

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Epoxy Composites Using Wood Pulp Components as Fillers

Douglas M. Fox, Noy Kaufman, Jeremiah Woodcock,
Chelsea S. Davis, Jeffrey W. Gilman, John R. Shields,
Rick D. Davis, Szabolcs Matko and
Mauro Zammarano

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65261>

Abstract

The components of wood, especially lignin and cellulose, have great potential for improving the properties of polymer composites. In this chapter, we discuss some of the latest developments from our lab on incorporating wood-based materials into epoxy composites. Lignosulfonate was used as a flame retardant and cellulose nanocrystals were used as reinforcing materials. Lignosulfonate will disperse well in epoxy, but phase separates during curing. An epoxidation reaction was developed to immobilize the lignosulfonate during curing. The lignosulfonate–epoxy composites were characterized using microcombustion and cone calorimetry tests. Cellulose also has poor interfacial adhesion to hydrophobic polymer matrices. Cellulose fibers and nanocrystals aggregate when placed in epoxy resin, resulting in very poor dispersion. The cellulose nanocrystal surface was modified with phenyl containing materials to disrupt cellulose interchain hydrogen bonding and improve dispersion in the epoxy resin. The cellulose nanocrystal–epoxy composites were characterized for mechanical strength using tensile tests, water barrier properties using standardized water absorption, glass transition temperatures using differential calorimetry, and aggregation and dispersion using microscopic techniques.

Keywords: cellulose, lignosulfonate, flammability, reinforcement, epoxy

1. Introduction

Wood is comprised of three of the most abundant natural polymers on earth: cellulose, lignin, and hemicellulose. Wood fibers and extracted cellulose fibers have good structural characteristics, and their use in polymers as an inexpensive filler for strength and stiffness improvements is well documented [1–5]. Lignin can also be used as a reinforcing filler, though its irregular structure and natural composition variability can lead to reduced toughness, while the phenolic moieties can promote heat instability [6–9]. Nevertheless, there are benefits, such as sustainability, cost reduction, and improved stiffness, to incorporating wood-based fibers into polymers.

Fiber composites can be prepared using either thermoplastics or thermosets. Thermoplastics have higher impact strength, are recyclable, and can be molded into a variety of shapes, while thermosets are typically stronger, easier to process, and less expensive. Most fiber-reinforced plastics in use today are thermosets. One of the most versatile and widely used thermosets is bisphenol-A-based epoxy systems [10, 11]. These polymers suffer from poor impact strength and are typically reinforced with glass, polymer, or carbon fibers.

Lignin has been used to increase stiffness and toughness in thermoset composites [7, 9, 12]. The addition of lignin was found to toughen neat epoxy [12] and hemp-reinforced epoxy composites [13]. And, lignin was found to increase the flexural strength in flax-epoxy composites [14]. Lignin has also been used as a condensed phase flame retardant. Initially, it was used as an additive to other flame retardants to reduce the flammability of polypropylene [15–17] and polylactic acid [18, 19]. More recently, lignin has been modified with phosphorous to enhance its flame retardancy, then blended with epoxy [20, 21], polybutylene succinate [22], poly(acrylonitrile-butadiene-styrene) [23], and wood plastic composites [24]. And, lignosulfonate has been used unmodified to reduce the flammability of epoxy composites [25]. More often, however, lignin is used as a raw material for the preparation of polymers. Due to the phenolic structure of lignin, it is most often used as a prepolymer for epoxy composites. Typically, the lignin is depolymerized, then epoxidated with epichlorohydrin to produce polyglycidyl phenolic monomers and oligomers [11, 26, 27]. In some cases, it has been aminated to act as a hardener in epoxy composites [28–30]. Recently, lignin has been fractionated using ethanol, then epoxidated using epichlorohydrin in the presence of a phase transfer salt, such as tetramethylammonium hydroxide [31, 32]. This isolates the lower molecular weight lignin to produce a liquid epoxy and minimize segregation between the lignin and the epoxy composite. The use of the phase transfer salt does add toxicity to the process and requires an additional liquid–liquid extraction step to remove it.

The main component of plant fiber that adds strength and stiffness is cellulose, making it a good reinforcement agent for polymer nanocomposites. Recently, cellulose nanocrystals, which are the short, highly crystalline regions in a cellulose fiber, have been identified as good candidates to add reinforcement while simultaneously reducing the weight and increasing the sustainability of the reinforced composite [5, 33–35]. Unfortunately, cellulose is hydrophilic while most polymers are hydrophobic, leading to poor adhesion and water absorption problems when blending the two. In addition, when the cellulose nanocrystals are dried they aggregate, and it is extremely difficult to re-separate these aggregates [36, 37].

There have been a variety of approaches to overcome this obstacle. In most studies, a covalently bonded coupling agent is used to improve the adhesion between the crystal and the polymer. Another approach for is to use solvent exchange and solvent casting or thermosetting with the aid of a solvent. In a two-component thermoset, each component can have significantly different chemistries and surface energies, creating opportunities to use processing techniques to improve dispersion of less compatible fillers. One of the most commonly studied epoxy composites are based on diglycidyl ether of bisphenol A epoxy resin and aliphatic diamines. Polyether diamines are typically used to improve flexibility, toughness, and color fastness of the composite. These diamines are significantly more hydrophilic than the epoxy resin or the final epoxy composite, and will have better adhesion with cellulose. Tang and Weder [38] prepared cellulose nanocrystal–epoxy composites by solvent exchange into dimethylformamide and Peng et al. [39] used acetone to create a nanocrystal gel network prior to adding a hydrophilic curing agent, followed by an epoxy resin. These approaches all suffer from laborious and high-energy processing steps. Further, the solvent is difficult to remove, can lead to the loss of desirable composite properties, and add an environmental burden to the process. And, Emami et al. [40] used a polypropylene oxide–polyethylene oxide block copolymer as a surfactant. Although dispersion was improved, there was a loss in tensile strength and elongation by adding the surfactant. We have recently developed a simple, scalable, ion-exchange method to alter the surface energy of cellulose nanocrystals while retaining much of the cellulose surface intact [41].

In this study, we modified wood components using simple procedures to improve their dispersion in epoxy matrices. Lignosulfonate was used as a flame retardant in epoxy composites. The lignosulfonate was epoxidized using epichlorohydrin and sodium hydroxide, then fractionated by extraction in ethanol to minimize migration in the epoxy during curing. The flammability was examined using microcombustion and cone calorimeters and the glass transition temperature was measured using differential scanning calorimetry (DSC). We also prepared cellulose nanocrystal–epoxy composites. A novel ion exchange method was used to eliminate the need for a reaction solvent, reduce the aggregation of the nanocrystals, and improve dispersion throughout the epoxy matrix. The glass transition temperatures were measured using DSC and the dispersion was visualized using confocal fluorescent microscopy.

2. Materials and methods¹

All the chemicals were used as-received unless otherwise indicated. A sulfonated ethoxylated kraft lignin (REAX825E) was provided by MeadWestvaco Corporation (Richmond, VA). Two forms of cellulose nanocrystals were obtained from the University of Maine: (a) an aqueous solution prepared using sulfuric acid, neutralized to the sodium form, and containing 0.95 % mass fraction sulfur on a dry basis and (b) freeze-dried powder, freeze-dried from an aqueous

¹ The policy of NIST is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

solution containing a 9 % mass fraction t-butanol. Ammonium polyphosphate (APP, Clariant EXOLIT AP422, $(\text{NH}_4\text{PO}_3)_{1000+}$) was used as control filler. Ammonium tartrate (AT, Aldrich) and melamine (ML, Melamine 003 fine, DSM) were used as blowing agents. An epoxy monomer (DER331, Dow Plastics) was cross-linked with a diamine-terminated polypropylene glycol (JA230, Jeffamine D230, Huntsman Corp.). Alkali lignin, Dowex 50 W-X2 (50–100 mesh, H^+ form) cation exchange resin and Rhodamine 6G (Rh, 95 %) were obtained from Sigma Aldrich. Methyltriphenylphosphonium bromide (MePh_3PBr , 98 + %) was supplied by Alfa Aesar.

Lignin sulfonate (Reax 825E, 20.6 g) was dispersed in 400 mL of 15 % mass fraction sodium hydroxide solution and stirred for 3 h. After stirring, the solution was filtered using vacuum filtration and a glass fiber filter to remove any undissolved lignin, yielding a dark red solution. The lignin solution was then heated to 50 °C and epichlorohydrin was added (60 g, 0.63 mol). The reaction was stirred for 4 h and then brought to room temperature. The reaction solution was again filtered to remove any precipitates. The majority of water and unreacted epichlorohydrin was removed under high vacuum. The glycidyl lignin sulfonate was extracted from the resulting opaque solid using ethanol (200 proof). The excess sodium hydroxide was removed through repetitive washings of the lignin sulfonate with 50/50 ethanol/isopropanol (volume fraction). Excess ethanol was removed under vacuum at 50 °C. The product was isolated as a viscous red oil (30.8 g). Epoxide content (275 g/equiv) was determined by titration with 0.1 N HBr in acetic acid using a crystal violet endpoint. Cellulose nanocrystals were exchanged using the process described previously [41]. The epoxy composites were prepared by in the following manner. For most composites, fillers were added to either the epoxy resin or amine curing agent using a high shear mixer (FlackTek Inc. SpeedMixer) for 10 min at 260 rad/s (2500 rpm). The other epoxy composite component was added in stoichiometric amounts and mixed again in a high shear mixer for 10 min at 2500 rpm. For some of the composites, fillers were added using a mechanical stirrer and final mixtures were placed in a sonication bath for 30 min. For all composites, the mixture was degassed for 5 min under vacuum and immediately transferred to silicone molds for cone calorimetry (25 g, 75 cm diameter disk), optical properties (22 mm diameter, 1 mm thick), tensile properties (type V, ASTM D 638-02a), and water absorption analysis (51 mm diameter \times 3.2 mm thick). Samples were also extracted using a 1 mL Teflon syringe before and after transferring to the silicone molds for thermal property measurements. These syringes were kept upright during the curing process. All epoxy samples were cured at room temperature for 24 h and 80°C for 2 h. For lignosulfonate containing composites, the total filler content was kept constant at 10 % mass fraction, and for cellulose containing composites, the filler content varied between 0.5 % and 5 % mass fraction.

Combustion properties were examined using microcombustion calorimetry (MCC) and cone calorimetry. The microcombustion calorimetry (MCC) samples (5 ± 0.1 mg) were tested with a Govmark MCC-2 microcombustion calorimeter at 1°C/sec heating rate under nitrogen from 200 to 600°C using method A of ASTM D7309 (pyrolysis under nitrogen). Each sample was run in triplicate to evaluate reproducibility of the flammability measurements. Cone calorimetry was conducted according to a standard testing procedure (ASTM E-1354-07) on a National Institute of Standards and Technology (NIST) prototype calorimeter. The cone was operated with an incident target flux of 35 kW/m² and an exhaust flow of 24 L/s. The sample was placed

in a pan constructed from heavy-gauge aluminum foil (Reynolds Heavy Gauge Aluminum Foil). The sides and bottom of the sample were covered by aluminum foil so that only the top surface of the sample was exposed to the Cone heater. The aluminum foil height was 5 mm higher than the sample to allow for expansion of intumescent samples. Exposure to the 35 kW/m² external heater caused pyrolysis of the sample. Once sufficient fuel (pyrolysis products) was released, ignition occurred, which was activated by a spark igniter. The test was over when there were no visible flames. The standard measurement uncertainty was $\pm 10\%$ of the reported reduction values and ± 2 s in time.

Optical images were obtained using a Zeiss ID03 inverted microscope, equipped with LD10, LD20, and LD32 phase contrast objectives and an AmScope 5.0MP Microscope USB Camera. A confocal laser scanning microscope (LSM 510 META Carl Zeiss, Germany) was used to examine the aggregation and dispersion of cellulose in epoxy. The excitation source was a 405 nm diode laser (30 mW) and an emission band pass filter (420–480 nm) was used. Images were collected at 5 \times , 50 \times , and 100 \times magnification. A TA Instruments Q-2000 differential scanning calorimetry (DSC) was used to determine extent of curing and glass transition temperatures. For each epoxy, 5.0 mg \pm 0.4 mg samples were placed in aluminum pans with unsealed lids and the cell was purged with nitrogen at a flow rate of 50 mL/min. The samples were equilibrated at -30 °C, heated to 200 °C at a scan rate of 10 °C/min, and cooled to -30 °C. The cycle was repeated five times, with the final four showing no changes between cycles. The uncertainties are $\sigma = \pm 0.4$ °C for the reported temperatures and $\sigma = \pm 0.3$ J/g for the heat flow. Tensile tests were performed on an MST Criterion Model 45 hydraulically driven test frame with a 5 kN load cell in accordance to the ASTM D 638-02a norm at a speed rate of 0.05 mm/s with a gauge length of 14 mm. All tests were averaged over a minimum of five measurements for each sample with a standard deviation of $\sigma = \pm 10\%$. Water absorption was measured after submersion in water for 1 day at 23°C, according to the ASTM D570 standard.

3. Lignosulfonate–epoxy composites

3.1. Migration of lignosulfonate

In a previous study, the flammability of epoxy composites containing lignosulfonate was initially measured using a radiative gasification apparatus [25]. This is a nonflaming technique used to study condensed phase flammability reductions in composites. The measured mass loss rate and time to peak mass loss rate are related to the heat release rate and time to peak heat release rate (PHRR) of materials in a standard cone calorimetry experiment. The results indicated that ethoxylated lignosulfonate can reduce the flammability of epoxy composites through the formation of char. Further, the addition of naturally derived gas-forming agents, such as melamine or ammonium tartrate, initially reduced mass loss rates by enhancing the quality of char rather than by inducing intumescence behavior. The addition of these gas-forming agents also induces cracks and debonding later in the burning process, leading to a loss of protection partway through the experiment.

The flammability of these materials was re-examined using cone calorimetry. The shape and relative heat release values mirrored the mass loss rate curves obtained using the gasification apparatus for all samples. The strong correlation observed indicates the reduced flammability when adding lignosulfonate is almost entirely through a condensed phase mechanism. The cone calorimetry data are summarized in **Figure 1**. The peak heat release rate (PHRR), which estimates how intense a fire will be and can help predict the time to flashover, is reduced by 24 % by adding 10 % lignin, 34 % by adding 10 % REAX825E, and 36 % by adding 7 % REAX825E + 3 % AT. The addition of ML instead of AT leads to an increase in PHRR compared to pure epoxy. Melamine produces more gases, leading to more cracks to the char layer, reducing its protective ability. The total heat release is reduced by as much as 14 % when using REAX825E. Since MCC suggests that 30 % to 40 % of lignosulfonate will volatilize during pyrolysis, this indicates an ability to prevent some of the epoxy from burning. One disadvantage to using lignin is that the time to ignition is significantly reduced. A number of factors contribute to the ignition time, including heat capacity, thermal conductivity, surface emissivity, oligomeric decomposition products, melt viscosity, and permeability of the solid. Pure epoxy is transparent with low surface emissivity, whereas lignin is brown or black in color with high surface emissivity. Accordingly, t_{ign} is reduced going from pure epoxy to epoxy + 10 % lignin to epoxy + 10 % REAX825E. The addition of gas-forming compounds, which degrade at temperatures lower than the pure epoxy, leads to a more porous solid as the sample heats up. So, it is not surprising that t_{ign} is further reduced going from epoxy + 10 % REAX825E to epoxy + 7 % REAX825E + 3 % AT to epoxy + 7 % REAX825E + 3 % ML.

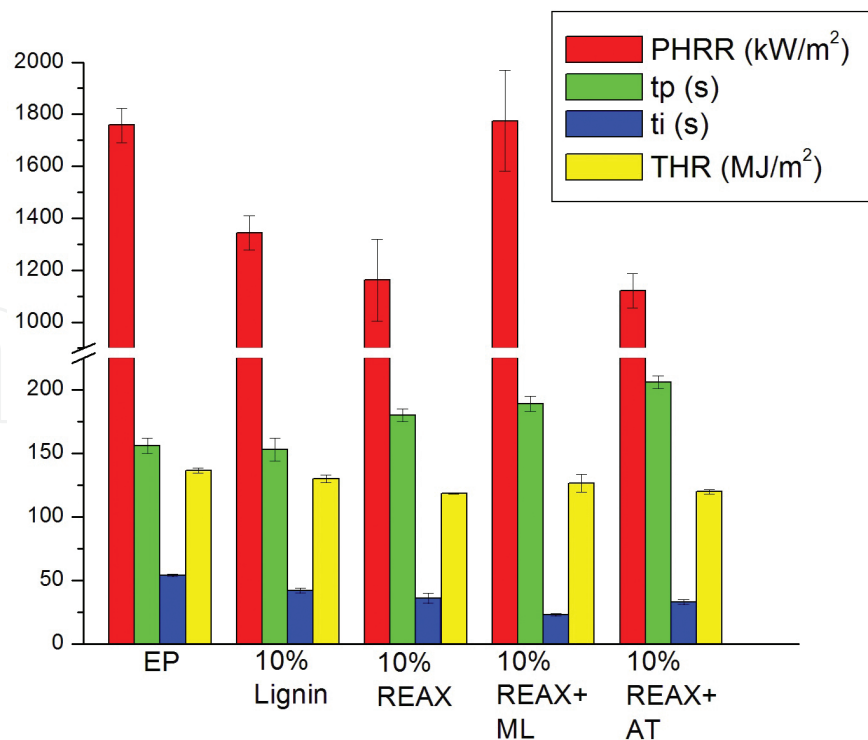


Figure 1. Cone calorimetry data for epoxy + lignosulfonate composites. Error bars represent 2σ .

The observed peeling of the char layer during combustion in the cone calorimeter suggested the lignin migrated and separated from the epoxy matrix during curing. The migration was verified using microcombustion calorimetry. Microcombustion calorimetry is a small scale (3 mg to 10 mg samples) test, where a sample is heated in nitrogen, similar to thermogravimetric analysis, and the pyrolyzed gases are mixed with oxygen and combusted in a separate chamber. The amount of oxygen consumed can be correlated to heat released. The heat release capacity (HRC) and heat of combustion (H_c) measured by the MCC are correlated to several flammability parameters obtained from other measurements, including peak heat release rate (PHRR) and total heat released (THR) from cone calorimetry experiments. As shown in **Table 1**, ethoxylated lignosulfonate has a lower flammability and higher char yield than alkali lignin, which is why it was chosen as the primary flame retardant in this study. Lignin and ethoxylated lignosulfonate have much lower flammabilities than epoxy. The use of these materials in epoxy significantly reduces the HRC by up to 45 % and the H_c by up to 20 %. A 5 mg sample was taken from the top and the bottom of an 8 mm thick epoxy + 10 % REAX825E sample. The results show that the lignosulfonate migrates to the top surface of the epoxy during the curing process. The higher char yield and lower apparent heat capacity are likely due almost entirely to the lignin, rather than uncombusted epoxy. The low H_c and char yield for AT verifies that it has potential as a gas-forming agent in intumescent formulations.

Sample	HRC (J/g · K)	H_c (kJ/g)	T_{peak} (°C)	Char (mass-%)
Epoxy	703	24.4	391	0
Lignin	29	3.5	252	56
Ethoxylated lignosulfonate (REAX825E)	19	1.7	251	64
Ammonium tartrate (AT)	233	4.3	250	6
Epoxy + 10% REAX825E (top)	385	19.7	393	24
Epoxy + 10% REAX825E (bottom)	489	24.8	398	14

Table 1. Microcombustion analysis of epoxy + lignosulfonate samples.

3.2. Variability of lignosulfonate

Additional ethoxylated lignosulfonate was obtained from the same source. Composites were prepared and tested in a cone calorimeter. Even though the exact same product was used, the two lots had significantly different properties. As shown in **Figure 2**, lot #RI27 had a later ignition time, but a 10 % higher PHRR and THR than lot #NK22. The addition of ammonium tartrate lowered the PHRR and reduced the time to PHRR to the same extent, so its interaction with the salt did not change. Most of the difference is due to the natural variability of the lignin composition. The color of lot #RI27 was darker than that of #NK22. In addition, the number of phenolic groups, sulfate groups, or average molecular weight may be different, depending on the source of the lignin and sulfonation process. Although there are variations, the general properties and potential use of lignosulfonate as a flame retardant remain promising.

3.3. Immobilization of lignosulfonate

To prevent the migration of the lignosulfonate, it was epoxidated using epichlorohydrin. It was then used to prepare epoxy + 10 % eLS composites, which were still opaque, but lighter in color than the REAX825E composites. The addition of glycidyl moieties did add to the fuel content of the lignin. Using MCC, eLS was found to have $H_c = 5.1$ kJ/g, $HRC = 72$ J/g · K, $T_{peak} = 340$ °C, and 44 % mass fraction residue. This is only a modest increase in flammability and the immobilization was expected to have a greater effect. As shown in **Figure 3**, by incorporating the lignosulfonate within the epoxy matrix, the char layer was more effective at reducing the heat released. The PHRR was reduced by 63 % and the THR was reduced by 27 % over neat epoxy. The one disadvantage is that the composite ignited the earliest of all composites tested. To improve the efficiency of the epoxidation process, the starting material was dissolved in ethanol and filtered to remove any insoluble material. The solubility of lignin in ethanol decreases as the molecular weight of lignin increases, so this likely removes the highest molecular weight lignin. This may account for the earlier time to ignition, though residual ethanol will also lower this characteristic. The char formed during the decomposition was thicker and did not peel away from the composite, which helps explain how it could effectively reduce the heat released during combustion.

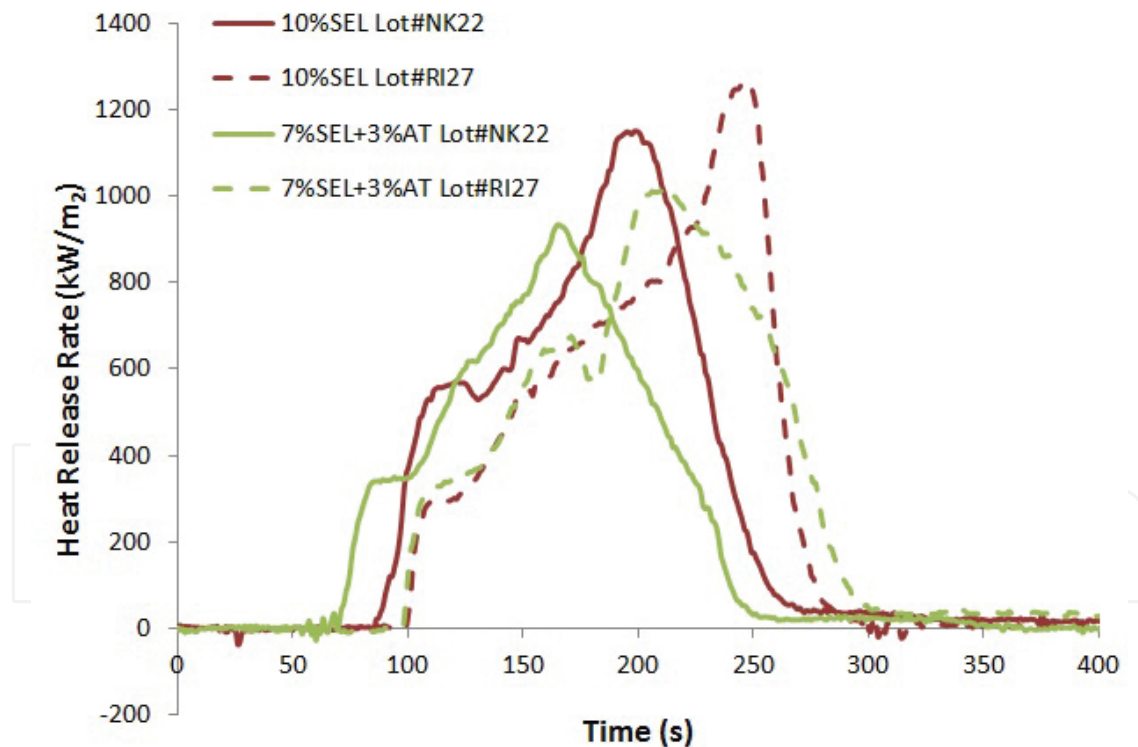


Figure 2. Heat release rate as measured in a cone calorimeter of epoxy flame retarded with lignosulfonate, using two different batches of ethoxylated lignosulfonate.

The addition of lignosulfonate significantly changed the glass transition temperatures (T_g). The measured T_g were 81.2 °C for neat epoxy, 88.7 °C for epoxy + 10 % REAX825E, and 75.7 °C for epoxy + 10 % eLS. Increases in T_g are typically associated with enthalpic interactions between

the filler and epoxy matrix. This may be π - π interactions between lignosulfonate and DGEBA or hydrogen bond interactions with the poly(propylether)diamine curing agent.

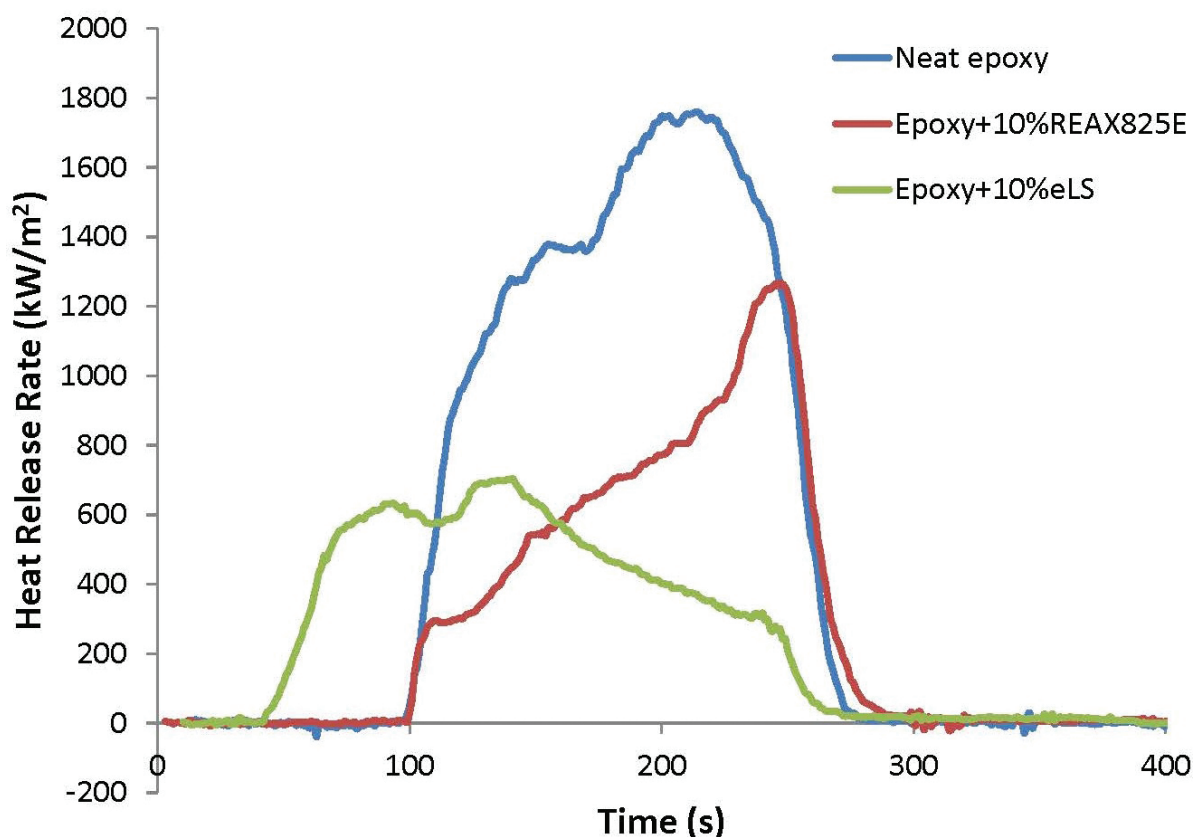


Figure 3. Heat release rate as measured in a cone calorimeter of epoxy + epoxidated lignosulfonate.

4. Cellulose–epoxy composites

4.1. Effects of processing methods of dispersion

The order of addition and the use of high speed centrifugal mixing were investigated to improve dispersion of unmodified sulfated cellulose nanocrystals (Na-CNC) in epoxy composites. The Na-CNC nanocrystals that were obtained as a dried powder were freeze dried in the presence of 9 % mass fraction t-butyl alcohol. This reduces the water crystal size during the freezing process and adds a small amount of an organic solvent to the crystal structure of the cellulose, which improves the microscopic dispersion of the crystals. Since these represent the “best case scenario” for dispersing unmodified sulfated cellulose nanocrystals in hydrophobic matrices, these were used to assess the effects of processing methods on dispersion. All the composites exhibited cellulose aggregation that was visible without magnification. Mechanical stirring and sonication resulted in the largest aggregates and high shear mixing with addition of cellulose to the diamine followed by addition of the epoxy resin resulted in

the smallest aggregates. In previous studies, both a polar, nonaqueous solvent and ultrasonication were required to form transparent composites free from visible aggregates.

4.2. Ion exchange of cellulose nanocrystals

A method has recently been developed to modify the surface of sulfated cellulose nanocrystals using a simply, scalable ion exchange process [41]. In this approach, rather than adding a surfactant, the sodium cation is exchanged with a surfactant cation. The exchange reduces the surface energy, reduces the water uptake, increases the thermal stability, and improves the polymer adhesion of the nanocrystals. This method also allows co-exchange of cations. In this study, the column was loaded with 1 % mass fraction rhodamine 6G and 99 % mass fraction methyl(triphenyl)phosphonium, (MePh₃P/Rh)-CNC. A Na-CNC control was prepared by using a column that was loaded with 1 % mass fraction rhodamine 6G and 99 % mass fraction Na⁺. The fluorescence of 2 % mass fraction cellulose nanocrystals in water is shown in Figure 4.

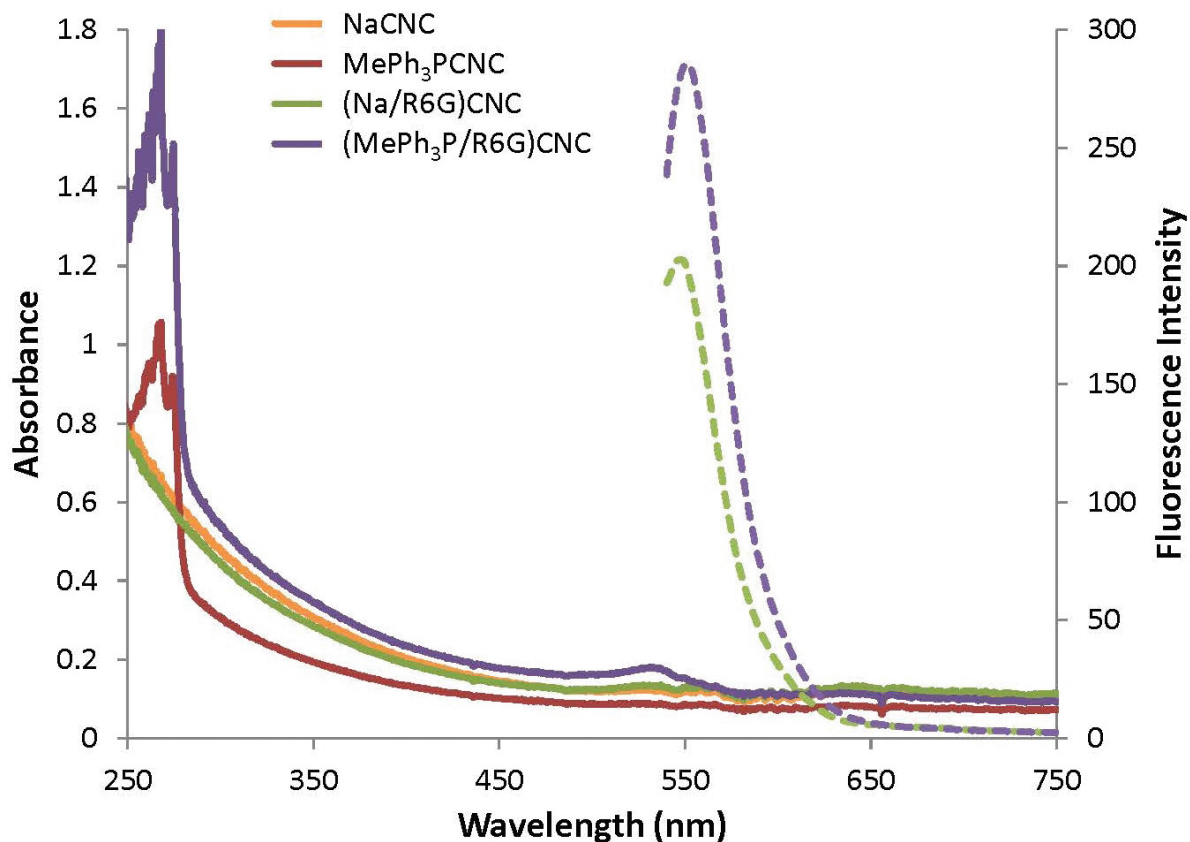


Figure 4. UV and fluorescence spectra of aqueous solutions of cellulose nanocrystals.

4.3. Improved dispersion with exchanged cellulose nanocrystals

The exchanged cellulose nanocrystals disperse readily in the epoxy resin, even without significant shear. Composites were initially prepared using a high shear, speed mixer. Optical

images (**Figure 5**) show large microscopic agglomeration for the Na-CNC composites, which disappear when using MePh₃P-CNC. There is still some agglomeration, but the lengths of the aggregates are smaller than 50 μm and the width of the aggregates is on the submicron scale.

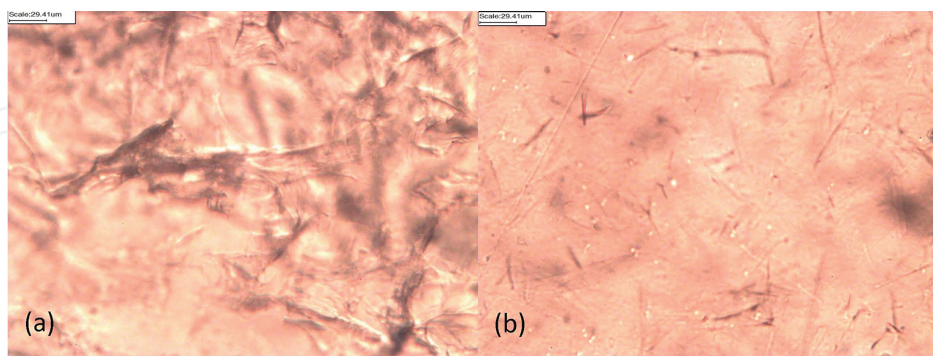


Figure 5. Optical images (20× magnification) of (a) 0.5 % Na-CNC in epoxy and (b) 0.5 % MePh₃P-CNC in epoxy.

When using an optical microscope, it is often difficult to differentiate cellulose crystals from matrix defects, such as cracks, bubbles, or impurities. To obtain a better representation of cellulose distribution, laser scanning fluorescent confocal microscopy was used to image epoxies containing rhodamine co-exchanged crystals (cf **Figure 6**). These images show larger Na-CNC agglomerates, since the (Na/Rh)-CNCs were freeze dried without t-butyl alcohol. They also show fewer microscopic (MePh₃P/Rh)-CNC than the optical images of MePh₃P-CNC containing epoxies (**Figure 5b**). The visible crystal sizes are similar to those observed for MePh₃P-CNC. This suggests that some of the features observed in the light microscope images are defects rather than cellulose crystals. It also indicates that there are crystals that are smaller than the limit of detection of optical microscopes, likely nanoscale in size. This mixed micro-scale/nanoscale size distribution of nanocellulose in polymer matrices has been observed previously [42].

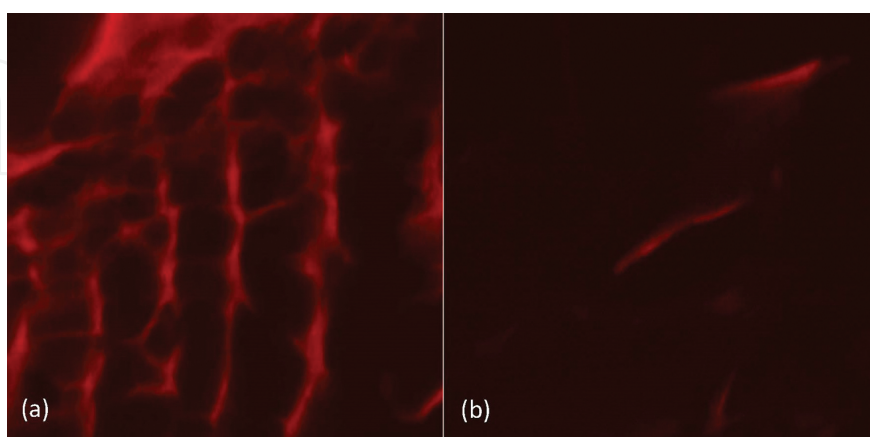


Figure 6. Fluorescent confocal images (100× magnification) of (a) 0.5 % Na-CNC in epoxy and (b) 0.5 % MePh₃P-CNC in epoxy.

Composites were also prepared by gently heating the epoxy resin to reduce viscosity, blending the cellulose using a stir plate, and use of a sonication bath to help separate some of the slower dispersing particles. Epoxies containing 2 % MePh₃P-CNC were visibly transparent, and the microscopic images (not shown) suggest similar levels of crystal separation and dispersion throughout the epoxy.

The differences in particle size and surface energy of the crystals resulted in differences in the glass transition temperatures (cf **Figure 7**). The cellulose nanocrystals interacts strongly with the epoxy matrix, leading to a 5 °C increase in the glass transition temperature at 2 % NaCNC loading. This behavior is consistent with other studies incorporating cellulose nanofibers [43] or nanocrystals [44]. The addition of MePh₃PCNC does not change the glass transition temperature relative to neat epoxy. The MePh₃P⁺ functionality lowers the surface energy of the cellulose, reducing both crystal–crystal interactions (less aggregation), and cellulose–polymer interactions (lower T_g). The differences in T_g between the epoxies prepared using high shear mixing and those using mechanical mixing were not statistically significant.

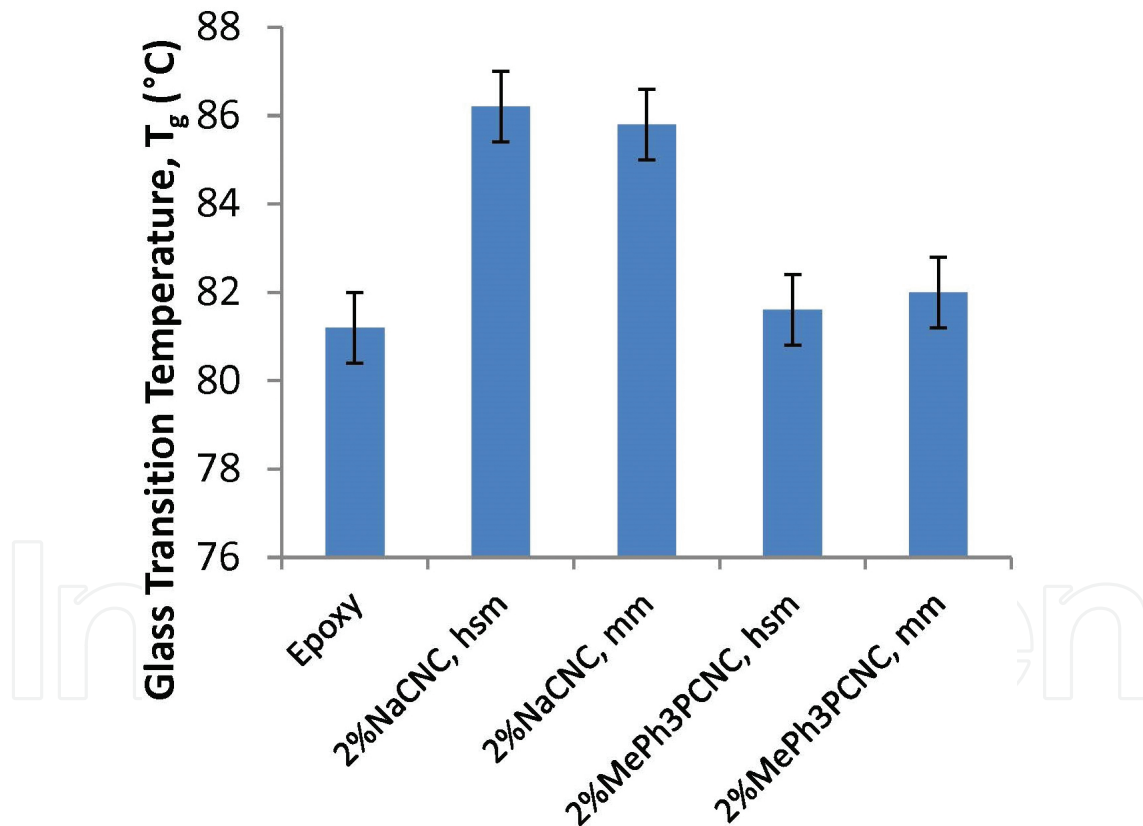


Figure 7. Glass transition temperatures of epoxy-cellulose nanocrystal composites using DSC. Error bars represent 2 σ .

The tensile properties of the epoxy composites are provided in **Table 2**. As expected, the incorporation of stiff crystals increased the modulus (E) of the epoxy composites. The addition of MePh₃P-CNC had a greater effect than the addition of Na-CNC, likely due to the smaller size of aggregates and better dispersion in these composites. The peak tensile strength (σ_p) of

the composites decreased, which may be due to heterogeneity in the cross-linking due to the presence of the crystals. The use of MePh₃P-CNC also reduced the tensile strength, but only half as much in the Na-CNC composites. A key advantage to using the modification is the reduction in hydrophobicity due to the presence of large, hydrophobic cations. The water absorption in Na-CNC epoxy after 1 day of water immersion (W_{1d}) was significantly higher than in neat epoxy, but the MePh₃P-CNC filled epoxies had nearly the same water absorption as neat epoxy.

Sample	E (GPa)	σ_p (MPa)	W_{1d} (% mass fraction)
Epoxy	2.03 ± 0.09	61.2 ± 2.1	0.24 ± 0.04
Epoxy + 1% NaCNC	2.10 ± 0.04	43.7 ± 2.6	0.33 ± 0.01
Epoxy + 1% MePh ₃ PCNC	2.15 ± 0.17	48.5 ± 3.7	0.25 ± 0.02
Epoxy + 5% NaCNC	2.23 ± 0.05	39.9 ± 2.3	0.53 ± n.d.
Epoxy + 5% MePh ₃ PCNC	2.33 ± 0.06	49.5 ± 3.9	0.30 ± n.d.

n.d. – not determined due to insufficient number of samples.

Table 2. Tensile properties and water absorption of cellulose nanocrystal–epoxy composites.

5. Conclusions

Epoxy composites were filled with lignocellulosic materials to improve their flammability and mechanical properties. Lignosulfonate was used as a condensed phase flame retardant. The lignosulfonate migrated during the curing process and resulted in delamination, reducing its effectiveness at maintaining a protective char layer during combustion. The lignosulfonate was successfully epoxidated and incorporated within the epoxy matrix. This reduced the migration and improved the fire performance of the composite. Cellulose nanocrystals were successfully incorporated in an epoxy composite without the aid of a solvent by modifying the crystals with a simple ion exchange process. This process minimized aggregation of cellulose without the use of nonaqueous solvents. The resulting composites were transparent, were stiffer, had a smaller loss in tensile strength, and absorbed less water than the composites with unmodified Na-CNC.

Acknowledgements

This material is based upon work supported by the NIST-EL Extramural Fire Research Grants Program. Research was carried out at the National Institute of Standards and Technology (NIST), an agency of the U.S. government and by statute is not subject to copyright in the United States. Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. Such

identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

Author details

Douglas M. Fox^{1*}, Noy Kaufman¹, Jeremiah Woodcock², Chelsea S. Davis², Jeffrey W. Gilman², John R. Shields³, Rick D. Davis³, Szabolcs Matko³ and Mauro Zammarano³

*Address all correspondence to: dfox@american.edu

1 Department of Chemistry, American University, Washington, DC, USA

2 Materials Science and Engineering Division, Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

3 Fire Research Division, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

References

- [1] Pickering K.L., editors. *Properties and Performance of Natural-Fibre Composites*. Cambridge, England: Woodhead Publishing; 2008. 576 p.
- [2] Hodzik A., Shanks R., editors. *Natural Fibre Composites: Materials, Processes and Properties*. Cambridge, England: Woodhead Publishing; 2014. 408 p.
- [3] Thomas S., Pothan L.A. *Natural Fibre Reinforced Polymer Composites: From Macro to Nanoscale*. Philadelphia, PA: Old City Publishing; 2009. 539 p.
- [4] Nabi Saheb D., Jog J.P. Natural fiber polymer composites: a review. *Advances in Polymer Technology* 1999;18:351–363.
- [5] Miao C., Hamad W.Y. Cellulose reinforced polymer composites and nanocomposites: a critical review. *Cellulose*. 2013;20(5):2221–2262.
- [6] Belgacem M.N., Gandini A., editors. *Monomers, Polymers and Composites from Renewable Resources*. Amsterdam: Elsevier; 2008. 552 p.
- [7] Faruk O., Sain M. *Lignin in Polymer Composites*. Amsterdam: Elsevier; 2015. 350 p.
- [8] Lora J.H., Glasser W.G. Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials. *Journal of Polymers in the Environment*. 10;2002:39–48.

- [9] Thakur V.K., Thakur M.K., Raghavan P., Kessler M.R. Progress in green polymer composites from lignin for multifunctional applications: a review. *ACS Sustainable Chemistry & Engineering* 2014;2:1072–1092.
- [10] Auvergne R., Caillol S., David G., Boutevin B. Pascault J.-P. Biobased thermosetting epoxy: present and future. *Chemical Reviews* 2014;114:1082–1115.
- [11] Ferdosian F., Yuan Z., Anderson M., Xu C. Sustainable lignin-based epoxy resins cured with aromatic and aliphatic amine curing agents: curing kinetics and thermal properties. *Thermochimica Acta* 2015;618:48–55.
- [12] Liu W., Zhou R., Goh H.L.S., Huang S., Lu X. From waste to functional additive: toughening epoxy resin with lignin. *ACS Applied Materials & Interfaces* 2014;6:5810–5817.
- [13] Wood B.M., Coles S.R., Maggs S., Meredith J., Kirwan K. Use of lignin as a compatibiliser in hemp/epoxy composites. *Composites Science and Technology* 2011;71:1804–1810.
- [14] Thielemans W., Wool R.P. Butyrate kraft lignin as compatibilizing agent for natural fiber reinforced thermoset composites. *Composites Part A: Applied Science and Manufacturing* 2004;35:327–338.
- [15] Gregorova A., Kosikovka B., Osvald A. The study of lignin influence on properties of polypropylene composites. *Wood Research*. 2005;50(2):41–48.
- [16] Galina A., Bravin E., Badalucco C., Audisio G., Armanini M., De Chirico A., Provasoli F. Application of cone calorimeter for the assessment of class of flame retardants for polypropylene. *Fire and Materials*. 1998;22(1):15–18.
- [17] De Chirico A., Armanini M., Chini P., Cioccolo G., Provasoli F., Audisio G. Flame retardants for polypropylene based on lignin. *Polymer Degradation and Stability* 2003;79:139–145.
- [18] Reti C., Casetta M., Duquesne S., Bourbigot S., Delobel R. Flammability properties of intumescent PLA including starch and lignin. *Polymers for Advanced Technologies*. 2008;19(6):628–635.
- [19] Zhang R., Xiao X., Tai Q., Huang H., Yuan H. Modification of lignin and its application as char agent in intumescent flame-retardant poly(lactic acid). *Polymer Engineering and Science* 2012;52:2620–2626.
- [20] Alalykin A.A., Vesnin R.L., Kozulin D.A. Preparation of modified hydrolysis lignin and its use for filling epoxy polymers and enhancing their flame resistance. *Russian Journal of Applied Chemistry*. 2011;84(9):1616–1622.
- [21] Howarter J.A., Mendis G.P., Bruce A.N., Youngblood J.P., Diertenberger M.A., Hasburgh L. Flame retardancy of chemically modified lignin as functional additive to epoxy nanocomposites. In: Wilkie C.A., editors. 26th Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials; May 18–20, 2015; Stanford, CT. BCC

Research; 2015. p. Session 3: Nanocomposites, 2–1 through Session 3: Nanocomposites, 2–8.

- [22] Ferry L., Dorez G., Taguet A., Otazaghine B., Lopez-Cuesta J.M. Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate. *Polymer Degradation and Stability* 2005;113:135–143.
- [23] Prieur B., Meub M., Wittemann M., Klein R., Bellayer S., Fontaine G., Bourbigot S. Phosphorylation of lignin to flame retard acrylonitrile butadiene styrene (ABS). *Polymer Degradation and Stability* 2016;127:32–43.
- [24] Liu L., Qian M., Song P., Huang G., Yu Y. Fu S. Fabrication of green lignin-based flame retardants for enhancing the thermal and fire retardancy properties of polypropylene/wood composites. *ACS Sustainable Chemistry & Engineering* 2016;4:2422–2431.
- [25] Zammarano M., Fox D.M., Matko S., Kashiwagi T., Gilman J.W., Davis R.D. Sustainable flame retardants: bio-derived products as intumescent materials. In: *Fire & Materials* 2011; San Francisco, CA. 2011. p. 337–342.
- [26] Koike T. Progress in development of epoxy resin systems based on wood biomass in Japan. *Polymer Engineering and Science* 2012;52:701–717.
- [27] Sun G., Sun H., Liu Y., Zhao B., Zhu N., Hu K. Comparative study on the curing kinetics and mechanism of a lignin-based-epoxy/anhydride resin system. *Polymer* 2007;48:330–337.
- [28] Pan H., Sun G., Zhao T. Synthesis and characterization of aminated lignin. *International Journal of Biological Macromolecules* 2013;59:221–226.
- [29] Mendis G.P., Hua I., Youngblood J.P., Howarter J.A. Enhanced dispersion of lignin in epoxy composites through hydration and Mannich functionalization. *Journal of Applied Polymer Science*. 2015;132(1):41263.
- [30] Pan H., Sun G., Zhao I., Wang G.H. Thermal properties of epoxy resins crosslinked by an aminated lignin. *Polymer Engineering and Science*. 2015;55(4):924–932.
- [31] Sasaki C., Wanaka M., Takagi H., Tamura S., Asada C., Nakamura Y. Evaluation of epoxy resins synthesized from steam-exploded bamboo lignin. *Industrial Crops and Products* 2013;43:757–761.
- [32] Asada C., Basnet S., Otsuka M., Sasaki C., Nakamura Y. Epoxy resin synthesis using low molecular weight lignin separated from various lignocellulosic materials. *International Journal of Biological Macromolecules* 2015;74:413–419.
- [33] Habibi Y., Lucia L.A., Rojas O.J. Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chemical Reviews* 2010;110:3479–3500.
- [34] Moon R.J., Martini A., Nairn J., Simonsen J., Youngblood J. Cellulose nanomaterials review: structure, properties, and nanocomposites. *Chemical Society Reviews* 2011;40:3941–3994.

- [35] Samir M., Alloin F., Dufresne A. Review of recent research into cellulosic whiskers, their properties, and their application in nanocomposite field. *Biomacromolecules* 2005;6:612–626.
- [36] Beck S., Bouchard J., Berry R. Dispersibility in water of dried nanocrystalline cellulose. *Biomacromolecules* 2012;13:1486–1494.
- [37] Khoshkava V., Kamal M.R. Effect of drying conditions on cellulose nanocrystal (CNC) agglomerate porosity and dispersibility in polymer nanocomposites. *Powder Technology* 2014;261:288–298.
- [38] Tang L., Weder C. Cellulose whisker/epoxy resin nanocomposites. *ACS Applied Materials & Interfaces* 2010;2:1073–1080.
- [39] Peng S.X., Youngblood J.P., Moon R.J. Design and characterization of cellulose nanocrystal-enhanced epoxy hardeners. *Green Materials* 2014;2:1–13.
- [40] Emami Z., Meng Q., Pircheraghi G., Mana-Zloczower I. Use of surfactants in cellulose nanowhisker/epoxy nanocomposites: effect on filler dispersion and system properties. *Cellulose* 2015;22:3161–3176.
- [41] Fox, D.M., Rodriguez, R.S., Devilbiss, M.N., Woodcock, J., Davis, C.S., Gilman, J.W. Simultaneously Tailoring Surface Energies and Thermal Stabilities of Cellulose Nanocrystals Using Ion Exchange: Effects on Polymer Composites Properties for Transportation, Infrastructure, and Renewable Energy Applications. *ACS Applied Materials & Interfaces*. <http://dx.doi.org/10.1021/acsami.6b06083>.
- [42] Zammarano M., Maupin P.H., Sing L.-P., Gilman J.W., McCarthy E.D., Kim Y.S., Fox D.M. Revealing the interface in polymer composites. *ACS Nano*. 2011;5(4):3391–3399.
- [43] Omrani A., Simonb L.C., Rostami A.A. Influences of cellulose nanofiber on the epoxy network formation. *Materials Science and Engineering A* 2008;490:131–137.
- [44] Xu S., Girouard N., Schueneman G., Shofner M.L., Meredith J.C. Mechanical and thermal properties of waterborne epoxy composites containing cellulose nanocrystals. *Polymer* 2013;54:6589–6598.

