Wood Science and Technology (2019) 53:1051–1060
https://doi.org/10.1007/s00226-019-01112-0

ORIGINAL

Modification of wood cell wall with water-soluble vinyl monomer to improve dimensional stability and its mechanism

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Received: 21 February 2019 / Published online: 3 July 2019

Abstract

In this work, a new simple and environmentally friendly wood modification method was used to improve the dimensional stability of fast-growing wood. The wood samples were submerged in a neutral aqueous solution of 40% *N*-isopropylacrylamide/2-hydroxyethyl methacrylate (NIPAM/HEMA) at a mass ratio of 1/6 in the presence of catalytic amounts of 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AAPH). The impregnated samples were heated at 60 °C for 12 h, followed by a heating period at 103 ± 2 °C for 12 h, in the course of which an in situ graft polymerization occurred in the cell wall. The results of scanning electron microscopy and energy-dispersive X-ray analyses indicate that the water-soluble vinyl monomers could effectively permeate into the wood cell walls. Infrared spectra showed that water-soluble monomers were in situ polymerized in wood. The results of XPS indicate that the water-soluble vinyl monomers could graft onto wood cell walls. The dimensional stability of poplar wood modified by the water-soluble vinyl monomers treatment was remarkably improved compared with that of untreated poplar wood.

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Introduction

Plantation wood is an ideal material for sustainable society. However, due to the inherent hygroscopicity of wood, the dimensional stability of wood is poor, which limits its application. The dimensional stability of wood can be improved by reducing the hydrophilic –OH group of cell wall components or bulking the cell wall with a modifier. There are many studies on dimensional stability of chemically modified wood. Typical modifications of wood are esterification (Hill and Jones 1999; Kumar 2007), etherification (Chang and Chang 2006), resin impregnation (Gindl and Gupta 2002; Furuno et al. 2004), silylation (Hill et al. 2004; Donath et al. 2004) and in situ grafting polymerization of monomers (Wang et al. 2018; Huang et al. 2019). Although chemical modification can improve wood properties, most treatments involve harmful chemicals or solvents, which may cause serious environmental and health problems in the process of processing and using modified wood.

N-isopropylacrylamide (NIPAM) is a water-soluble vinyl monomer and of low toxicity (Naha et al. 2009; Ghavami et al. 2010). Poly-(*N*-isopropylacrylamide) [p(NIPAM)] is one of the most widely studied thermoresponsive polymers, with a lower critical solution temperature (LCST) near human body temperature in aqueous solutions. When the water solution temperature of p(NIPAM) is higher than the LCST, p(NIPAM) changes from hydrophilic to hydrophobic (Śliwa et al. 2017; Raju et al. 2018). Cabane et al. (2016) grafted NIPAM onto wood by ATRP to prepare thermosensitive wood. Modified wood has lower dimensional stability at lower temperatures and higher dimensional stability at higher temperatures. Keplinger et al. (2016) synthesized a novel smart hierarchical bio-based material by grafted NIPAM thermosensitive hydrogel onto wood cells in two steps. The temperature dependence of thermosensitive hydrogels was studied by Raman spectroscopy.

2-Hydroxyethyl methacrylate (HEMA) is a water-soluble organic monomer with low toxicity and no irritating smell. P(HEMA) has good biocompatibility and is insoluble in water (Horák et al. 1997; Walther et al. 2004). P(HEMA) is widely used in contact lens manufacturing, dental fillers, tissue engineering scaffolds and drug delivery (Miyasaka and Nakabayashi 1999; Lou et al. 2004; Abraham et al. 2005). Chen-Yang et al. (1998) used HEMA and hexachlorocyclotriphosphazene to prepare reaction intermediates and then used UV radiation to initiate in situ polymerization to improve wood flame retardancy. Cleland et al. (2009) used X-ray to initiate in situ polymerization of HEMA in wood cell wall. The results showed that the polymer could not be extracted from the cell wall.

In this paper, environment-friendly modification methods were used to improve wood dimensional stability. The mechanism of the grafting reaction between vinyl monomers and wood cell wall was studied by X-ray photoelectron spectroscopy (XPS). The results of this study can provide a framework for improving wood water resistance with water-soluble monomers and water as solvents.

Materials and methods

Materials

Poplar wood (*Populus euramericana* cv.I-214) was obtained from a fast-growing plantation located in Hebei Province, China. 2-Hydroxyethyl methacrylate (HEMA), *N*-isopropylacrylamide (NIPAM) and 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AAPH) were purchased from Aladdin Industrial Corporation (Shanghai, China). Deionized (DI) water was used as solvent for the preparation of the impregnation solutions.

Chemical modification of wood blocks

The functional monomers HEMA and NIPAM were mixed at a mass ratio of 6/1 and added to deionized (DI) water resulting in an aqueous solution with 40% monomers content. Moreover, 1% of AAPH (by wt. based on the functional monomers) was added and stirred at room temperature for 10 min. Then, a vacuum/pressure treatment was applied for impregnation (− 0.1 MPa for 30 min followed by 0.8 MPa for 120 min) of the experimental blocks. After removal from the solution, the sample surfaces were washed with deionized (DI) water. The impregnated samples were heated at 60 °C for 12 h, followed by heating at 103 ± 2 °C for 12 h. After the polymerization, the modified wood blocks were immersed in aqueous solution for half an hour to wash off the residual modifiers on the surface. The weight percent gain (WPG) was determined by weighing, which was around 43% (the standard deviation was 2.8 according to the weight gain rate of 20 samples).

Characterization

The surface of wood was sliced smoothly by a rotary microtome (LEICA RM2255, Germany). The morphology of the wood was characterized by field-emission scanning electron microscopy (FESEM) (Hitachi S-8010, Japan) equipped with an energy-dispersive X-ray (EDX) detector for mapping (Horiba Scientific, Japan). Fourier transform infrared spectra (FTIR) of samples were recorded on a Nicolet 6700 instrument by the KBr pellet pressing method (Thermo Scientific, USA). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 spectrometer (Thermo Scientific, USA).

Physical properties

Measurements of weight percent gain (WPG), water uptake (WU), mass loss (ML) and antiswelling efficiency (ASE) were taken with 10 replicates of cubic samples with a size of 20 mm × 20 mm × 20 mm (longitudinal × radial × tangential). Samples were submerged in deionized water at 25 °C for 120 h and then dried in an oven at 65 °C until constant mass was obtained. ASE and MS were calculated after measuring the volume and weight of samples before and after immersion. The oven-dry wood blocks were immersed in deionized water for 30 days, weights were measured at intervals and water uptake (WU) was calculated.

The weight percent gain (WPG) was calculated as:

$$\mathrm{WPG}\ (\%) = (\mathrm{Wt} - \mathrm{Wu})/\mathrm{Wu} \times 100$$

where Wt represents the oven-dried weight of chemically modified sample, Wu represents the oven-dried weight of unmodified sample.

The mass loss was calculated by the following formula:

$$\mathrm{ML}\ (\%) = (\mathrm{Wa} - \mathrm{Wb})/\mathrm{Wa} \times 100$$

where Wa represents the oven-dry weight of samples before each cycle of soaking, and Wb is the oven-dry weight of samples after each cycle of soaking.

Water uptake (WU) was calculated as:

$$\mathrm{WU}\ (\%) = (\mathrm{Ws} - \mathrm{Wd})/\mathrm{Wd} \times 100$$

where Wd represents the weight of sample before each cycle of soaking, and Ws is the weight of sample after each cycle of soaking.

ASE was calculated from the wet and oven-dried volumes of the treated and untreated wood specimens:

$$\mathrm{ASE}\ (\%) = (\mathrm{Su} - \mathrm{St})/\mathrm{Su} \times 100\%$$

where Su is the volumetric swelling coefficient of the untreated blocks, and St is the volumetric swelling coefficient of the treated wood blocks.

Volumetric swelling coefficient was calculated as follows:

$$S(\%) = (V2 - V1)/V2 \times 100\%$$

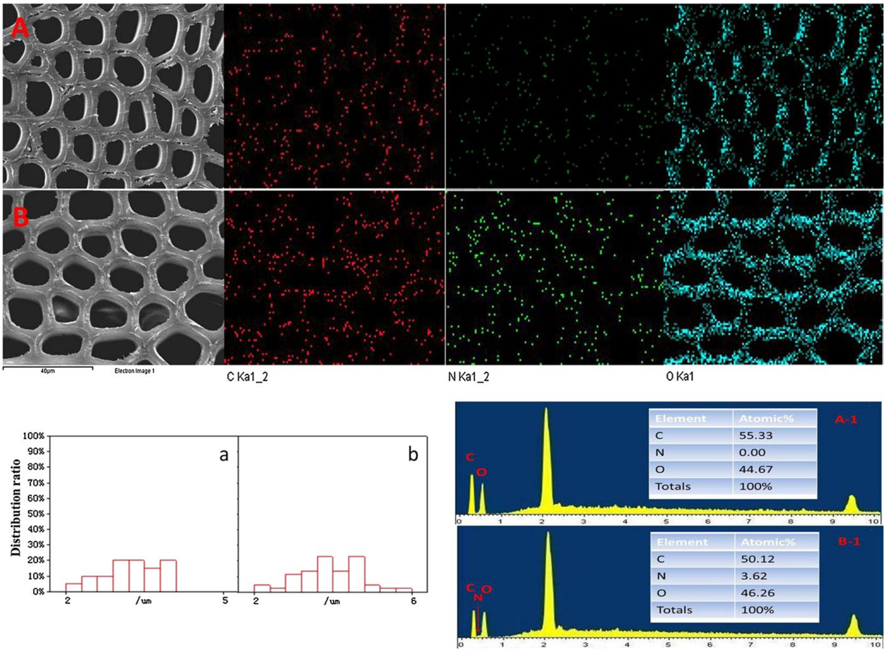
where $V2$ is the volume of the water-saturated wood blocks, and $V1$ is the volume of the oven-dried wood blocks.

Results and discussion

SEM–EDX analyses

Figure 1 shows the SEM images of untreated (A) and treated samples (B). It was observed that in the unmodified wood, there are many gaps between cell walls and the CML. However, in the modified sample, there is no space between cell walls and the CML. By comparison, the average thickness of the modified wood cell wall becomes thicker than before modification. According to the Nano Measure software statistics, the average thickness of the untreated cell walls was 3.10 ± 0.5 μm (a), and the average thickness of the treated wood cell walls was 3.90 ± 0.5 μm (b) (distribution ratio: the ratio of the number of cell walls corresponding to the thickness to the total number of cell walls measured). This could be related to the two monomers penetrated into the cell wall and copolymerized in the cell wall, bulking the cell wall and grafting into cell wall.

Columns 2–4 show EDX elemental maps of C, N and O to identify the distribution of the different elements within the samples. The content of nitrogen



Element	Atomic%
C	55.33
N	0.00
O	44.67
Totals	100%

Element	Atomic%
C	50.12
N	3.62
O	46.26
Totals	100%

Fig. 1 SEM images of unmodified wood (**A**) and modified wood (**B**). Elemental maps of C, N and O are shown for each class. Element content of modified wood (**B-1**) and natural wood (**A-1**). Thickness distribution of untreated cell wall (**a**) and treated cell wall (**b**)

in the cell wall increased from 0 before modification to 3.6% after modification, indicating that the modifier penetrated into the cell wall. From the distribution of carbon, nitrogen and oxygen in the cell wall of wood before and after modification, it can be seen that the elements are evenly distributed in the cell wall, indicating that the modifier penetrates into the cell wall of wood evenly [element content of modified wood (B-1) and natural wood (A-1)].

FTIR analyses

Figure 2 shows the FTIR spectra of the unmodified wood, modified wood and polymer. The spectrum of grafted wood exhibits main peaks at 1650 and 1542 cm^{-1} corresponding to the characteristic peaks for amide I and amide II, respectively. The strong and narrow absorption peak shown at 1730 cm^{-1} (–COO–) confirms the presence of the carbonyl group of ester (Liu et al. 2014; Jin et al. 2018). The absorption bands located at 3400–3500 cm^{-1} correspond to aromatic and aliphatic hydroxyl groups; 1590 and 1510 cm^{-1} correspond to aromatic rings (Chang and Chang 2006; Wang et al. 2018). Infrared spectra showed that water-soluble monomers were in situ polymerized in wood.

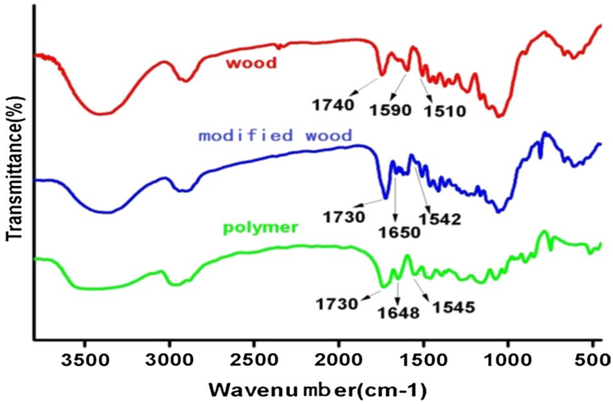


Fig. 2 FTIR spectra of unmodified wood, modified wood and polymer

XPS analyses

Wood blocks were ground into wood flour with a particle size of about 300 microns and then studied by XPS. The XPS survey spectra are presented in Fig. 3. The main elements detected are oxygen (532.6 eV), carbon (285.3 eV) and nitrogen (398.9 eV). Nitrogen is present in the form of amide functional groups. Nitrogen content increased from 0.65% before modification to 1.73% after modification.

According to most data in the literature, the carbon spectrum (C1s) was deconvoluted into four types. C1: carbon atoms bonded only to carbon or hydrogen (C–C, C=C, C–H). C2: carbon atoms bonded to a single noncarbonyl oxygen (C–O, C–O–C). C3: carbon bonded to a carbonyl or two noncarbonyl oxygen (C=O, O–C–O). C4: carbon atoms bonded to a carbonyl and a noncarbonyl oxygen (O–C=O, C(=O)OH) (Bryne et al. 2010; Tuong and Li 2011; Fernández-Fernández et al. 2014).

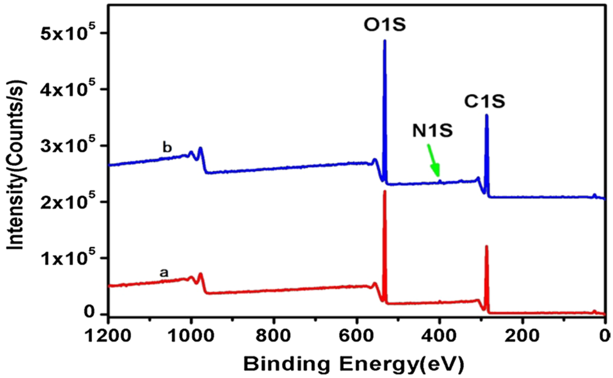


Fig. 3 XPS survey spectrum of unmodified (a) and modified wood (b)

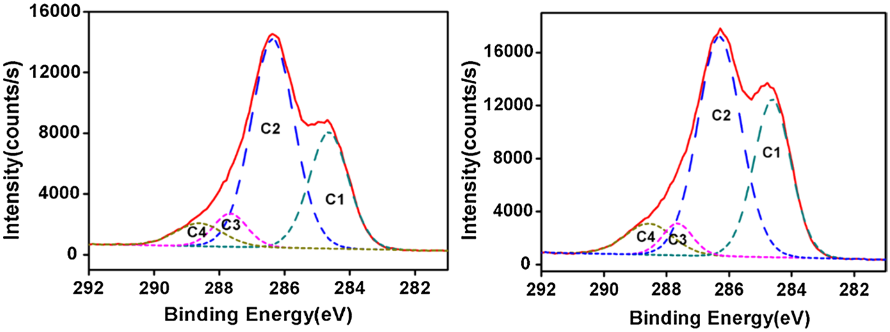


Fig. 4 XPS high-resolution spectra of C1s for modified wood (right) and unmodified wood (left)

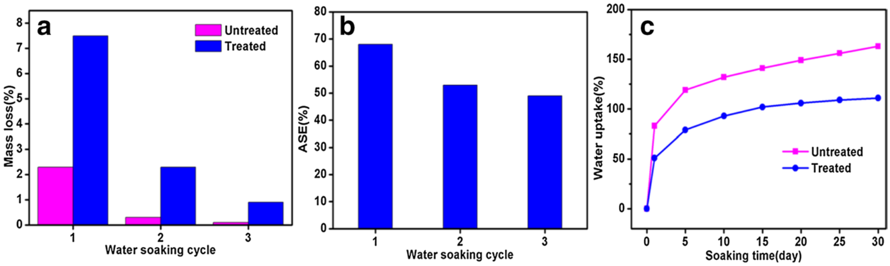


Fig. 5 Mass loss (**a**), dimensional stability (**b**) and water uptake behavior (**c**) of the wood samples

Figure 4 shows the XPS high-resolution spectra of C1s. Typical BE values for the samples are C1: C–C and C–H at 284.6 eV, C2: C–O and C–O–C at 286.2 eV, C3: C=O and O–C=O at 287.6 eV and C4: O–C=O and C(=O)OH at 288.6 eV. Water-soluble ethylene monomer treatment increases C1 slightly from 28.83 to 32.91%, whereas C2 reduces from 57.10 to 53.35%. In addition, the content of C4 increased from 3.5% before modification to 5.5% after modification, indicating that the monomer was grafted onto the C–O of the wood cell wall.

Improved wood properties

The weight loss of samples during repeated immersion is due to the removal of extracts and unreacted water-soluble vinyl monomers. The mass loss value of the sample after the immersion cycle is shown in Fig. 5a. The extracts of untreated samples were removed after two immersion cycles, but for treated wood samples, most of the unreacted water-soluble vinyl monomers were removed after three immersion cycles.

After three soaking cycles, the ASE value of modified wood is as high as 50%, which means that the insoluble resin formed by water-soluble monomers can be well anchored on the cell wall of wood, effectively reducing the water absorption of wood, while preventing the swelling of wood due to water absorption (Fig. 5b).

Water-soluble monomers of small molecules can enter the cell wall and polymerize in the cell wall. The insoluble polymer formed will swell the cell wall and hinder the entry of water, thus improving the dimensional stability of treated wood.

Figure 5c shows the results of deionized water immersion during 30 days. As visible, both the untreated and treated wood absorb water quickly within the first 5 days. Then, the curves flatten. During the whole observation period, the treated wood absorbs less water than the untreated one. The final water uptake of the treated wood decreased from 163 to 109% when compared to untreated wood. The polymers bulk the cell walls, thereby preventing water from entering the cell walls.

In summary, the graft copolymerization improved the dimensional stability and water uptake behavior.

Mechanism of graft polymerization

Based on the results of the current experiment, the mechanism of the grafting copolymerization between wood and water-soluble vinyl monomers is proposed. As depicted in Fig. 6, the initiator decomposes into free radicals under mild conditions (reaction 1), which are able to abstract hydrogen from wood to form wood macromolecular radicals (reaction 2). It is presumed that once the wood macromolecular radicals are generated, they can support active grafting sites to monomer to anchor onto the wood (reaction 3) (Qiu et al. 1999; Ivanova et al. 2016).

Conclusion

In this study, water was used as solvent to improve wood dimensional stability by in situ polymerization of water-soluble vinyl monomers. The results showed that the dimensional stability (ASE) of modified wood reached 50%. The results from

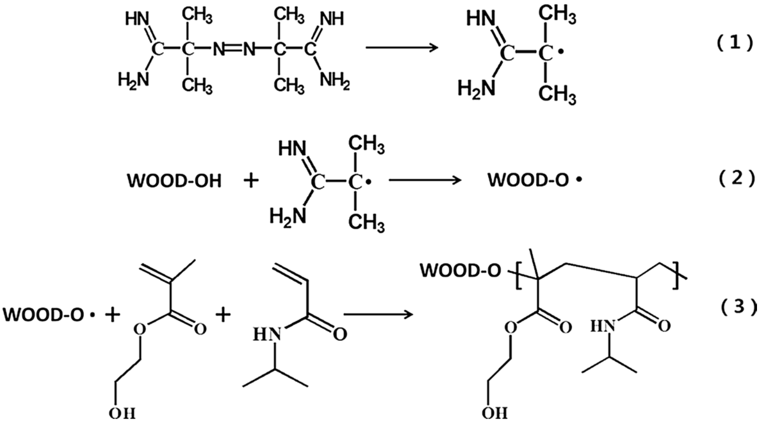


Fig. 6 Proposed mechanism of graft copolymerization of water-soluble monomers onto wood using AAPH initiator

FTIR and XPS indicate that the free radical reaction could graft vinyl monomers onto wood.

Acknowledgements The authors are very grateful for financial support from the National Key Research and Development Program of China (2017YFD0600203).

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

References

Abraham S, Brahim S, Ishihara K, Guiseppi-Elie A (2005) Molecularly engineered p (HEMA)-based hydrogels for implant biochip biocompatibility. Biomaterials 26:4767–4778

Bryne LE, Lausmaa J, Ernstsson M, Englund F, Wålinder ME (2010) Ageing of modified wood. Part 2: determination of surface composition of acetylated, furfurylated, and thermally modified wood by XPS and ToF-SIMS. Holzforschung 64(3):305–313

Cabane E, Keplinger T, Künniger T, Merk V, Burgert I (2016) Functional lignocellulosic materials prepared by ATRP from a wood scaffold. Sci Rep 6:31287

Chang HT, Chang ST (2006) Modification of wood with isopropyl glycidyl ether and its effects on decay resistance and light stability. Bioresour Technol 97:1265–1271

Chen-Yang Y, Chuang J, Yang Y, Li C, Chiu Y (1998) New UV-curable cyclotriphosphazenes as fire-retardant coating materials for wood. J Appl Polym Sci 69:115–122

Cleland MR, Galloway RA, Berejka AJ, Montoney D, Driscoll M, Smith L, Larsen LS (2009) X-ray initiated polymerization of wood impregnants. Radiat Phys Chem 78:535–538

Donath S, Militz H, Mai C (2004) Wood modification with alkoxysilanes. Wood Sci Technol 38:555–566

Fernández-Fernández M, Sanromán MA, Moldes D (2014) Potential of laccase for modification of *Eucalyptus globulus* wood: a XPS study. Wood Sci Technol 48(1):151–160

Furuno T, Imamura Y, Kajita H (2004) The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. Wood Sci Technol 37:349–361

Ghavami S-M, Mesbahi A, Pesianian I, Shafaee A, Aliparasti M-R (2010) Normoxic polymer gel dosimetry using less toxic monomer of N-isopropyl acrylamide and X-ray computed tomography for radiation therapy applications. Rep Pract Oncol Radiother 15:172–175

Gindl W, Gupta H (2002) Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. Compos A Appl Sci Manuf 33:1141–1145

Hill CAS, Jones D (1999) Dimensional changes in corsican pine sapwood due to chemical modification with linear chain anhydrides. Holzforschung 53:267–271

Hill CA, Farahani MM, Hale MD (2004) The use of organo alkoxysilane coupling agents for wood preservation. Holzforschung 58:316–325

Horák D, Červinka M, Půza V (1997) Hydrogels in endovascular embolization: VI. Toxicity tests of poly (2-hydroxyethyl methacrylate) particles on cell cultures. Biomaterials 18:1355–1359

Huang Y, Li G, Chu F (2019) In situ polymerization of 2-hydroxyethyl methacrylate (HEMA) and 3-(methacryloxy) propyltrimethoxysilane (MAPTES) in poplar cell wall to enhance its dimensional stability. Holzforschung 73(5):469–474

Ivanova AV, Gerasimova EL, Gazizullina ER, Kozitsina AN, Matern AI (2016) Kinetics of the thermal decomposition of 2, 2′-azobis (2-methylpropionamidine) dihydrochloride studied by the potentiometric method using metal complexes. Russ Chem Bull 65:419–424

Jin C, Song W, Liu T, Xin J, Hiscox WC, Zhang J, Kong Z (2018) Temperature and pH responsive hydrogels using methacrylated lignosulfonate cross-linker: synthesis, characterization, and properties. ACS Sustain Chem Eng 6(2):1763–1771

Keplinger T, Cabane E, Berg JK, Segmehl JS, Bock P, Burgert I (2016) Smart hierarchical bio-based materials by formation of stimuli-responsive hydrogels inside the microporous structure of wood. Adv Mater Interfaces 3:1600233

Kumar S (2007) Chemical modification of wood. Wood Fiber Sci 26:270–280

Liu X, Xu Y, Yu J, Li S, Wang J, Wang C, Chu F (2014) Integration of lignin and acrylic monomers towards grafted copolymers by free radical polymerization. Int J Biol Macromol 67:483–489

Lou X, Munro S, Wang S (2004) Drug release characteristics of phase separation pHEMA sponge materials. Biomaterials 25:5071–5080

Miyasaka K, Nakabayashi N (1999) Combination of EDTA conditioner and phenyl-P/HEMA self-etching primer for bonding to dentin. Dent Mater 15:153–157

Naha PC, Casey A, Tenuta T, Lynch I, Dawson KA, Byrne HJ, Davoren M (2009) Preparation, characterization of NIPAM and NIPAM/BAM copolymer nanoparticles and their acute toxicity testing using an aquatic test battery. Aquat Toxicol 92:146–154

Qiu J, Gaynor SG, Matyjaszewski K (1999) Emulsion polymerization of n-butyl methacrylate by reverse atom transfer radical polymerization. Macromolecules 32:2872–2875

Raju R, Bandyopadhyay S, Sharma A, Gonzalez S, Carlsen P, Gautun O, Glomm W (2018) Synthesis, characterization and drug loading of multiresponsive p [NIPAm-co-PEGMA](core)/p [NIPAm-co-AAc](Shell) nanogels with monodisperse size distributions. Polymers 10:309

Śliwa T, Jarzębski M, Andrzejewska E, Szafran M, Gapiński J (2017) Uptake and controlled release of a dye from thermo-sensitive polymer P (NIPAM-co-Vim). React Funct Polym 115:102–108

Tuong VM, Li J (2011) Changes caused by heat treatment in chemical composition and some physical properties of acacia hybrid sapwood. Holzforschung 65:67–72

Walther UI, Siagian II, Walther SC, Reichl FX, Hickel R (2004) Antioxidative vitamins decrease cytotoxicity of HEMA and TEGDMA in cultured cell lines. Arch Oral Biol 49:125–131

Wang K, Dong Y, Yan Y, Zhang S, Li J (2018) Improving dimensional stability and durability of wood polymer composites by grafting polystyrene onto wood cell walls. Polym Compos 39:119–125