

189   mm/min, and the force was recorded with a 0.05 kN load cell. Apparent densities of the strips were

190   estimated from multiple measures of each sample's dimensions and mass, while specific

191   mechanical properties were reported as the average of three repeats.

192   **Results and discussion**

193   **Acetylation in the presence of the functionalizing agent**

194   When sulfuric acid and hyamine were present with acetic anhydride, the acetylation of

195   lignocellulose needed no solvent to improve the wetting of the fibrous mass. Since sulfuric acid is

196   a catalyst for esterification, the functionalizing agent served this purpose as well as wetting agent.

197   The interaction of sulfuric acid with hyamine was essential for the dispersion of lignocellulose in

198   the non-solvent reaction system; otherwise, reaction conditions were notably poor with hyamine

199   alone. Fig. 1a shows the wood pulp displayed no dispersion in the reaction system without sulfuric

200   acid, maintaining its granular form. With the inclusion of sulfuric acid, the molar ratio between

201   sulfuric acid and hyamine played an important role in dispersing lignocellulose in the non-solvent

11

202 reaction system. Over a sulfuric acid/hyamine ratio from 0.25-0.5, the pulp became increasingly

203 easier to disperse in the reaction medium as the ratio increased. Fig. 1b shows visible fibrous mass

204 still present at the end of the reaction for a sulfuric acid/hyamine ratio of 0.25 but then, an almost

205 homogenous system was seen (Fig. 1c) at a ratio of 0.49. Further increasing the sulfuric

206 acid/hyamine ratio kept the lignocellulose homogenously dispersed, but with a corresponding

207 increase in degradation, denoted by the blackening of the reaction medium (referring to the inserted

208 photo in Fig. 1d).
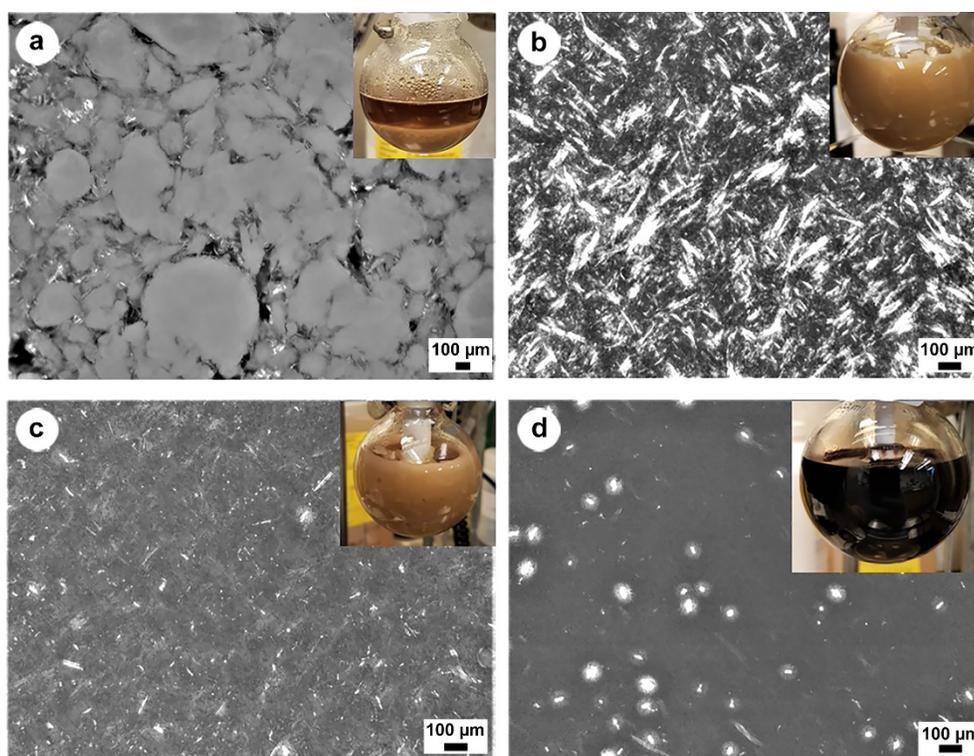
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210 **Fig. 1** Light microscope images of the solution dried onto a glass slide at the end of the reaction with the (a) presence
211 of hyamine or (b-d) sulfuric acid/hyamine with different ratios (0.25, 0.49 and 1.96). Inserted photo shows the state
212 of the reaction vessel at the end of the reaction

213 Degradation of pulp from the modification was quantified by measuring the inherent viscosity

214 of the soluble part of the modified samples dissolvable in DMSO. This analysis was not possible

215 for the sample using 13.4% (w/w) sulfuric acid at a 0.25 molar ratio of sulfuric acid/hyamine

216   because it had negligible solubility in DMSO, similar to the original pulp. Since a baseline

217   viscosity measurement for the original lignocellulose was not possible, this discussion is limited

218   to commenting on trends seen in the data. As shown in Fig. 2, the lowest inherent viscosity

219   corresponded to a 1.96 molar ratio of sulfuric acid/hyamine (sulfuric acid content fixed at 13.4%

220   (w/w) relative to the pulp), producing the black liquid mentioned before; with lower sulfuric

221   acid/hyamine ratios, intrinsic viscosity increased as noted by the climbing intercept values for the

222   curves. Sulfuric acid is only considered as a solvent, with no degradative nature, towards cellulose

223   at very low temperatures (-20 °C) (Huang et al. 2016b). The presence of hyamine significantly

224   decreased the extent of degradation by sulfuric acid, even at high reaction temperature (120 °C),

225   but also maintained the solvation properties of the sulfuric acid. The benzethonium-based salt

226   recovered from the acetic anhydride solution displayed an additional chemical shift at 9.65 ppm

227   within the ^{1}H NMR spectra not seen with pure hyamine (Fig. 3). The shift corresponds to a

228   bisulfate (Zare et al. 2020), indicating that benzethonium bisulfate had formed in the solution. The

229   weaker acidity of the system reduced the degradative effects on lignocellulose, but still displayed

230   a solvation or deconstruction ability to lignocellulose. To optimally disperse lignocellulose and

231   minimize degradation, a molar ratio of 0.49 appeared ideal.
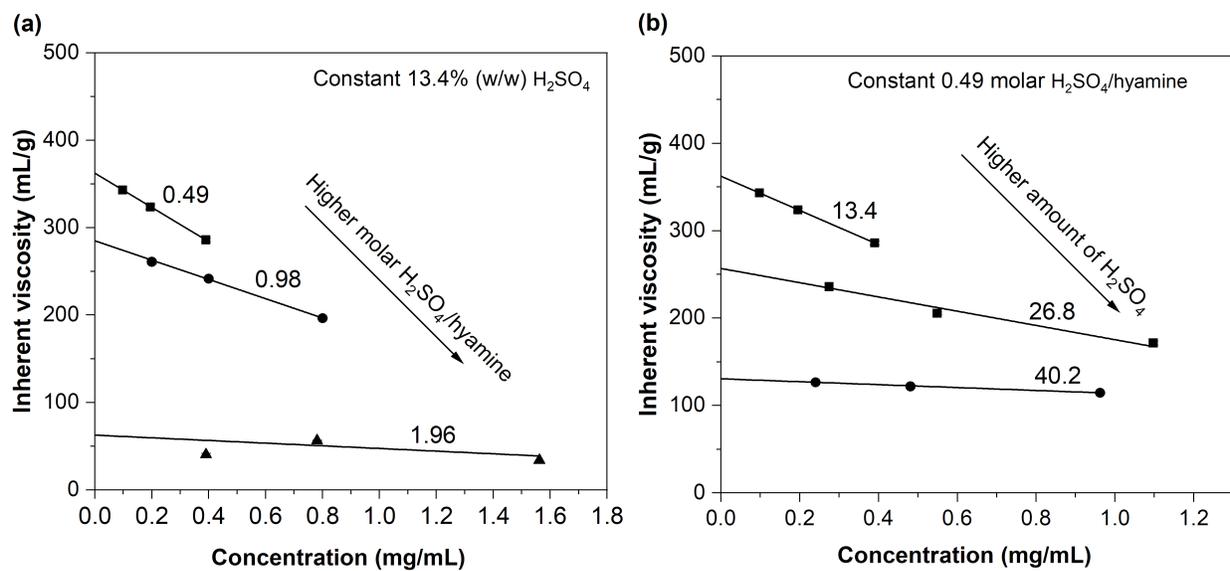
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233   **Fig. 2** Inherent viscosities of modified pulp samples in the first (a) and the second (b) set of trials

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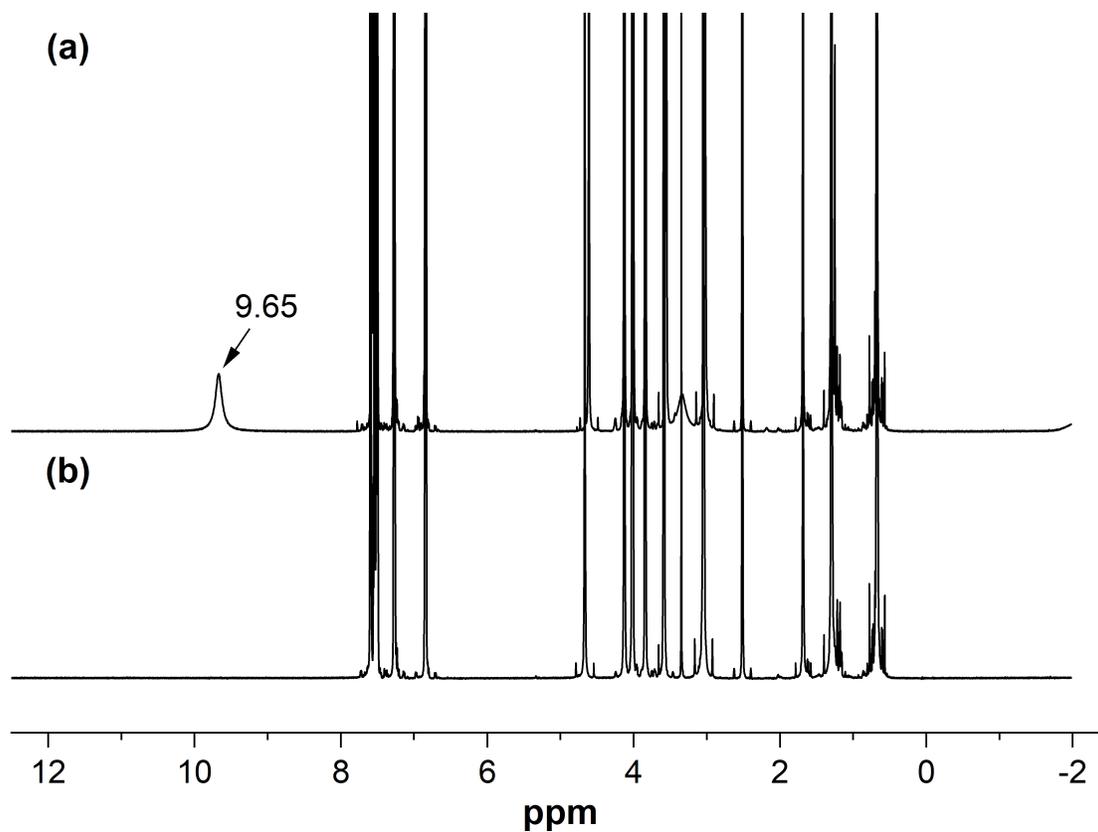
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236   **Fig. 3** ^{1}H NMR spectra of hyamine (a) and the "hyamine" (b) regenerated from its acetic anhydride solution with the

237   presence of sulfuric acid

Chemical structures of the modified lignocellulosic wood pulp

Characteristic peaks for the acetyl groups of polysaccharide acetates are seen in the spectra at 1740 cm^{-1} (C=O ester stretching), 1365 cm^{-1} (C-H bending of acetyl groups) and 1230 cm^{-1} (-C=O-stretching of acetyl groups) (Zhen et al. 2016). Although lignocellulose naturally has trace acetyl groups, the characteristic peaks in the modified sample were much stronger than the original material (Fig. 4), showing successful acetylation in the presence of the sulfuric acid/hyamine. Correspondingly, there was a decrease in hydroxyl functionality in the modified sample, noted by the disappearance of the strong absorbance at 3330 cm^{-1} originally seen in the lignocellulose (Fig. 4).
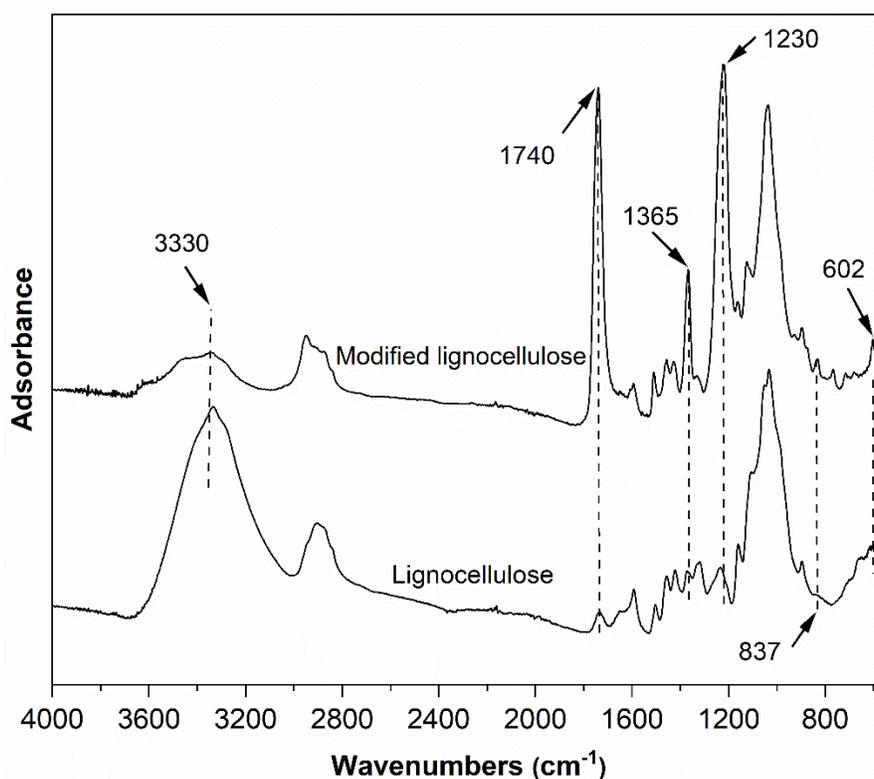
Fig. 4 FTIR spectra of lignocellulose and modified lignocellulose using 13.4% (w/w) sulfuric acid and 0.49 molar ratio of sulfuric acid to hyamine

250   The acetylation was also evident by solution-state ^{13}C NMR. Fig. 5 shows two significant

251   groupings of chemical shifts in the modified lignocellulose at 168.90-171 ppm and 20-20.55 ppm,

252   corresponding to the carbonyl and methyl groups of the acetyl functionality, respectively (Kono et

253   al. 2017). Solution-state ^{13}C NMR also found the hyamine attachment by comparing the spectrum

254   of the modified pulp versus hyamine. The spectrum for the modified sample includes all chemical

255   shifts attributed to hyamine, as labelled with solid arrows (downward pointed) in Fig. 5. The

256   benzethonium cation was not readily detected by FTIR, being low in concentration and typically

257   present between 1200-1500 cm^{-1} which were indistinguishable from the broad lignocellulose peaks.

258   However, a sulfate functionality was detected in the modified sample, at 837 cm^{-1} (C-O-S

259   symmetrical vibration) and 602 cm^{-1} (bending mode of sulfate) (Böke et al. 2004; Chen et al. 2013).

260   To investigate the nature of functionalizing agent attachment based on reaction conditions,

261   elemental analysis was conducted.

262
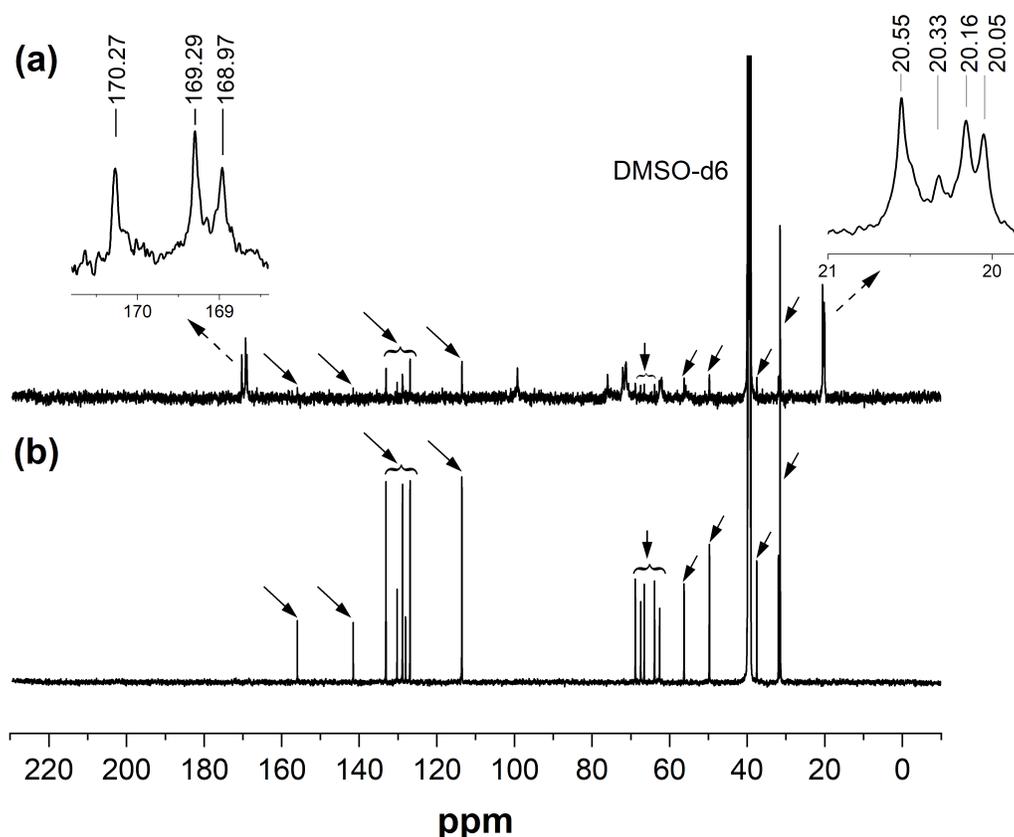
Fig. 5 ^{13}C NMR spectra of modified lignocellulose using (a) 13.4% (w/w) sulfuric acid and 0.49 molar ratio of sulfuric acid to hyamine, and (b) pure hyamine. Downward pointed arrows highlight the chemical shifts of hyamine in the modified pulp, while upward dashed arrows are related expanded peak regions to the original spectrum

Results of the elemental analysis are presented in Fig. 6. In its received form, the lignocellulosic had a small but detectable elemental nitrogen (N) and sulfur (S) content; the elements showed up in repeated testing and thus were concluded as trace contaminants in the supplied wood pulp. Modified samples showed a substantial increase in N and S content when acetylated in the presence of the functionalizing agent (sulfuric acid/hyamine), reaffirming the findings by infrared and ^{13}C NMR analysis that hyamine and sulfate species had chemically bonded to the pulp acetates during the reaction. In the presence of only hyamine but no sulfuric acid (highlighted by a rectangle symbol in Fig. 6a), the modified sample showed no increase in S relative to the supplied pulp, and only a slight increase in N; since lignocellulose itself can be negatively charged as a result of

17

275   pulping (Boufi et al. 2004), the small increase in N without sulfate groups present is plausible. The

276   need for sulfuric acid in grafting hyamine to the lignocellulose species suggested that it was

277   primarily attached as a benzethonium sulfate. Sulfate groups readily form in lignocellulose within

278   the presence of bisulfates or sulfuric acid (Chen et al. 2013; Mao et al. 2015), making this mode

279   most likely. The grafted benzethonium sulfate formed either directly by reaction of benzethonium

280   bisulfate (which has been notably detected in the acetic anhydride solution) or by a two-step

281   reaction via sulfation by sulfuric acid first, and then interaction with the benzethonium cation of

282   hyamine (Salajková et al. 2012; Shimizu et al. 2014). The molar ratio (R) of N to S elements in

283   the modified samples provided greater details on the modes of attachment:

284   $$R = \frac{(N - N_i)/14}{(S - S_i)/32} \hspace{3cm} (3)$$

285   where N and S corresponded to a modified pulp while N_i, and S_i corresponded to the sample

286   modified with the presence of only hyamine. The R values for the two experimental series were

287   included in Fig. 6 as dashed curves. For most sulfuric acid/hyamine conditions, R was around 1.2,

288   which was slightly above molar equivalence. Excessive benzethonium surrounding the bound

289   sulfate was thought to be adsorbed via hydrophobic interactions with bound hyamine (Alila et al.

290   2005). The only case where R dropped below unity was at a sulfuric acid/hyamine ratio of 1.96

291   where N and S values closely resembled the case where only hyamine was used (i.e. sulfuric

292   acid/hyamine ratio of zero in Fig. 6a). Functional agent attachment was not significantly evident

293   at both low and excess concentrations of sulfuric acid in these tests.
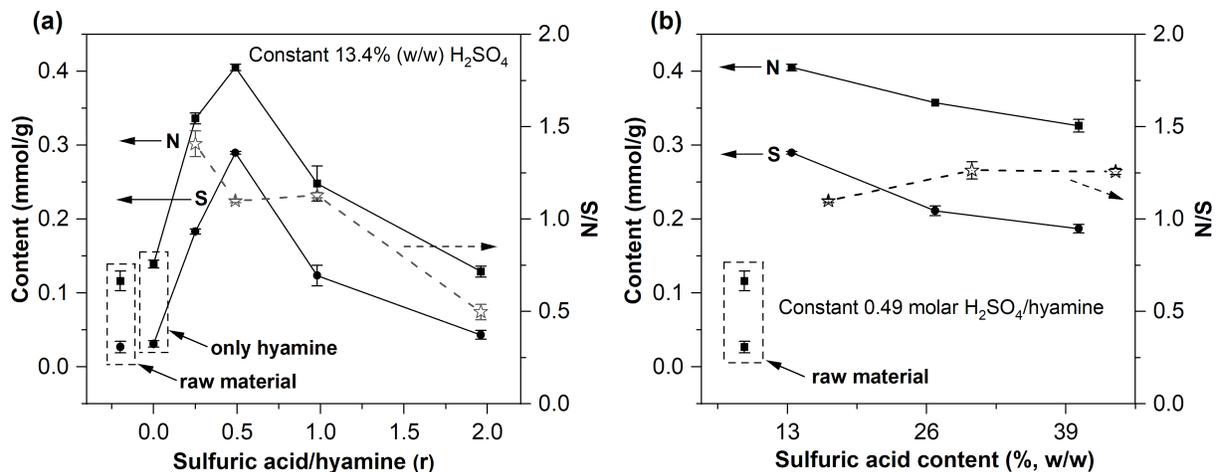
Fig. 6 Nitrogen (N) and sulfur (S) elemental content and N/S ratio detected in the original lignocellulose and modified lignocellulose samples from the (a) first set and (b) second set of trials

Influence of reaction conditions

In the course of acetylating lignocellulose in the presence of functionalizing agent, hydroxyl groups were substituted with acetyl, benzethonium sulfate and possibly sulfate species; hyamine could be chemically bound to the lignocellulose pulp via sulfate anion (moiety 1) or associated with already bound benzethonium via hydrophobic end group attraction (moiety 2). For the purpose of estimating the extent of conversion, we assume the amount (mmol/g) of moiety 1 was molar equivalent to the sulfur content of the modified sample after subtraction of S content of the original pulp. The amount of moiety 2 was the molar difference between N and S content of the modified sample after subtraction of S and N content of the sample modified in the presence of hyamine, as indicated by Equation (4):

$$Moiety\ 2\ (mmol/g) = (N - N_i) - (S - S_i) \tag{4}$$

where N, S and N_i, S_i were nitrogen, sulfur contents (mmol/g) of the modified wood pulps with the presence of sulfuric acid/hyamine and only hyamine, respectively. In the cases of both moieties, sulfate attachment without hyamine was ignored in the calculations though at the highest

19

311 sulfuric acid/hyamine ratio, such attachments may have existed. Acetyl content was estimated by

312 NaOH hydrolysis and titration. A summary of acetyl content as well as estimated moiety 1 and

313 moiety 2 attachments are given in Fig. 7. Although NaOH can also hydrolyze sulfate group,

314 hydrolysis of sulfate species at low NaOH concentration (0.5 wt%) will be limited (Jordan et al.

315 2019), especially for sulfates with a large counterion (benzethonium), which normally improves

316 stability (Dong and Gray 1997; Beck and Bouchard 2014). The error associated with the titration

317 should be considered small since the amount of sulfate esters (0.01-0.26 mmol, based on elemental

318 analysis), was minor as compared to the acetyl content value determined by titration (2.4-8.9

319 mmol).

320   In the first experimental series (Fig. 7a), the acetylation content increased with the increasing

321 sulfuric acid/hyamine ratio, though the rate of modification relative to the ratio was highest up to

322 0.49. However, it was only above a ratio of 1.0 that the rate of modification significantly declined.

323 The sample acetylated without sulfuric acid showed the lowest acetyl content of 2.5 mmol/g. All

324 prepared samples had a lower acetyl content compared to the sample prepared by the acetic acid

325 solvent method (10.2 mmol/g). Comparatively, functionalizing agent attachment increase with the

326 sulfuric acid/hyamine ratio up to 0.49 (both moiety forms) and then declined at higher ratios. When

327 sulfuric acid/hyamine ratio was lower than 0.49, excessive hyamine tended to convert sulfuric acid

328 into bisulfate that had a low reactivity towards lignocellulose and catalyzing ability for the

329 acetylation (Mao et al. 2015). When the sulfuric acid/hyamine ratio was higher than 0.49, the

330 declining presence of hyamine in the reaction system (fixed sulfuric acid content) increased the

331 system acidity that was beneficial to the acetylation of lignocellulose (Kuo and Bogan 1997), but

332 improved acetylation subsequently decreased the hydroxyl functionality sites for the

333 functionalization agent attachment since the competition between the two reactions. The declining

334 presence of hyamine was not beneficial to the formation of benzethonium sulfate. Others have

335 reported that sulfate groups ($-SO_3H$) will be partially replaced by acetyl group (Malm et al. 1946;

336 Chauvelon et al. 2003), when sulfation and acetylation occur simultaneously in the reaction, but

337 sulfate with large counterion (benzethonium) was more structural stable (Dong and Gray 1997;

338 Beck and Bouchard 2014). Additionally, high acidity causing degradation would reduce the sulfur

339 content, thus decreased the functionalizing agent attachment in the final product (Chen et al. 2015).

340 The degradation of wood pulp did not have any observed negative effect on the acetylation, which

341 was because of the degree of acetylation was much higher than that of the functionalization by

342 sulfuric acid/hyamine.

343   In the second set of experiments, influence of the amount of functionalizing agent on the reaction

344 was examined (Fig. 7b). The sulfuric acid/hyamine ratio was constant (at 0.49, seemingly optimal

345 in the first experiments) in this series while the sulfuric acid content was increased. The acetyl

346 content showed little change as the sulfuric acid content increased, indicating the higher amount

347 of functionalizing agent present did not improve the rate of reaction. In general, increasing the

348 sulfuric acid content (and functionalizing agent content) in the reaction system resulted in small

349 decreases in both acetyl content and moiety 1 content whereas moiety 2 showed a slight increase.

350 However, significant hydrolysis occurred in the presence of the higher sulfuric acid was noted by

351 intrinsic viscosity measurements earlier, indicating that system acidity was increasing. The rising

352 acidity may explain the decrease in moiety 1. Conversely, the large amounts of hyamine in the

353 reaction system, while beneficial to coordinating with those moiety 1 groups attached, resulting in

354 a higher moiety 2 content, may have also reduced accessibility of the hydroxyl groups of the

355 lignocellulose to acetic anhydride (Ass et al. 2004).
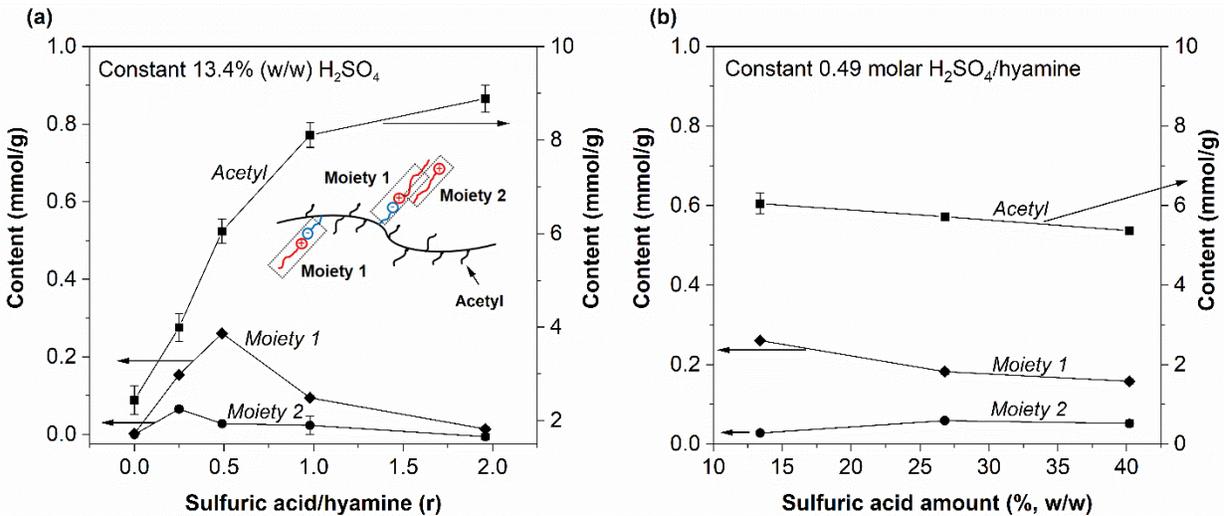
Fig. 7 Extent of acetylation and functionalization by the functionalizing agent in the modified lignocellulose, based on the (a) first series and (b) second series of experimental trails

Influence of lignin

Table 2 shows that under the same reaction conditions, lignocellulose with its inclusion of lignin obtained a higher degree of modification than α-cellulose. For each reaction condition, acetyl content was three to five times greater and benzethonium sulfate addition was three to nine times greater in lignocellulose versus α-cellulose. In the case of both functional groups, the relative reactivity of cellulose increased with higher sulfuric acid content. The amorphous structure of lignin seemed to offer greater access for chemical modification, though intensified acid hydrolysis offered similar benefits to the highly organized cellulosic polymer chains. A similar observation was reported by Gan et al. (2018), who found the hydroxyl groups rof lignin exhibited preferential reactive in lignocellulosic modification.

370　**Table 2** Comparison between modified lignocellulose and cellulose in term of degree of modification and
371　thermoplasticity

| Pulp (g)	Sulfuric acid/pulp (w/w, %)	Sulfuric acid/hyamine (molar/molar)	Acetyl content (mmol/g)	Benzethonium sulfate (mmol/g)	Thermoplasticity*
L	0	0	2.4 ± 0.31	0	-
C	0	0	0.53 ± 0.02	0	-
L	13.4	0.49	6.05 ± 0.26	0.26 ± 0.01	+
C	13.4	0.49	1.2 ± 0.15	0.03	-
L	26.8	0.49	5.72 ± 0.01	0.18 ± 0.01	+
C	26.8	0.49	1.6 ± 0.2	0.04	-
L	40.2	0.49	5.37 ± 0.01	0.16 ± 0.01	+
C	40.2	0.49	2.1 ± 0.05	0.06	-/+

372　* The flowability attributed to thermoplastcity in this paper was evaluated by compression molding at 190 ℃,
373　+:compression moldable, -:non-compression moldable, -/+: partially compression moldable

374

Thermoplasticity

376　Fig. 8 presents the DSC thermogram of the original pulp and sample acetylated in the presence of

377　only hyamine showed an endothermic transition at 133 °C but no glass transition. The extractives

378　in the wood pulp, including fats, phenolics, resin acids and waxes, contributed to this seemingly

379　endothermic peak. This peak was not found in samples with sufficient acetylation to disrupt the

380　hydrogen bonding of the pulp, confirming the poor extent of reaction for the sample prepared in

381　the presence of only hyamine. The highly acetylated lignocellulose prepared by the acetic acid

382　solvent method displayed an apparent glass transition temperature (T_g) at 164 °C, which is lower

383　than the 180-200 °C reported for pure cellulose acetate due to the inclusion of acetylated lignin

384　(Teramoto 2015). The modified pulp with functionalizing agent showed a glass transition at around

385   161 °C (T_{g1}), close to the acetic acid solvent modified sample, and another at 123 °C (T_{g2}). The

386   bulky size and sparse attachment of the benzethonium group afforded greater chain mobility as a

387   distinct phase in the modified pulp. The improved thermoplasticity seen in subsequent tests for the

388   modified pulp by the sulfuric acid/hyamine approach compared to conventional acetylation can be

389   directly attributed to this newly emerging phase.
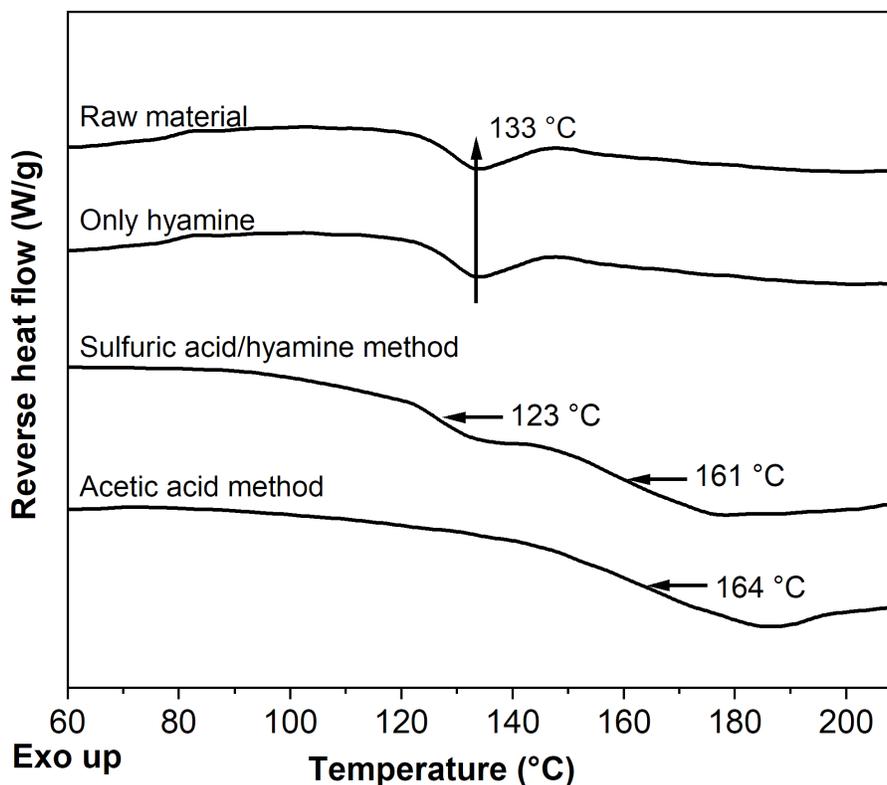
390

391   **Fig. 8** Modulated DSC results of the raw material and modified pulps by three different processes. The lignocellulose
392   acetate had an acetyl content of 10.2 mmol/g prepared by the acetic acid method compared to 2.5 mmol/g for the case
393   prepared with hyamine only. The modified lignocellulose prepared by sulfuric acid/hyamine method had an acetyl
394   content of 6.0 mmol/g and 0.3 mmol/g functionalizing agent (moiety 1)

395   Thermoplasticity of the modified pulp was qualitatively determined by the moldability of

396   samples from compression molding. Inserted images in Fig. 9 show a semi-transparent yellow film

397   was produced with the modified pulp using the functionalizing agent whereas the highly acetylated

398   pulp sample by the acetic acid method mostly charred without evidence of flow. The modified

24

399   pulp by the sulfuric acid/hyamine method appeared to be showing flow attributes comparable to

400   synthetic plastics while the purely acetylated pulp retained its fibrous structure and solid-like

401   nature in the mold. As compared with modified α-cellulose (Table 2), the presence of lignin

402   afforded lignocellulose with a higher degree of modification and consequently, a better

403   compression modability. Quantitively, thermoplasticity of the modified pulp was evaluated

404   rheologically by DMA, though results were limited to those samples suitably ductile for testing

405   which did not include the sample prepared by the acetic acid method or the highly degraded sample

406   from the first experimental series with a sulfuric acid/hyamine ratio of 1.96. Fig. 9 shows the loss

407   factor measured for the molded films of the modified lignocellulose; the measure is often a better

408   indicator of processability whereas DSC results are more insightful into the composition. A single

409   peak is seen for each modified sample tested by DMA whereas the DSC results had found two

410   glass transitions for the modified samples, reflecting the dominant nature of the acetylated domain

411   despite the benefits of the benzethonium-based domain on overall moldability.

412   Fig. 9a shows results for the first series of experiments where the thermoplasticity of the

413   modified wood pulp appeared to be mainly determined by the degree of benzethonium sulfate

414   modification. At a sulfuric acid/hyamine ratio of 0.25, the loss factor had no definitive peak in the

415   tested temperature range which indicated that there was no significant transition from the solid-

416   like deformational nature of this lignocellulose at its low degree of acetylation and benzethonium

417   sulfate attachment. A well-defined peak was found centered at 169 °C at a ratio of 0.49, increasing

418   to 176 °C for a ratio of 0.96; the higher temperature required to transition from a solid-like to more

419   liquid-like deformational response at the higher ratio negated considerations that the measure was

420   influenced by molecular weight since the extent of degradation was greater according to intrinsic

421   viscosity measurements. The greater tendency to flow at lower temperatures, which is a reasonable

422 definition of thermoplasticity for this study, is noted at the optimal condition for benzethonium

423 sulfate attachment. Fig. 9b shows results for samples from the second set of experiments. As

424 sulfuric acid content increased from 13.4% to 26.8% (w/w), the peak remained at 169 °C though

425 it narrowed to reflect a sharper transition in flowability. Since the acetyl content and benzethonium

426 sulfate attachment was not significantly different between the two conditions, the narrowing may

427 be attributed to degradation which was significant with 26.8% sulfuric acid addition. The peak

428 shifted to 159 °C at the highest sulfuric acid content of 40%. This improved thermoplasticity might

429 be influenced by the ever-increasing degradation to the pulp from such high usage of sulfuric acid

430 in the reaction; however, considering its small influence on the other results and greater sensitivity

431 to the benzethonium group, it seems more reasonable to attribute to the increase in moiety 2. In

432 general, the analysis shows the importance of the benzethonium sulfate attachment rather than

433 acetyl content or extent of degradation on the thermoplasticity of the modified lignocellulose.
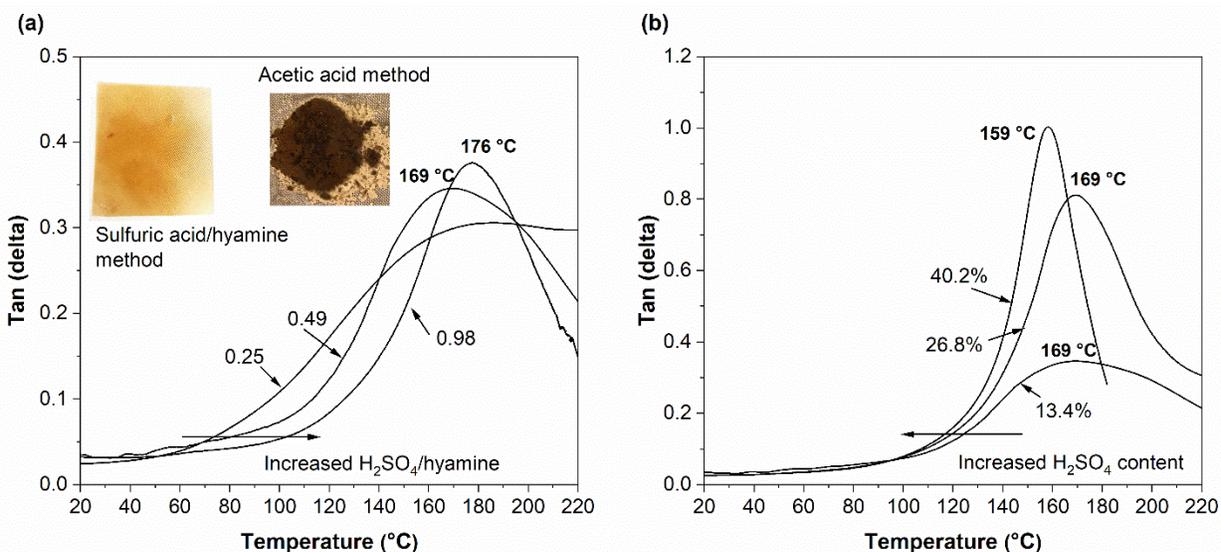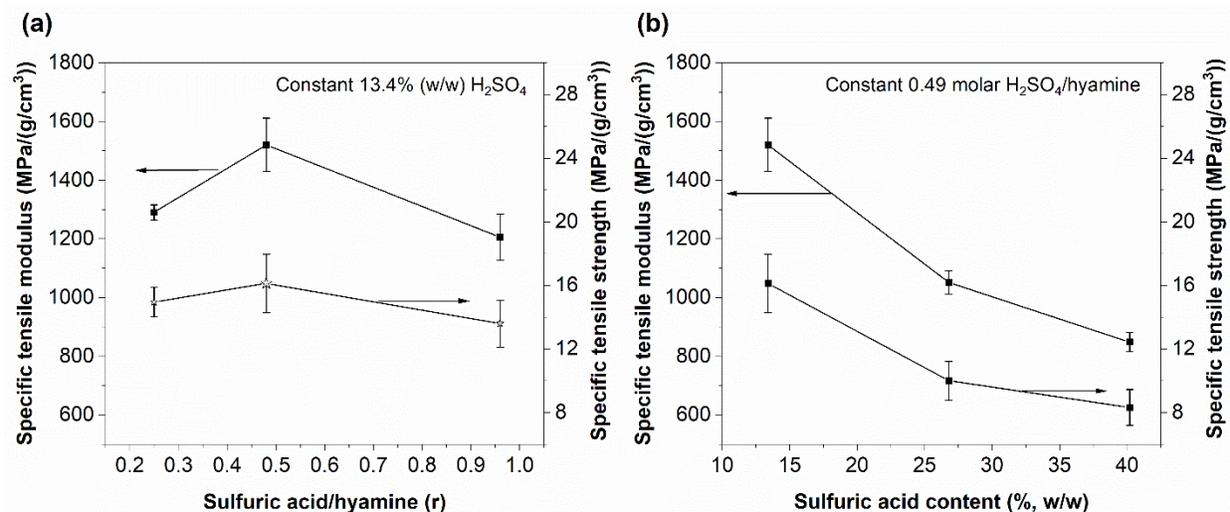
434

435 **Fig. 9** Loss factor (tan(δ)) determined by DMA testing of the modified pulp-thermoplastics of (a) the first set, sample
436 modified with a 1.96 molar ratio of sulfuric acid/hyamine was brittle for the testing and (b) the second set of trials.
437 Inserted images are hot-pressed samples of modified pulps by two different methods

438   Mechanical properties

439   Fig. 10 shows the specific tensile properties of the modified pulp which has been established above

440   as a thermoplastic. The molded films exhibited high stiffness at room temperature with specific

441   Young's moduli in the range of 0.9-1.6 GPa and a low tensile strain of less than 1% (elongation at

442   break). For the first set of experiments, Fig. 10a shows that the modified wood pulp prepared at

443   the ideal sulfuric acid/hyamine ratio of 0.49 had the highest modulus and strength. Though

444   degradation should have been lowest at the ratio of 0.25, the modified sample exhibited a lower

445   stiffness due to its relatively poor thermoplasticity. Its lower acetyl and functionalizing agent

446   content meant it exhibited a more discrete fibrous behavior, yielding poor stress transmission

447   through the film. Comparably, at a ratio of 0.96, the brittle film was more prone to crumble under

448   deformation, making the result questionable. At least the sample at the ratio of 0.49 showed

449   thermoplastic properties and produced a reliable test specimen, which meant the analysis of

450   samples of the second set of experiments was likely the most informative on the material properties

451   affecting its mechanical nature.

452   Fig. 10b shows a significant drop in both modulus and strength as the sulfuric acid content was

453   increased for a fixed ratio of 0.49; the decline in tensile properties matched the loss in molecular

454   weight detected by intrinsic viscosity. Considering the small changes in acetyl content and

455   benzethonium sulfate attachment among these samples, the tensile properties were related to the

456   extent of degradation. Such high levels of sulfuric acid in the reaction, as used in the second set of

457   experiments, would seem undesirable if the goal of the synthesis is to retain the excellent

458   mechanical properties inherent to cellulose pulp. Fortunately, the modulus and strength of the

459   optimal modified pulp in these tests seems to be a reasonable substitute for many synthetic

460   polymers (though more ductility would be beneficial).

461

462 **Fig. 10** Specific tensile modulus and strength of modified wood pulp-thermoplastics of (a) the first set, sample
463 modified with a 1.96 molar ratio of sulfuric acid/hyamine was brittle for the testing and (b) the second set of
464 trial, the apparent density of the thermoplastic was in the range of 1.01-1.07 g/cm^3

465

Conclusions

467 The functionalizing agent based on hyamine and sulfuric acid was seen to effectively wet the

468 lignocellulose fibrous mass for the acetylation of lignocellulose. The presence of hyamine was

469 essential for homogenously dispersing lignocellulose and minimizing degradation. More

470 significantly, with regards to the goal of producing a thermoplastic from the wood biomass, was

471 the spectral and elemental results demonstrating that the benzethonium species had become

472 chemically bonded during the reaction. The grafted benzethonium sulfate rather than acetyl species

473 appeared to influence strongly the thermoplasticity of the modified lignocellulose, which resulted

474 in flow attributes comparable to synthetic plastics. The resulting bio-thermoplastics exhibited high

475 stiffness at room temperature with Young's moduli in the range of 0.9-1.6 GPa and a low tensile

476 strain of less than 1%.

28

482 **Compliance with ethical standards**

483 **Conflict of interest**   The authors associated with McMaster University declare no conflict of
484 interest. David J. W. Lawton is an employee of the Xerox Research Centre of Canada, a division
485 of Xerox Canada.

486

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