Transparent Wood Biocomposites by Fast UV-Curing for Reduced Light-Scattering through Wood/Thiol–ene Interface Design

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ABSTRACT: Transparent wood (TW) is an interesting polymer biocomposite with potential for buildings and photonics applications. TW materials need to be eco-friendly and readily processed with few defects, for high optical transmittance and low transmission scattering at wide angles (haze). Two wood templates with different lignin-content are impregnated with a new thiol–ene thermoset system. The more eco-friendly bleached wood template results in transparent wood with high optical transmission and much reduced transmission haze, due to strong reduction of interfacial air gaps. Characterization includes template composition, thiol–ene distribution, and polymerization in wood cell wall by EDX and confocal Raman microscopy, also NMR and DSC, tensile testing and FE-SEM fractography for morphology and wood/thiol–ene interface adhesion assessment. The wood template is a true nanocomposite with thiol–ene polymer located inside the nanoporous wood cell wall. Advanced TW applications require not only appropriate wood template modification and careful polymer matrix selection but also tailoring of the process to impregnation and polymerization mechanisms, in order to reduce optical defects.

KEYWORDS: cellulose, polymer composite, optical properties, haze, debonding

INTRODUCTION

Transparent wood (TW) was first proposed as a method for optical investigation of wood anatomy1 but has recently garnered interest as an application of wood as an advanced and eco-friendly biocomposite material. TW exhibits high transmittance of light, good mechanical properties, and low heat transfer2,3 and can be scaled up to load-bearing multifunctional structures through lamination.4 TW shows promise in solar cell applications.5,6 Additional functionalization has been demonstrated, such as lasing,7 heat shielding,8 thermal energy storage,9 electroluminescent devices,10 and combined with conducting polymers in electromechanical devices.11

Wood is the starting point for TW, and the tissue consists of fibrous, tubular cells oriented in parallel to the stem of the tree. A typical fiber diameter is 20–30 μm, with a cell wall thickness of 2–8 μm. In transparent wood, the empty pore space at the center of the fiber is filled by a polymer. Preparation is a two-step process where the chromophores in lignin are first removed, and the porous wood template is then impregnated by polymer precursors of matching refractive index. If lignin is completely removed by delignification, the resulting wood template becomes completely white.2,3

Optical transmission is important, but haze, the fraction of light diffusely scattered compared to the total light transmitted, is also critical in many applications. The microstructural parameters controlling this property are not well understood for TW materials, although interfaces between the wood template structure and the polymer phase are likely candidates. Since light may also be reflected at interfaces, transmittance is commonly lower for high haze materials. It is often desirable to have thick material structures combining high transmittance with low haze, but the ability to control optical properties by tailored composition and microstructure is the major engineering science goal.

In previous work, Li et al.12 used poly(methyl methacrylate) (PMMA) and Zhu et al.13 used an epoxy resin to prepare TW with high transmittance and high haze (above 80%), based on delignified templates. Later speculations suggested that high haze is caused by mismatch of refractive indices between wood and polymer as well as optical defects, such as interfacial debond gaps between the wood cell wall and the matrix, resulting in highly scattering interfaces.3 Li et al.14 tried to increase template adhesion to the matrix by acetylation of the wood template, resulting in haze ≈50% for 1.5 mm thick
samples. This method, however, requires a separate chemical modification step using acidic chemicals.

Later, TW was prepared using strong hydrolysis treatment of the wood structure and a haze of 10% was achieved for 0.7 mm thick samples of low wood volume fraction.15,16 Haze depends strongly on sample thickness for TW17 and the same TW of 1.5 mm thickness showed a haze of around 40%.15 The lowered haze compared with reference materials was attributed to removal of noncellulosic wood components and ease of polymer infiltration due to partial delamination of the wood structure. A disadvantage of strong hydrolysis treatment is that TW strength properties may be reduced, due to lowered cellulose molar mass and microfibril length.

An alternative method for wood template preparation is lignin modification by bleaching, using a dilute sodium hydroxide-hydrogen peroxide solution. The wood structure is better preserved and up to 80% of lignin is retained by selective chromophore removal. This bleaching treatment is also milder and more eco-friendly than delignification, resulting in higher yield. PMMA-based TW from bleached templates did, however, result in high haze.18 Possibly, the haze-inducing optical defects are related to the PMMA polymer matrix and its polymerization. Lignin contains phenols,19 which can form resonance stabilized radicals, and are commonly used as monomer stabilizers.20,21 The phenol content is also known to increase during bleaching.19,22−24 It is therefore possible that oxygen and phenols may inhibit PMMA-polymerization inside wood templates, and contribute to optical defect formation. PMMA has been used also for transparent biocomposites from wood fibers.25 Alternative polymer systems are therefore of interest and could possibly improve optical properties of TW.

Thiol−ene polymers form homogeneous thermoset networks by rapid, stepwise free radical polymerization,26 see mechanism in Figure 1. The reaction has high yield, is carried out from solvent-free mixtures and is readily carried out by photopolymerization. Curing inhibition by oxygen is negligible for thiol−ene systems27,28 and phenols have limited negative effects.29 During free radical chain polymerization of vinyl monomers, such as MMA, phenoxy radicals are generated from lignin, which can terminate polymerization, see Figure S1. Although phenoxy radicals may also form during thiol−ene curing, the reaction is not terminated. Instead thiyl radicals are formed, which can continue the curing reaction, see Figure S1.

Another advantage of thiol−ene curing is low residual curing strain. The reason is that curing proceeds in a stepwise mechanism, so that gelation takes place at high degree of reaction. Since cure shrinkage then primarily takes place in liquid state, shrinkage strains in the composite will be very low. In addition, the sulfur content in the thiol increases refractive index,30 and monomers can thus be selected to better match the refractive index of wood templates. Although thiol−enes are commonly petroleum-based with low glass transition temperature (Tg), higher Tg systems from renewable resources are explored.31

In this work, a thiol−ene thermostet was investigated as a new polymer category for eco-friendly biocomposites for applications where high optical transmittance and low haze are desirable. The thiol−ene polymer family has not been used for transparent wood and rarely for other cellulose biocomposites.
but may offer reduced residual curing strains, energy-efficient and rapid UV-curing as a new TW processing concept, better refractive index matching with the template, and reduced inhibition of curing reactions from wood lignin. The engineering science objectives are 2-fold. (1) For manufacturing purposes, the in situ curing mechanisms for thiol—ene in the presence of wood templates need clarification. (2) The main micro- and nanostructural biocomposite characteristics influencing optical properties need to be identified in order to facilitate optical performance tailoring of transparent wood for applications exemplified in refs 4—11. Two different wood templates are studied. One is highly delignified, whereas in the “bleached” template only lignin chromophores are removed. The bleached template is of extra interest, since bleaching is a more sustainable method for wood template preparation.

**EXPERIMENTAL SECTION**

**Materials and Chemicals.** Balsa wood with a density of 90—110 g cm−3 was supplied from Material AB (Sweden). Hydrogen peroxide (30%), 1-hydroxycyclohexyl phenyl ketone (UV sensitive radical initiator), pentaerythritol tetras(3-mercaptopropionate) (PETMP, tetrafunctional thiol monomer), sodium acetate, sodium silicate, and 1,3,5-triaryl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO, trifunctional ene monomer) were supplied from Sigma-Aldrich. Acetone, ethanol absolute (99%), and sodium hydroxide were supplied from VWR. Acetic acid (Honeywell), diethylallyltriamine, acetone, ethanol absolute (99%), and sodium hydroxide were supplied from VWR. Acetic acid (Honeywell), diethylallyltriamine-penta acetic acid (DTPA, Acros Organics), magnesium sulfate (Scharlau), and sodium chloride (40%, Alfa Aesar) were bought from other suppliers.

**Chemical Treatment of Wood.** 15 × 15 mm2 (length × width) wood templates with lengthwise fiber orientation were cut, using a razor blade, from rotary cut balsa veneers of 0.9—1.2 mm. Bleaching (lignin modification) of wood templates was performed with sodium silicate (3.0 wt %), sodium hydrosilicate (3.0 wt %), magnesium silicate (0.1 wt %), DTPA (0.1 wt %), and hydrogen peroxide (4.0 wt %) in deionized water at 70 °C for 1 h or until templates turned white, according to the published method.18 Delignification of wood templates was performed with sodium chlorite (1.0 wt %) in an acetate buffer (pH 4.6) at 80 °C for 6 h, according to published method.19 The templates were washed with deionized water after treatment.

**Transparent Wood Preparation.** wood templates underwent sequential solvent exchange to ethanol and acetone by submersion under reduced pressure. Stoichiometric mixtures according to thiol and alky functionalities of PETMP and TATATO were mixed with the UV-initiator 1-hydroxycyclohexyl phenyl ketone (0.5 wt %). Templates were infiltrated overnight at 55 °C, followed by 5 h vacuum infiltration. Samples were sandwiched between glass slides and cured for 4 min by illumination from four 9 W 365 nm UV-lamps: two on opposite sides of and two above the sample, which rested on a reflective surface.

**Single Monomer Treatment of Wood Templates.** Single monomer treatment of templates followed the protocol for TW preparation but with two exceptions. Either pure PETMP or TATATO were mixed with initiator (0.5 wt %) prior to template infiltration and samples were sequentially washed with acetone and water after UV illumination. Homopolymerization of TATATO was attempted by mixing pure monomer with initiator (0.5 wt %) and subjecting the mixture to 4 min of UV illumination in the previously mentioned set up.

**Measurement and Characterization.** Template weight fractions were calculated using average weight losses of freeze-dried templates from oven-dried wood (105 °C) and the weight of finished TW. Transmittance and haze were measured with a broad wavelength light source (quartz tungsten halogen light source, model 66181 from Oriel Instruments) coupled to an integrating sphere, according to ASTM D1003-13.22

**RESULTS AND DISCUSSION**

**Processing of Transparent Wood Biocomposites.** Transparent wood biocomposites (TW) were prepared by a two-step process (schematic overview in Figure 1). White wood templates were obtained by chromophore removal; either by bleaching or delignification (Figure S2). The effects from different wood template composition on TW structure and properties were investigated. The impregnation method is related to what is commonly used for fiber composite product applications based on man-made fibers. During processing, the pore space in the wood templates is impregnated by reactants for the thiol—ene thermoset, a new class of polymers for TW preparation. Water was solvent-exchanged via ethanol to acetone, a reactant solvent, in the template mediated reactant impregnation. The acetone was then evaporated during impregnation at 55 °C.

For polymer matrix, the tetrafunctional thiol PETMP and the trifunctional ene TATATO were selected as monomers to create a three-dimensional thermoset network by free radical addition polymerization. Monomer structures and basic reaction mechanisms are presented in Figure 1. This reaction combines photopolymerization advantages with formation of homogeneous networks. The glass transition temperature of the neat thermoset was 49 °C (Figure S3). The reactant infiltration and acetone evaporation was followed by rapid UV-curing for 4 min which resulted in two different TW
grades; low haze TW based on bleached wood template and high haze TW based on delignified wood template; see photographs in Figure 1. The bleaching approach, where only chromophores are removed, is a more eco-friendly preparation method compared with delignification. The method is faster, requires less energy, and the use of chlorinated and toxic compounds is avoided.12,18 The rapid curing of thiol–ene systems by low intensity UV-light reduces energy requirements further compared with thermal curing. This processing route adds to the advantages of wood biocomposites of high optical transmittance.

Optical Properties and Interface Analysis. Total transmittance and transmitted diffuse light (for calculating haze) was measured using a broad wavelength light source and an integrating sphere, according to ASTM D1003-13.32 Data proved sensitive to structural details of the materials and values at 550 nm wavelength are presented in Figure 1. Optical properties are strongly affected by surface roughness. Samples were, therefore, fixated between glass slides during curing to produce even surfaces. Both materials show high optical transmittance. Low haze TW showed improved transmittance (90%) compared with high haze TW (85%). The difference in haze is, however, dramatic and confirms the sensitivity of diffuse light (haze) to details of the composition and the nano- and microstructure in TW. Low haze TW showed 36% haze compared with 63% haze for high haze TW (Figure 2). Low haze TW is based on eco-friendly chromophore removal only (bleaching), rather than delignification, which means that the yield is higher and the wood cell wall is better preserved.18

Table 1. Optical Properties (Measured at 550 nm) and Material Characteristics for TW

| sample                          | wood species | thickness [mm] | wood– [vol %] | transm. [b] [%] | haze [%] |
|---------------------------------|--------------|----------------|---------------|----------------|---------|
| low haze TW (bleached)          | balsa        | 1.2            | 4.3 ± 0.3     | 90 ± 0.1       | 36 ± 0.4|
| high haze TW (delignified)      | balsa        | 1.2            | 5.0 ± 0.1     | 85 ± 0.4       | 63 ± 0.7|
| bleached/thiol–ene              | ash          | 1.3            | 21.6          | 84 ± 1.4       | 74 ± 1.5|
|                                 | birch        | 1.1            | 16.5          | 89 ± 0.6       | 61 ± 0.5|
|                                 | pine         | 0.9            | 12.5          | 90 ± 0.6       | 60 ± 2.9|
| delignified/PMMA12              | balsa        | 1.2            | 5.0           | 85 ± 0.1       | 71 ± 0.5|
| lignin modified (bleached)/PMMA16 | balsa      | 1.5            | 83 ± 0.5      | 83 ± 0.5       | 75 ± 0.5|
|                                 | ash          | 1.5            | ~57           | ~64           | ~80 ± 0.5|
|                                 | birch        | 1.5            | ~64           | ~70           | ~80 ± 0.5|
|                                 | pine         | 1.5            | ~70           | ~80           | ~80 ± 0.5|
| acetylated/PMMA14               | balsa        | 1.5            | 5.0           | 92 ± 0.5       | 50 ± 0.5|
| clear wood/epoxy15              | basswood     | 0.7            | 2.9           | 90 ± 0.1       | ~10 ± 0.1|
|                                 |              | 1.5            | 2.9           | 85 ± 10        | 40 ± 10|
| clear wood/PVA16                | balsa        | 0.8            | 92 ± 0.5      | 15 ± 0.5      | 15 ± 0.5|
| sulfate/epoxy13                 | basswood     | 2              | ~80           | ~85           | ~85 ± 0.5|
| sulfate/PVP6                    | basswood     | 0.1–1          | 90 ± 0.5      | 80 ± 5        | 80 ± 5|

“Wood template content in finished TW. bTransmittance.

Figure 2. Left, optical transmittance and haze as a function of wavelength for specimens of 1.2 mm in thickness. Right, SEM images of freeze-fractured cross sections of low haze TW and high haze TW at different magnifications. Fiber pull-out, matrix protrusions, cell wall porosity, and interfacial debond gaps indicated by colored arrows. Lettering corresponds to F, fibers; R, rays; V, vessels; L, lumen; CW, cell wall.
Dashed lines indicate cell wall edges, L and CW corresponds to lumen and cell wall, respectively. Large refractive index mismatch between air (2.0 for water, 1.5 for wood) results in highly light scattering interfaces, due to the formation of air voids or defects. In addition, formation of air voids or defects during monomer impregnation and polymerization can occur due to mismatch of refractive index between polymer and cell wall, microscale phases. Dashed lines indicate cell wall edges, L and CW corresponds to lumen and cell wall, respectively.

In a previous study, the reported haze of TW based on an acetylated wood template was 30% at 1.5 mm thickness, with preserved wood microstructure. The present low haze TW shows lower haze (36%) and has reduced embodied energy (energy needs for materials preparation) and reduced use of chemicals, since the acetylation step is avoided.

TW materials based on the same wood template treatment can be compared to evaluate the effect of polymer matrix on optical properties. Bleached templates with PMMA has a significantly higher reported haze, 75% as reported in Table S1, than thiol–ene based low haze TW, 36%. For this class of wood biocomposites, such a large difference can only be explained by reduced presence of wood/thiol–ene interfacial debond gaps.

The interface between the polymer in the lumen space, and the cell wall is critical for optical properties such as transmittance and haze (forward scattering). Scattering of light takes place due to mismatch of refractive index between microscale phases. In addition, formation of air voids or debond gaps during monomer impregnation and polymerization results in highly light scattering interfaces, due to the large refractive index mismatch between air (~1.00) and the TW components (Table S1). Wood/polymer interfacial debond gaps can form due to poor wood/polymer compatibility and from polymer shrinkage during polymerization.

Fracture surfaces from freeze-fractured sample were investigated using FE-SEM (Figure 2). Low haze TW display an even fracture surface with little to no wood fiber pull-out. This is a sign of strong interfacial adhesion between fibrous reinforcement and polymer, since little interface debonding takes place during fracture. Higher magnification micrographs neither show interfacial debond gaps nor obvious presence of voids. The wood-polymer interface is not only improved but also subjected to less strain from polymer shrinkage after gelation when compared to PMMA. The current thiol–ene system has a significantly lower reported volume shrinkage, 4.1% than PMMA, 21.0%. Haze is, thus, lowered by limiting interfacial gap formation in low haze TW.

Improving matching of refractive index (1.56 for thiol–ene, Table S1), will also contribute somewhat to reduced haze since retention of lignin increases the effective refractive index of the bleached template, but this effect on haze is weaker. Reports on refractive indices of lignin-containing wood are few but a rough comparison can be made with reported refractive indices for softwoods, 1.55–1.58 (Table S1).

The delignified templates with thiol–ene (high haze TW) investigated here show a smaller difference in haze compared with PMMA, 63% versus 71% for PMMA-based TW, see Table 1. In contrast to low haze TW, fracture surfaces of high haze TW shows apparent fiber pull-out and long protrusions of the polymer matrix, from which the surrounding cell wall has been detached (indicated by arrows in Figure 2). This is a sign of weaker interfacial adhesion. Higher magnification micrographs reveal both visible interfacial debond gaps and porous cell walls with separated cell wall layers (indicated by arrows in Figure 2). It is then apparent that the main mechanism for reduced haze in low haze TW is the reduced presence of wood/polymer interfacial debond gaps, due to improved interfacial adhesion and retention of cell wall integrity.

For materials design, both selection of polymer (refractive index matching, polymerization shrinkage) and wood template treatment (polymer matrix interaction) have strong effects on haze; primarily through effects on interface gap defects, which depend on the physical and chemical nature of wood-thiol–ene interface interactions.

Bleached templates have shown versatility in a variety of PMMA-based TW biocomposites from various wood species of hardwoods: balsa, ash and birch, and softwoods: pine. Thiol–ene based TW have the same versatility, and TW was produced from balsa, and higher density wood species: ash, birch and pine. The optical transmittance for higher density species is much improved for bleached templates with thiol–ene matrix, compared with bleached templates and PMMA matrix, see Table 1, although differences in sample thickness limit the comparison. Transmittances for the same thicknesses are therefore recalculated for some PMMA-data (ash and birch), by fitting values for attenuation coefficients, see the procedure by Chen et al. For the present bleached template...
TW from ash and thiol–ene, see Table 1, the transmittance is 84%, whereas ash/PMMA at the same 1.3 mm thickness is predicted to have 71% transmittance. For the bleached 1.1 mm birch/thiol–ene in Table 1, the transmittance is 89%, whereas the predicted value for 1.1 mm bleached birch/PMMA is only 72%.

**Thiol–ene Distribution and Degree of Cure.** The distribution of the polymer phase is of major importance for the interpretation of structure–property relationships. Wood is a complex polymeric template, where monomers may infiltrate the nanoporous wood cell wall. Based on EDX and confocal Raman mapping, thiol–ene polymer was found inside the cell wall of both low haze TW and high haze TW, although there was a difference in the distribution of thiol and ene components, see Figure 3 and Table 2. Raman data for the cell wall reveal peaks for both thiol (thiol stretching 2572 cm$^{-1}$, ester stretching 1735 cm$^{-1}$) and ene monomers (ketone stretching 1755 cm$^{-1}$). This shows that both components are present in the cell wall of low haze TW and high haze TW. Solvent-assisted preparation is likely to have facilitated monomer diffusion into the cell wall. Raman measurements were acquired with a beam size of 1.5 μm, which is equal or smaller than the double cell wall thickness (1.5–2.5 μm). Polymer in the fiber cell lumen (central pore space) and cell wall data in TW could be readily separated, since a strong peak at 1600 cm$^{-1}$ corresponds to cell wall lignin.40

EDX measurements revealed sulfur (thiol component) and nitrogen (ene component) in the cell wall of both low haze TW and high haze TW, see Figure 3 and Table 2. The infiltration of thiol monomers into the cell wall is very much improved in bleached templates whereas the ene diffusion is similar for both templates (nitrogen content 2.7% (bleached) and 3.3% (delignified)). Low haze TW had more than twice the mole percentage of sulfur, 8.1%, compared with high haze TW, 3.2%. The thiol content is thus much higher in the more lignin-rich low haze TW template, and strong interactions are expected between polymer in the lumen and inside the cell wall. Variations in cell wall impregnation of each monomer can result in local stoichiometric imbalances in the thiol–ene polymer. Systems of off-stoichiometry thiol–enes have been studied extensively and effects on the thermostet properties are small if the stoichiometry mismatch is small.41

The degree of cure of the thiol–ene reactants after polymerization was calculated by comparing relative Raman peak intensities of thiol stretching (2575 cm$^{-1}$) and allyl bending (1645 cm$^{-1}$) to ketone stretching (1755 cm$^{-1}$) before and after curing, see Figure 3 (left). Degrees of cure are presented in Table 3. Thiol–ene polymer in lumen and in cell wall regions are characterized separately, by shifting the microscopic location of the beam. In both low haze TW and high haze TW, the degrees of cure of the thiol monomer in lumen and cell wall are well above 90% (Table 3), similar to the neat thiol–ene (Figure S4). For high haze TW, the ene monomer show decreased degree of cure, around 85%, in both lumen and cell wall. Low haze TW show degrees of ene cure of around 96% in both lumen and cell wall.

Since the overall degree of cure is high also inside the cell wall, it is concluded that thiol–ene inhibition reactions caused by oxygen or phenols in wood are negligible. This is a major advantage compared with free-radical chain polymerization of acrylates, commonly used for TW.

**Monomer/Cell Wall Interaction.** EDX and Raman data confirm that both reactant components, thiol and ene, are located inside the nanoporous wood cell wall for both templates (Figure 3). The question is if thiol and ene monomers may react with chemical groups of wood components? Bleached and delignified templates were therefore impregnated by either thiol or ene monomers, containing a UV sensitive radical initiator, followed by exposure to UV-light. In addition, bleached templates were treated with neat ene monomer, without radical initiator, to examine whether a radically initiated reaction was required. Before analysis, unreacted monomers were washed away after UV-exposure and no homopolymer formation occurred based on these single monomers.

Confocal Raman spectroscopy data are presented in Figure 4 for the bleached templates. No chemical reaction occurs between thiol monomer and wood components, since no peaks related to thiol monomers were observed for either template after thiol treatment, (spectra for delignified templates in Figure S5). All reacted thiol monomers in both TW grades must, therefore, have bonded with ene monomers. The stoichiometric excess of thiol monomers with a high degree of cure in the cell wall of low haze TW are in support of chemical reactions between the polymer in the lumen and thios in the cell wall.

In this model experiment, the peaks for the trifunctional ene monomer: allyl stretching (3095 cm$^{-1}$), allyl bending (1650 cm$^{-1}$), and ketone stretching (1765 cm$^{-1}$), were present inside the cell walls of ene-treated bleached templates and remained after additional washing. The ene monomer was therefore anchored inside the wood cell wall by covalent bonds to wood biopolymers from free radical reactions. If no initiator was added, the ene monomer was readily removed by washing. To exclude oligomer formation by ene homopolymerization, pure ene monomer with radical initiator was subjected to UV light and analyzed by NMR spectroscopy. No formation of dimer or higher oligomers was observed (NMR signals matched the pure ene monomer, Figure S6). For delignified templates, all ene monomers were washed out after ene treatment, as no

### Table 2. EDX Data from Point Measurements of Samples

| sample          | area      | sulfur   | nitrogen | carbon | oxygen |
|-----------------|-----------|----------|----------|--------|--------|
| low haze TW     | cell wall | 8.1 ± 5.2| 2.7 ± 1.3| 80.0 ± 3.8| 9.1 ± 2.2|
|                 | lumen     | 9.0 ± 1.2| 9.0 ± 1.0| 75.3 ± 1.1| 6.8 ± 1.7|
| high haze TW    | cell wall | 3.2 ± 0.3| 3.3 ± 1.0| 81.2 ± 1.8| 12.3 ± 2.1|
|                 | lumen     | 11.0 ± 2.6| 7.8 ± 1.4| 75.3 ± 0.5| 5.8 ± 0.8|

“Data correspond to mole percentages, converted from measured weight percentages.

### Table 3. Degree of Cure of Thiol and Ene Monomers

|          | neat thiol–ene | low haze TW | high haze TW |
|----------|----------------|-------------|--------------|
| thiol    | 92.2%          | 96.2%       | 92.4%        |
| ene      | 92.8%          | 98.7%       | 100%         |

“*Discernible peak to measure (Figure 3).”
peaks were visible in the Raman spectrum (Figure S5). The results show that ene monomers only bonds to bleached templates, strongly suggesting that the retained lignin covalently bonds to the ene monomers.

An interesting detail is that ene monomers attached to the bleached template (“ene-only” experiment), contain unreacted double bonds, since allyl stretching and bending modes (3095 and 1650 cm\(^{-1}\)) are visible (Figure 4). In TW preparation, ene molecules reacting with the cell wall are still able to covalently bond with thiol monomers. This enhances interfacial adhesion by bonding the polymer matrix with the cell wall.

**Mechanical Properties.** Mechanical properties in tension of both grades of TW and of neat thiol–ene were studied, with structural material function in mind. Stress–strain curves are presented in Figure 4 and the data in Table S2. The reinforcement effect from the wood template is apparent, compared with the neat thiol–ene (Figure 4). The tensile strength of low haze TW increases from 47.2 to 59.0 MPa and the modulus from 2.0 to 3.4 GPa, compared with the neat thiol–ene. The effective cell wall modulus of the template was estimated using the rule of mixtures for composite modulus\(^3\) and found to be 34.6 GPa, almost 20 times the modulus of thiol–ene thermoset. The improvement was slightly lower for High Haze TW, 53.7 MPa in tensile strength and 3.2 GPa in Young’s modulus.

Low haze TW and high haze TW show a large decrease in strain to failure in comparison with neat thiol–ene, due to failure of the wood template reinforcement. When the wood reinforcement is failing at low strain, the whole composite fractures due to redistribution of stress from wood reinforcement to the polymer matrix.

The tensile properties of TW are highly dependent on the volume fraction of wood, where an increased wood content results in improved mechanical properties.\(^{12,42}\) The tensile properties of low haze TW and high haze TW was compared with literature data of TW with similar wood content (Table S2). It reveals that the improved optical properties of low haze TW do not come at the expense of mechanical properties. In fact, there is a small improvement in tensile strength and elastic modulus, with the exception of poly(vinyl alcohol) (PVA) based TW.\(^{16}\)

The dynamic mechanical properties were measured in order to learn about the nature of the thermoset network in neat thiol–ene and in the wood biocomposites, see Figure S7 and more detailed analysis in SI. Neat thiol–ene forms a homogeneous thermoset network characterized by a narrow glass transition in storage modulus. For transparent wood composites, no major change in polymer structure takes place in the large thiol–ene fraction located outside the cell wall. The presence of thiol–ene polymer inside the cell wall is further supported by a broadening of the thiol–ene tan delta damping peaks in transparent wood biocomposites.

**CONCLUSIONS**

Transparent wood is a new application for polymer-impregnated wood templates. Here, a new transparent wood (TW) biocomposite in the form of low haze TW with high transmittance and very low haze is prepared by removing chromophores in wood templates, followed by successful impregnation with thiol–ene thermoset precursors. Chromophore removal (bleaching), rather than more complete delignification, offers faster and more eco-friendly wood template pretreatment. In addition, a processing concept is developed based on rapid (four minutes) and scalable in situ UV-curing using energy-efficient and low intensity UV-light. The resulting transparent wood biocomposite combines eco-friendly processing with improved optical properties.

The high optical transmittance and very low haze reported are related to improved interfacial adhesion between thiol–ene polymer and the bleached wood template, rather than improved matching of wood-polymer refractive indices. Compared with the wood-PMMA composites common in literature, scattering from wood-polymer interface air gaps and the corresponding haze are strongly reduced. The main reasons are lower polymerization shrinkage and improved wood-polymer interface adhesion. Note that haze is confirmed to be highly sensitive to structural details, in particular optical defects.

An unexpected consequence of the specific preparation procedure is that a true nanocomposite is formed, where thiol and ene components of the polymer phase are found inside the nanoporous wood template cell wall. This is confirmed by both EDX and micro-Raman data. The in situ polymerization mechanism is influenced by the bleached template, since the ene monomer by itself could react and form covalent links with the bleached wood template. Remaining allyl groups could...
then bond to the thiol component. The presence of thiol–ene components in the cell wall of the TW composites contributes to interfacial adhesion, since the polymer network extends into the wood phase. Although the monomers are not compatible with wood, solvent-assisted monomer impregnation (industrially used for high-strength fiber composites) facilitate monomer diffusion into the wood template cell wall. Considering the nanoscale porosity of the cell wall, the polymer domains must be primarily distributed at the nanoscale. As a consequence, thiol–ene contributes to hierarchical structuring, since thiol–ene domains are present both at the scales of tens of micrometers (lumen space) and a few nanometers (wood cell wall).

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c12505.

Schematic and description of phenolic inhibition of radical polymerization. Photographs of native balsa, delignified template and low haze TW. DSC of thiol–ene thermoset. Table of refractive indices of various materials. Raman spectra of thiol–ene and TW. Raman spectra of single monomer treated delignified templates. H-NMR of attempted homopolymerization of ene monomer. Table of mechanical properties for TW and thiol–ene (PDF).

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