In-situ modification of cellulose nanofibrils by organosilanes during spray drying

Lu Wang a,b, J.Elliott Sanders a,b, Douglas G. Gardner a,b,*, Yousoo Han a,b

a School of Forest Resources, University of Maine, 5755 Nutting Hall, Orono, Maine 04469-5755, USA
b Advanced Structures and Composites Center, University of Maine, 35 Flagstaff Road, Orono, ME, 04469-5791, USA

A R T I C L E   I N F O
Article history:
Received 26 October 2015
Received in revised form 27 January 2016
Accepted 3 February 2016
Available online xxx

Keywords:
Cellulose nanofibrils
Spray drying
Modification
Morphology
Particle size
Surface energy

A B S T R A C T
Cellulose nanofibrils (CNFs) have shown their potential as the sustainable choice for reinforcements in thermoplastic composites. Studies on surface properties are important because they directly relate to the compatibility between CNFs and polymer matrices. In this study, CNF suspensions were treated with two different organosilane functionalities before being spray-dried (SD). Three concentration levels of organosilane solution were applied based on the mass of the CNFs in suspension: 1 wt. %, 3 wt. % and 5 wt. %. Morphological and surface properties of the CNFs were measured to understand changes induced by the organosilane modification. Scanning electron microscopy analysis shows some aggregation of larger particles as well as many small twisted rectangular particles. Particle size distribution analysis (PSD) indicates certain differences among treated and untreated CNFs. Inverse gas chromatography (IGC) reveals that the organosilane treatment reduces the dispersion component of surface energy of dried CNFs and changed the acid-base characteristic of CNFs by the attachment of different functional end-groups.

1. Introduction

Nanocellulose refers to various celluloseic nanoparticles that include: cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs) and bacterial cellulose (BC). CNFs are prepared by mechanical fibrillation, very much like producing wood pulp with additional fibrillation by high-pressure homogenization, grinding or refining. CNCs are made by acid hydrolysis of pulp and BCs are synthesized from the bottom up by bacteria (Moon et al., 2011). Nanocellulose is formed through the aggregation of cellulose macromolecular chains by hydrogen bonding. Each cellulose chain comes from the polymerization of β-D-glucose at C1 and C4 positions with a degree of polymerization ranging from 1000 to 1500. Nanocellulose cross-sectional dimensions are within the nano-scale size range, imparting them very unique properties: (1) large surface area, (2) high modulus of elasticity and high tensile strength (Moon et al., 2011), (3) transparency (Okahisa et al., 2009) and (4) low thermal expansion and high thermal conductivity (Shimazaki et al., 2007). Compared to other forms of nanocellulose, CNFs are relatively cheaper to produce and much closer to commercial utilization. In most instances, the dimensions of CNFs and micro fibrillated cellulose are on the same length scale. They are all referred to as CNFs in this paper. The strength properties of the cellulose show promising results for additive use in thermoplastics (Yang et al., 2011). Because of their superior mechanical properties, CNFs are as emerging nanomaterials are proving to be a suitable replacement for polymer composite reinforcements, like glass fibers. The advantages cellulose nanofibrils hold over conventional composite reinforcements are their availability on a global scale, a sustainable life cycle and ecofriendly properties. There have been a number of literature reviews done on CNFs covering their structure, preparation, characterization, modification and applications, which addresses their importance as a nanomaterial (Khalil et al., 2012; Siró and Plackett, 2010; Lavoine et al., 2012; Missoum et al., 2013; Khalil et al., 2014; Kaila et al., 2014; Osong et al., 2016; Gandini and Belgacem, 2015). For most thermoplastics, which are hydrophobic, the hydrophilicity is the biggest disadvantage for mixing with CNFs. The CNFs cannot be adequately wetted by polymer matrices and weak bonds are formed between the two phases. As a result, mechanical stresses cannot be transferred to CNFs efficiently and their reinforcing potential cannot be fully achieved. Moreover, during compounding, CNFs tend to aggregate by hydrogen bonding. These aggregates are unevenly distributed within polymer matrices. Stress concentrations may occur when...
composites are under load. Therefore, surface modification of CNFs is a first step in utilizing them in hydrophobic polymers.

Silane coupling agents, one of the numerous modification methods, are found to be both a convenient and effective way to treat cellulose fibers: a small quantity added during processing generates significant improvements in material properties. Applying silanes to cellulose fibers has already been well addressed (Lu et al., 2000; Belgacem and Gandini, 2005; Hubbe et al., 2008; Xie et al., 2010). A few articles regarding silane treatment of CNFs were reported. CNFs were modified by isopropyl dimethylchlorosilane in toluene (Goussé et al., 2004). The modified CNFs maintained their nano scale in aqueous suspension and their dispersity in organic solvents increased. The viscosity of modified CNFs suspensions decreased because of reduced hydrogen bonding. The same silane was used to hydrophobilize the CNFs (Andresen et al., 2006). A reduced surface energy was indicated by a very high water contact angle on a film prepared from silane modified CNFs. Reduced surface energy of CNF aerogels was also found by perfluorodecytrichlorosilane or octyltrichlorosilane treatments via chemical vapor deposition (CVD) (Aulin et al., 2010; Cervin et al., 2012). CNFs were treated by 3-aminopropyltriethoxy silane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) in acetone (Lu et al., 2008) and better adhesion between CNFs and epoxy resin was found, resulting in improved mechanical properties. Lu and Drzal treated CNFs with APS then solvent cast a CNF/cellulose acetate (CA) composite films from an acetone suspension (Lu and Drzal, 2010). The mechanical properties of CA were significantly enhanced by the APS treated CNFs. The mechanical property improvement came from the good dispersion of fibers and covalent bonding with the matrix induced by APS. The thermal stability of APS treated CNF/CA composite was slightly increased which was attributable to reduced CNF hydroxyl groups and better fiber adhesion to the matrix. Silanes are also used in industry for modifying glass fibers. The success of applying silanes to CNFs should expedite commercial scale composite production.

Currently, CNFs are processed and dispersed in aqueous suspensions because of their hydrophilicity. The aqueous suspension is expensive to transport and is detrimental to thermoplastic processing such as extrusion and injection molding (Peng et al., 2012a,b). Therefore, drying CNF is a necessary procedure before their utilization. Oven drying, freeze drying, supercritical drying and spray drying were compared to investigate which one is more effective and economical (Peng et al., 2012a,b). Spray drying CNF was proven to be a scalable and inexpensive method with controllable particle size distribution (Peng et al., 2012a,b).

Usually, the introduction of coupling agents to cellulose fiber is done either during compounding or it requires a specific procedure. If the coupling agents are added during compounding, their efficiency is not high because not all of them can react with the cellulose fibers. If the modification step is performed separately, it is time-consuming and the cost increases. Hence, in-situ modification of cellulose surface during spray drying is an innovative way to satisfy the requirements for both CNF modification and processing costs. Moreover, the condensation reaction between silane and the hydroxyl groups of cellulose takes place only when the temperature is above 100°C (Xie et al., 2010) which can be easily achieved and maintained during spray drying.

In-situ modification of CNFs with silanes during spray drying was reported in our patent (Gardner et al., 2013). Because silanes will react with the hydroxyl groups of CNFs and reduce the sites for hydrogen bonding, they have the potential to reduce the size of spray dried CNF particles. Yet, to the best of our knowledge, there is no report on the effect of silanes on the particle size of CNFs produced during spray drying.

This research applied organosilane treatment to CNFs during spray drying, taking full advantage of the heat generated during drying to promote the silanization reaction. Morphological properties (particle morphology and particle size distribution) and surface properties (dispersion component of surface energy and acid-base characteristics) of modified CNFs were studied.

2. Experimental

2.1. Materials

CNF suspensions with a solids content of 3.4 wt.% from the Process Development Center at the University of Maine, were the primary materials tested in this experiment. Two organosilanes (Fig. 1) used were purchased from Sigma–Aldrich. They are (3-Glycidyloxypropyl) trimethoxysilane (GPS), >98%, molecular weight 236.34 g/mol and vinyltrimethoxysilane (VTS), >98%, molecular weight 148.23 g/mol. Other chemicals included ethanol (95%), acetic acid (reagent plus, >99%) and distilled water. Ethanol is used as a dispersion agent. Distilled water helps hydrolysis. Acetic acid manipulates the pH level of solution and produces an acid-catalyst environment which favors hydrolysis over self-condensation of silanes (Salon et al., 2007).

2.2. Suspension preparation

The solution used for hydrolysis was prepared by first mixing an 80/20 (w/w) ethanol/water solution. Then, acetic acid was carefully added to the solution to adjust the pH values. The pH level of solution was monitored by an Orion 420A pH meter until it read 4. Constant agitation of the mixture provided a consistent acetic acid solution. Organosilanes were measured by three weight percentages (1, 3, 5 wt.%) based on CNFs mass and added into the solution. The concentration of organosilane in the solution was targeted at 1 wt.%. The organosilane mixture stayed covered in a fume hood for 6 h to allow the hydrolysis reactions to occur. Previous research showed that 2 h was good to generate the most available silanol (Salon et al., 2007). CNF suspensions were diluted to 0.7% with distilled water. The hydrolyzed solution was poured into the suspension and kept in an ultrasonic mixer for 30 min. The ultrasonic mixer helps disperse the CNFs along with the organosilane mixture. Following ultrasonic mixing, the solution was mixed by magnetic stirrer for 3 h. The solution was finally mixed using a Speed Mixer (Flack Tek Inc., US) at 2000 rpm for 2 min. Spray drying was done immediately after this mixing step.

Please cite this article in press as: Wang, L., et al., In-situ modification of cellulose nanofibrils by organosilanes during spray drying. Ind. Crops Prod. (2016), http://dx.doi.org/10.1016/j.indcrop.2016.02.004
2.3. Spray-drying

The spray dryer used was a Mini Spray Dryer B-290 (Buchi, Switzerland). By changing the spray drying parameters, particles with different morphologies and sizes can be obtained (Peng et al., 2012a,b). For our experiments, the Spray Dryer (SD) inlet temperature was set to 175 °C. Compressed nitrogen gas was sent through the SD nozzle at 540L/min, atomizing the suspension particles flowing through it. The outlet gas temperature ranged from 80 to 90 °C. The aspirator ran at 100% with the gas flow rate set at 8 mL/min or 35 mm on the flow gauge. All samples were collected in vials and sealed properly.

2.4. Scanning electron microscopy (SEM)

Qualitative information of the morphology was obtained by observing spray dried CNF powders using a Hitachi Tabletop Microscope SEM TM 3000 (Hitachi High-Technologies Corporation, Tokyo, Japan). The set accelerating voltage was 15 kV. Various magnifications were used for obtaining CNF images.

2.5. Particle size distribution analysis (PSD)

Quantitative information of morphology was achieved using a Malvern Mastersizer and the Sirocco dry particle analysis cell (Malvern Instruments, Ltd., Malvern, Worcestershire, UK). The basic theory for this analysis is based on Mie theory which deals with spherical particles (Mie 1908). Because particles are not always spherical, a technique called “equivalent spheres” is used. This device uses the volume of the particle to calculate diameter. A sphere that has the same volume of a measured particle is generated by the software and its diameter is taken as the diameter of that particle. This is the so called “equivalent sphere diameter.” A pre-set standard of operation was used to automatically perform the analysis. First, the system checks the background electrical noise and scattering data from the dust on the optics. Adding samples to a tray (around 1 g) until the obscuration bar in the screen reaches a green

Please cite this article in press as: Wang, L., et al., In-situ modification of cellulose nanofibrils by organosilanes during spray drying. Ind. Crops Prod. (2016), http://dx.doi.org/10.1016/j.indcrop.2016.02.004
area. After closing the lid of the tray, a vacuum draws samples in and the instrument runs the analysis automatically. Parameters of the operation used for this study were 4 bar of air pressure and 20% of feeder capacity. Five replicates were measured for each sample.

2.6. Inverse gas chromatography (IGC)

The dispersion component of surface energy and acid-base characteristics of dried powders were measured and calculated based on a SMS-IGC device (Surface Measurement Systems, London, UK). A more detailed mechanism and description of IGC can be found elsewhere (Peng et al., 2013). A specific type of pre-silanized glass tube, 30 cm in length and 4 mm in inner diameter was plugged at one end by silanized glass wool. CNF powders were introduced into the tube by a hopper and an electric vibrator. After an amount of sample was added into the tube, the other end of the glass tube was also plugged by silanized glass wool. Once the glass tube was in place, helium was used as the carrier gas and methane was used as a reference gas. Conditions for running the test were 0% of RH and 10 standard cubic centimeters per minute (sccm) of carrier gas flow rate. Before running a test, columns were conditioned in situ for 4 h at 30 °C. Vapor concentration of the probe molecules applied was 0.03%/p0 (p is the partial pressure, p0 is the vapor pressure). The detection method of retention times of the probe gases was flame ionization detector. The peak maximum method was used to determine the retention time of all probe gases (Conder and Young 1979). The dispersion component of surface energy was calculated (Schultz et al., 1987). Acid-base characteristics were calculated based on the theories of Gutmann (1978), Schultz and Lavielle (1989) and Fowkes (1964). Each IGC test was run in duplicate.

3. Results and discussion

3.1. Surface modification mechanism

Silane molecules undergo hydrolysis to form –OH groups necessary for grafting. The time needed for hydrolysis is speculated to be a minimum of 2 h (Abdelmolleh et al., 2002). During this time, the ethoxy part of silane molecules reacts with water to form silanols (Salon et al., 2007). Silanols are then adsorbed on the CNFs by intermolecular forces (Salon et al., 2007). At this point, covalent bonds are possible upon heating (over 100 °C), forming the Si–O–C bridge. Self-condensation among silanols is also possible (Salon et al., 2007). Stabilization of molecules available to graft on cellulose and reduction of self-condensation is controlled through manipulating acidity values in the mixture (Salon et al., 2007). Lower pH values significantly favor hydrolysis over self-condensation. However, strong acidity may also degrade the CNFs. Therefore, a pH = 4 was used here.

According to Fig. 2, if the CNFs are not treated, they will agglomerate by forming hydrogen bonding among fibers. On the contrary, if the hydroxyl groups of CNFs react with the silanols, Si–O–C will be formed to prevent the hydrogen bonding. Moreover, two silanes adopted in this research impart CNF lower surface energy (Table 2), which will reduce the fiber aggregation from a thermodynamic perspective. The discussion below will be based on this mechanism.

3.2. Morphology of dried CNFs

SEM results showed very similar morphologies of the dried CNFs and they are shown in Fig. 3. Both nano and micro scale particles are found in those images. Large agglomerates, ranging from 50–150 μm, are seen throughout all treatment types and concentrations. Significant differences are difficult to determine because of the lack of consistent dispersion among samples. These particles easily reach the tens of microns in width and length. Larger groupings are mostly rectangular in shape and dispersed fairly regularly. Morphology of the particles is mostly irregular or bent rectangular forms. Former research has shown that CNF particles, formed during spray drying, initially extend outside of the surface of the water droplets in which the particles are encased (Peng et al., 2012a,b). The shrinkage that occurs around the particles during spray drying causes irregular formation of various agglomerates, similar to the ones seen in Fig. 2. The more spherical the particles in the beginning, the more wrinkled they become after drying (Peng et al., 2012a,b).

3.3. Particle size distribution (PSD)

PSDs of all samples are displayed in Fig. 4. Overall, the silane treatment does not affect the spray dried CNFs. A small percentage of nano-scale particles still exist. However, as a proof for the SEM results, there is little difference of PSD among treated and untreated groups. This finding conforms to previous research where CNFs were modified with maleic anhydride polypropylene (MAPP) emulsion during SD (Peng et al., 2014). It was pointed out that the MAPP emulsion treatment did not change the morphology of CNF. A possible reason why the PSD remains consistent is that the concentration of organosilane used may be too little to have an effect on dry particle formation. Former researchers have adopted much higher molar ratios of silane to glucose in CNF silane modification. For example, molar ratios of 4:1 and 2:1 were used to modify CNFs with isopropylidimethylchlorosilane (Gouss et al., 2004). Molar ratios of 3:1 and 6:1 were used in another study to modify CNFs with silane (Andresen et al., 2006). To modify CNFs for an epoxy matrix, a molar ratio about 2:1 was used (Lu et al., 2008). The highest molar ratio adopted here, corresponding to a concentration of 5 wt. %, was around 0.05:1. The use of organosilane as an additive would increase composite costs and dosage should be kept small from a commercial view point.

ANOVA results for equivalent sphere diameters are presented in Table 1. D(v, n), the equivalent sphere diameter, means that 100’n vol.% of the tested sample is smaller than this diameter. As seen in Table 1, the p values of silane type and concentration are sometimes smaller than 0.05, which means they alone may have a significant effect on the diameter. However, the p values of interaction effects of silane type and concentration are smaller than 0.0001 in every case, meaning the two factors together, instead of a single factor, affect the diameter. In other words, the combination of silane type and concentration influence the equivalent sphere diameter of dried CNFs at all percentile levels. However, the changing trend is different in each percentile, which is discussed below.

Fig. 5 shows average equivalent sphere diameters for each CNF treatment. Letters above the columns show the difference in diameter of each sample: same letter means no significant difference in diameter among those groups, while different letters show significant difference. As seen in (a), GPS 1% (2.4 μm) and VTS 5% (2.5 μm) both significantly increase the D(v, 0.1), while GPS 3% (2.1 μm) and GPS 5% (2.2 μm) reduced the D(v, 0.1), compared to control CNF.
Table 1
Two-way analysis of variance on equivalent sphere diameters.

<table>
<thead>
<tr>
<th>DF</th>
<th>Source</th>
<th>Degree of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Corrected total</td>
<td>39</td>
<td>0.983</td>
<td>0.002</td>
<td>21.86</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>model</td>
<td>7</td>
<td>0.813</td>
<td>0.116</td>
<td>28.22</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Silane</td>
<td>1</td>
<td>0.149</td>
<td>0.149</td>
<td>2.77</td>
<td>0.0576</td>
</tr>
<tr>
<td></td>
<td>concentration</td>
<td>3</td>
<td>0.044</td>
<td>0.014</td>
<td>38.62</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Silane*concentration</td>
<td>3</td>
<td>0.618</td>
<td>0.206</td>
<td>28.22</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>32</td>
<td>0.17</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>Corrected total</td>
<td>39</td>
<td>11.115</td>
<td>1.444</td>
<td>46.01</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>model</td>
<td>7</td>
<td>10.111</td>
<td>1.444</td>
<td>8.71</td>
<td>0.0059</td>
</tr>
<tr>
<td></td>
<td>Silane</td>
<td>1</td>
<td>0.273</td>
<td>0.273</td>
<td>41.77</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>concentration</td>
<td>3</td>
<td>9.333</td>
<td>3.111</td>
<td>62.69</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Silane*concentration</td>
<td>3</td>
<td>5.004</td>
<td>1.668</td>
<td>41.77</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>32</td>
<td>1.005</td>
<td>0.0314</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>Corrected total</td>
<td>39</td>
<td>88.012</td>
<td>2.222</td>
<td>22.15</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>model</td>
<td>7</td>
<td>72.952</td>
<td>10.421</td>
<td>41.77</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Silane</td>
<td>1</td>
<td>1.031</td>
<td>1.031</td>
<td>21.9</td>
<td>0.1487</td>
</tr>
<tr>
<td></td>
<td>concentration</td>
<td>3</td>
<td>41.528</td>
<td>14.509</td>
<td>30.83</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Silane*concentration</td>
<td>3</td>
<td>28.394</td>
<td>9.464</td>
<td>20.11</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>32</td>
<td>15.059</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Indicates the interaction between silane and concentration.

Table 2
Dispersion component of surface energy of CNFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion component of surface energy $\gamma_{Iw}$ (mj/m²)</th>
<th>$d$</th>
<th>$\gamma_{Iw}/dT$ (mj/m²/K)</th>
<th>$k^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>51.0</td>
<td>48.4</td>
<td>45.9</td>
<td>-0.255</td>
</tr>
<tr>
<td>VTS 1%</td>
<td>49.2</td>
<td>45.9</td>
<td>43.7</td>
<td>-0.275</td>
</tr>
<tr>
<td>VTS 3%</td>
<td>50.0</td>
<td>47.2</td>
<td>44.4</td>
<td>-0.28</td>
</tr>
<tr>
<td>VTS 5%</td>
<td>48.2</td>
<td>44.1</td>
<td>39.6</td>
<td>-0.43</td>
</tr>
<tr>
<td>GPS 1%</td>
<td>44.9</td>
<td>42.6</td>
<td>38.7</td>
<td>-0.31</td>
</tr>
<tr>
<td>GPS 3%</td>
<td>44.7</td>
<td>41.9</td>
<td>38.3</td>
<td>-0.32</td>
</tr>
<tr>
<td>GPS 5%</td>
<td>41.8</td>
<td>39.7</td>
<td>37.5</td>
<td>-0.215</td>
</tr>
</tbody>
</table>

(2.2 μm). In (b), GPS 1% (8.3 μm) and VTS 5% (8.9 μm) increase the $D(v, 0.5)$ of control sample (7.4 μm), while other treatments do not result in a statistically significant difference in particle size. The situation changes in $D(v, 0.9)$ where only VTS 1% (20.3 μm) and 3% (18.8 μm) maintain the diameter compared to control sample (19.5 μm), all others increase the diameter. The possible explanation why the same treatment has different effects on $D(v, 0.1)$, $D(v, 0.5)$ and $D(v, 0.9)$ lies in the diameter calculation method of the software. Laser diffraction is a volume based characterization technique where the influence of small particles on the average equivalent sphere diameter can be neglected. A numerical example can be used to illustrate this issue. Assume that only two particles with different equivalent sphere diameters within the range of this study are considered. One has a diameter of 2 μm and the other one has a diameter of 10 μm. So the volume of the large particle is 125 times bigger than the small particle. The contribution from the volume of the small particle to the total volume is only 0.8%. Values of $D(v, 0.1)$, $D(v, 0.5)$ and $D(v, 0.9)$ will all be 10 μm. The analysis indicates that although small particles exist in the samples, the distribution calculations reduce their impact. There are few papers addressing the size of dried CNFs with surface treatments. A simple description of silane treated CNFs will aggregate strongly after drying was found in a former paper (Lu et al., 2008). In-situ modification of CNFs with MAPT emulsion during SD did not affect the size of dried CNF (Peng et al., 2014). As a comparison, silane treatment has better potential in reducing the diameter of treated CNFs after drying.

3.4. Surface energy and acid-base characteristics

The dispersion component of surface energy ($\gamma_{Iw}$) of dried CNFs at different temperatures is shown in Table 2. The $\gamma_{Iw}$ of cellulose material mainly depends on the presence and concentration of free hydroxyl groups on the surface (Garnier and Gasser, 1996). More hydroxyl groups on the surface are concurrent with higher values of $\gamma_{Iw}$ (Peng and Gardner, 2015). With the temperature increases, the $\gamma_{Iw}$ decreases because the thermal energy can reorient the surface hydroxyl groups away from the surface, thus reducing the amount of free hydroxyl groups on the surface (Peng et al., 2013). The $\gamma_{Iw}$ of the control CNF in this research (51.01 mj/m² at 30°C, 48.42 mj/m² at 40°C and 45.94 mj/m² at 50°C) conforms well with previous CNF literature (53.7 mj/m² at 30°C, 50.9 mj/m² at 40°C and 48.2 mj/m² at 50°C) (Peng et al., 2013). Compared to the control CNF, the organosilsane treated CNF exhibits a lower $\gamma_{Iw}$. Earlier cellulose silane modification research found a similar tendency with amino and alky silanes which decrease the $\gamma_{Iw}$ of lyocell fiber (Tze et al., 2006). Also, $\gamma_{Iw}$ of silica was reported to drop after silanized with GPS or VTS (Kimura et al., 2000). When silane concentration increases, the $\gamma_{Iw}$ decreases. A lower $\gamma_{Iw}$ of hydroxyl groups on the surface of cellulose (Garnier and Gasser, 1996). This indicates that silanes are either chemically or physically adsorbed on the surface of CNFs, decreasing the number of free hydroxyl groups on the surface. The GPS treated groups had lower $\gamma_{Iw}$ than the VTS treated groups. The lower $\gamma_{Iw}$ may be attributed to the glycidyl functional group. As shown from Table 2 and Fig. 5, VTS at 5 wt% reduced the $\gamma_{Iw}$ of CNFs by 2% at 30°C. In contrast, the GPS at 5 wt% decreased the $\gamma_{Iw}$ by 18% at the same temperature. The temperature coefficients of dispersion component of surface energy ($d\gamma_{Iw}/dT$) align well with the reported values, which are between -0.22 and -0.35 mj/m² K, except VTS 5% treated cellulose (Tze et al., 2006). An increase in $d\gamma_{Iw}/dT$ suggests an increased entropic contribution to the surface energy which could result from either increased randomness in the system or a more energeti-
which justifies the increase in $K_a$. The increase in $K_a$ comes from the fact that the $s$ orbital property in $sp^3$ hybrid orbital of the vinyl group is greater than $sp^2$, making the carbon atoms of the vinyl group more electronegative. Consequently, the terminal hydrogen atom is easily released as a proton (Kimura et al., 2000). Another source for the increased acidity is the existence of uncondensed silanols on the CNF surface at high silane loading level. Compared to the VTS treated CNFs which alter the basicity of CNFs at 5 wt.%, the GPS increases the basicity of CNF as concentration increases. At 3 wt.%, the basicity of the GPS treated CNFs is around 2. The ratio between $K_a$ and $K_b$ of GPS also increased as silane concentration increased. Therefore, the GPS treated CNF is a more effective electron donor. The chemical structure of GPS verifies this finding where two oxygen atoms in the glycidoxyloxy can both donate electrons. This conclusion conforms well to previous research where GPS was found to increase the basidity of silica (Kimura et al., 2000).

4. Conclusions

SEM results show modest morphological and size changes among each spray-dried CNF particle type. The PSD analysis indicates the silane treatment decreases the size of dried CNFs.

After silane treatment, the CNFs exhibit different surface properties. The dispersion component of surface energy of CNFs treated by GPS is decreased. A reduction in surface energy is beneficial to their interaction with thermoplastic matrices. The VTS at 5 wt.% increased the acidity and basicity of CNFs, while the GPS treatments only increased the basicity of CNFs.

5. Future work

The laser diffraction technique used here provides diameter data based on volume of particles, which impacts the effect from small particles that are low in volume. A different measurement technique could be used to accurately interpret the particle size, for example, a technique based on optical imaging. Understanding whether chemical or physical reactions occur between CNFs and silanols during spray drying is very important. Chemical reaction is preferred because it provides strong covalent bonding between CNFs and silanols. A higher molar ratio of CNFs to silanes should be studied to investigate its effect on particle size and surface chemistry. Other types of coupling agents could be explored based on cost and ease of treatment.

Acknowledgements

We acknowledge the Maine Agricultural and Forestry Experiment Station McIntire-Stennis Project ME0-M-8-00527-13 “Renewable nanocomposites made from lignocellulosic fillers and transparent polymer matrices” and the National Science Foundation Research Experience for Undergraduates Project EEC-106 307 Explore It! Building the Next Generation of Sustainable Forest Bioproduct Researchers for financial support. Much appreciation goes to The Process Development Center at the University of Maine for providing the nanofibrillated cellulose suspension.

References
