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Improvement of interfacial interaction in impregnated wood via grafting methyl methacrylate onto wood cell walls

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Abstract: Improving the interaction between the wood cell wall and a modifying agent is fundamental to enhancing the efficacy of wood modification. The extent of interaction is, nevertheless, difficult to evaluate due to the highly heterogeneous nature of the modified wood. In this study, methacryl groups were grafted onto the wood cell wall polymers, via the reaction between 2-isocyanatoethyl methacrylate (IEMA) and hydroxyl groups, to improve their compatibility and reactivity. Subsequently, methyl methacrylate (MMA) was introduced into methacrylated wood and copolymerized with the bonded methacryl groups. The distribution of IEMA and poly MMA (PMMA) in the wood cell walls was investigated by scanning electron microscopy (SEM) and confocal Raman microscopy. The results showed that MMA penetrated the wood cell walls and formed strong interfacial interaction, which was confirmed by confocal Raman microscopy combined with principal component analysis (PCA). With copolymerization, the highest anti-swelling efficiency (ASE) (57%) was achieved, because of the effect of methacrylation. Compared to the reference, the water

resistance and hardness were significantly improved. In addition, the dynamic wettability was also altered largely due to copolymerization.

Keywords: copolymerization, impregnated wood, interfacial interaction, principal component analysis (PCA), Raman microscopy

Introduction

Wood, as a natural and renewable material, has been used in construction, tools, furniture and decorations for thousands of years due to its high strength-to-weight ratio, ease of processing and pleasant aesthetic appearance. Faced with a dwindling supply of high-quality lumber from natural forests and growing environmental awareness, fast-growing wood species have been considered as an alternative wood source due to their short cultivation time (Dong et al. 2016a; Kadir and Khairul 2018; Zhang et al. 2018). However, these wood species exhibit several disadvantages, such as low density, dimensional instability and poor durability (Wang et al. 2016; Che et al. 2018; Jiang et al. 2018).

Wood impregnation, combining the characteristics of wood and polymers, offers an efficient approach to improving the properties of solid wood, and has received considerable attention in the past few decades (Bütün et al. 2019). Various monomers, oligomers or polymers have been employed, such as vinyl monomers (Li et al. 2013; Mattos et al. 2015), ϵ -caprolactone (Ermeýdan et al. 2019), polyethylene glycol (Dong et al. 2016b) and formaldehyde-based resins (Hosseinpourpia and Mai 2016; Qin et al. 2019). These impregnated wood products display increased density, strength, dimensional stability and durability. However, the main problem encountered with these types of composites is the rather poor interfacial adhesion between the hydrophilic wood and the hydrophobic polymers (Ermeýdan et al. 2014). This could result in a micro-phase separation in the impregnated wood. Thus, water could still act on the wood cell

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wall, resulting in an unsatisfactory modification efficiency and low durability during the service life of the wood products. In addition, efficient penetration of the monomers into the cell wall is required to improve dimensional stability, instead of simply filling the cell lumens (Hill 2006; He et al. 2016; Wang et al. 2016). To overcome the incompatibility, copolymerization could be an efficient route, through the grafting of short-chain molecules or polymers onto the wood cell wall by means of radical-induced adhesion promoters (Cabane et al. 2014; Keplinger et al. 2015; Dong et al. 2016b). In this way, the interfacial interaction between wood components and a polymer could be improved so that the dimensional stability of the impregnated wood could be significantly enhanced. Additionally, the mechanical properties can also be enhanced by the incorporation of polymers into the cell walls (Ermeýdan et al. 2014).

2-isocyanatoethyl methacrylate (IEMA) is a bi-functional monomer possessing a polymerizable double bond and an isocyanate group. The isocyanate group can react with the hydroxyl groups of the wood components, while the double bond on the other side of the monomer can react with other monomers [e.g. styrene or methyl methacrylate (MMA)] by free-radical copolymerization. Hence, IEMA could be used to activate the wood cell walls, and graft copolymerization could be carried out to improve the interfacial interaction between wood cell walls and the chemical, thus permanently improving the wood properties.

The cellular-level distribution of modifiers is, however, difficult to evaluate, and our understanding of the interaction mechanism is thus incomplete. Confocal Raman microscopy is finding ever-increasing applications in the field of wood science due to its ability to characterize chemical changes in the wood cell wall in the context of its microstructure (Salmén and Burgert 2009; Gierlinger 2018). The layers of the wood cell wall can be clearly distinguished in two-dimensional (2D) Raman images, calculated by integrating the intensity of the characteristic spectral bands (Gierlinger et al. 2012; Belt et al. 2017). Therefore, it is possible to investigate the distribution of modifiers in the wood structure using Raman microscopy. Ermeýdan's researches suggested that the distribution of modifying agents in wood cell wall can be visualized using Raman microscopy (Ermeýdan et al. 2012, 2014). However, a large Raman imaging data set and the overlap of components in some modified wood complicate interpretation and make it more difficult to obtain accurate information. It has been confirmed that multivariate methods, such as principal component analysis (PCA), can normally resolve the important variations in

spectral data in a few interpretable dimensions (Zhang et al. 2015).

In this study, impregnated wood was prepared by grafting MMA onto poplar wood cell walls using free-radical copolymerization. First, the wood cell walls were activated via the reaction between IEMA and hydroxyl groups. The bound methacryl groups were then copolymerized with MMA. Finally, confocal Raman microscopy combined with PCA analysis was employed to distinguish the components of the modified wood and to visualize the distribution of the modifier in the wood cell walls. The dimensional stability, water uptake (WU), dynamic wettability, mechanical properties and morphology of the impregnated wood were evaluated.

Materials and methods

Materials: MMA and IEMA were purchased from Tianjin Heowns Biochem LLC (Tianjin, China). Dibutyltin dilaurate (DBTL) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Jinke Chemical Research Institute (Tianjin, China). Dry dimethylsulfoxide (DMSO) and other reagents were obtained from Xiya Reagent (Chengdu, China).

Preparation of impregnated wood: Straight-grained air-dried sapwood portions of fast-growing poplar wood (*Populus tomentosa* Carr.) were machined to dimensions of 20 (radial) × 20 (tangential) × 10 (longitudinal) mm³. The samples were solvent extracted using a mixture of toluene/ethanol/acetone (4:1:1 by volume) for 12 h using a Soxhlet apparatus, then oven-dried at 105°C, and finally sorted into four groups (10 samples per group). The oven-dried density of the wood samples was about 0.33 ± 0.02 g cm⁻³.

The IEMA with 1.0% DBTL as a catalyst was first dissolved in dry DMSO to 5 wt% concentration. Two groups were immersed into this solution under vacuum (ca. 950 mbar) for 30 min and impregnated under atmospheric pressure for 2 h. The impregnated samples, along with the solution, were poured into a three-necked flask. The mixture was degassed by bubbling N₂ for 10 min, and then heated to 85°C for 4 h under reflux and continuous stirring.

After reaction, one methacrylated group and one untreated group were impregnated with a solution of MMA in dry DMSO (70:30 v/v, containing 1% of AIBN as initiator) under vacuum (ca. 950 mbar) for 30 min and immersed under atmospheric pressure for 6 h to guarantee uniform impregnation of MMA. After impregnation, the samples were wrapped with aluminum foil and placed into an oven to polymerize the MMA for 20 h at 85°C. The rest of the untreated group was used as the reference wood. To evaluate the degree of copolymerization and remove solvent and unreacted MMA and IEMA, all samples were again solvent extracted using toluene/ethanol/acetone (4:1:1 by volume) for 12 h and then oven-dried at 105°C to constant weight.

Finally, the weight percent gain (WPG) and bulking effect (BE) of all samples were calculated as follows:

$$\text{WPG (\%)} = (W_2 - W_1) / W_1 \times 100 \quad (1)$$

$$BE(\%) = (V_2 - V_1) / V_1 \times 100 \quad (2)$$

where W_1 and W_2 are the oven-dried weights of samples before and after the treatment, respectively; V_1 and V_2 are the oven-dried volumes of samples before and after the treatment, respectively.

The degree of hydroxyl substitution (in mmol g⁻¹ oven-dry wood) after IEMA treatment was calculated as in Equation (3) (Hill et al. 2006):

$$\text{Hydroxyl substituted (mmol/g)} = \left[\frac{W_2 - W_1}{MW} \times 1000 \right] / W_1 \quad (3)$$

where MW is the molecular weight of the IEMA.

Scanning electron microscopy (SEM): In order to observe the morphologies of the untreated and treated samples, the cross-sections of the samples were cut with a sliding microtome (Yamato REM-710, Japan). These were then mounted on stubs with conductive adhesive and sputter coated with gold, after which they were observed using SEM (Hitachi S-3400N, Japan) using an accelerating voltage of 5 kV. The nitrogen distribution in the methacrylated sample was also observed with an energy-dispersive X-ray spectrometer (EDS) to evaluate the reaction of IEMA and cell walls.

Fourier transform infrared spectroscopy (FTIR): The untreated and treated wood samples was analyzed using a Nicolet 6700 infrared spectrophotometer (Thermo Scientific, Waltham, MA, USA) equipped with an attenuated total reflection (ATR) accessory with a scanning range of 4000–650 cm⁻¹ at 4 cm⁻¹ resolution for 32 scans. All spectra were corrected using advanced ATR correction and baseline correction.

X-ray diffraction (XRD): The reference and treated samples were analyzed by XRD, using a Bruker D8 Advance diffractometer (Karlsruhe, Germany). Preset parameters: Cu-K α radiation with a graphite monochromator, 40 kV, 40 mA and 2 θ scan range of 5–40° with a scanning speed of 2° min⁻¹.

X-ray photoelectron spectroscopy (XPS): The chemical composition of wood samples was investigated by XPS (KAlpha, Thermo Scientific) with a monochromatic Al K α X-ray source. Survey spectra were collected in the binding energy range from 0 to 1350 eV at a pass energy of 200 eV. High resolution scans of the C1s were collected at a pass energy of 50 eV.

Confocal Raman microscopy and PCA: Cross-sections with a thickness of 20 μ m were prepared using a rotary microtome (Leica RM 2255, Wetzlar, Germany). Each section was moved on an objective slide together with a droplet of deionized water and covered with a glass coverslip (thickness 0.17 mm) with the edges sealed by nail polish. The Raman measurements were conducted with an alpha300 RA Confocal Raman microscope (Witec GmbH, Ulm, Germany) at ambient conditions. Raman spectra were collected by using a frequency-doubled Nd: YAG laser (532 nm, 10 mW) and a DU970-BV EMCCD camera behind a 600-lines mm⁻¹ grating. A 100 $\times$ immersion oil objective (numerical aperture=1.25; 0.17 mm cover glass correction) was used. For mapping, Raman spectra were taken on 175 lines and 175 points per line on an area of 35 $\times$ 35 μ m² using an integration time of 0.3 s.

The individual images were preprocessed through baseline correction, normalization and random spike removal. Only wavelengths within 300–3550 cm⁻¹ were used to exclude unnecessary noise. Baseline was corrected using a second-order polynomial,

and the normalization was based on the vector length of each spectrum. Random spikes were replaced by the median of a 3 $\times$ 3 pixel moving window. After preprocessing, the images were combined into a mosaic and decomposed using PCA after mean centering according to the report of Belt et al. (2019). A scree plot (Supplementary Figure S1) suggested four principal components (PCs), but only three were used, as the fourth PC provided little meaningful information.

Contact angle analysis: Contact angle measurements on the tangential surfaces of samples were performed parallel to the grain. For measurement, 3 μ l droplets of deionized water were placed on the wood surface using a micro-syringe. Contact angles were measured on each side of the drop, diametrically opposite to each other, at intervals of 0.1 s for a total duration of 120 s. Once collected, the average of these angles was calculated to obtain an estimate of dynamic hydrophilicity. Six measurements of contact angles for deionized water were conducted.

Water uptake and dimensional stability: The unextracted MMA-alone-treated wood sample was used in this section instead of extracted ones. Both untreated and treated wood samples were immersed in deionized water at room temperature and the weight and dimensions were taken after different time intervals (12, 24, 48, 96 and 144 h). WU was expressed as follows:

$$WU(\%) = (W_3 - W_2) / W_2 \times 100 \quad (4)$$

where W_3 denotes the sample weight after immersion in deionized water.

The volumetric swelling (S) was calculated as follows:

$$S(\%) = (V_4 - V_3) / V_3 \times 100 \quad (5)$$

where V_3 and V_4 denote sample volume before and after 48 h immersion in deionized water, respectively.

Thereafter, the anti-swelling efficiency (ASE) was calculated based on the swelling difference between the untreated and treated samples as follows:

$$ASE(\%) = (S_u - S_t) / S_u \times 100 \quad (6)$$

where S_u and S_t are used for the volumetric swelling of the untreated and treated wood samples, respectively.

Nano-indentation test: The sample preparation and quasi-static indentation tests followed the procedure described by Wang et al. (2018). Briefly, the transverse sections (2 mm $\times$ 2 mm) of the reference and copolymerized samples were polished using a Leica EM UC7 ultramicrotome (Wetzlar, Germany) equipped with a diamond knife, and tested using a TriboIndenter (Hysitron Inc., Minneapolis, MN, USA) equipped with a diamond Berkovich tip operating in open-loop control. The target load was 200 μ N for all indents.

Results and discussion

Weight percent gain, bulking effect and substituted hydroxyl groups

The methacrylated wood showed an average WPG of 24% with a standard deviation (SD) of 1.9% and average

BE of 3.7% with an SD of 1.8%. A schematic diagram of the reaction between IEMA and the wood components is shown in Figure 1a. The degree of hydroxyl substitution was 1.54 mmol g^{-1} , which coincided with the result from a previous work (Li et al. 2011). These results indicated the successful covalent interaction of IEMA and the components of the wood cell walls. The copolymerization scheme is shown in Figure 1b. The copolymerized wood obtained a mean WPG of 118% (SD=10%) and BE of 8.4% (SD=3.1%). The mean WPG of sole MMA treatment was 97% (SD=13%) before extraction and 38% (SD=8.9%) after extraction. This was due to the leachability of poly MMA (PMMA) by the mixed solvent. However, the polymer could not be extracted from the copolymerized wood samples, which suggested that the polymer was affixed to the wood cell wall by graft copolymerization. Chemical interfacial interactions between the wood cell walls and the chemical were thus formed. The BE of the MMA-treated sample was only 2.0% (SD=1.2%), which was lower than that of methacrylated and copolymerized samples.

Chemistry changes of wood

Figure 2 displays the FTIR spectra of reference, methacrylated, copolymerized wood, IEMA, and PMMA. For the spectrum of IEMA, the apparent band at 2261 cm^{-1} was attributed to the asymmetric stretching vibration of the isocyanate group. The bands at 1719 and 1634 cm^{-1} were related to the carbonyl and the alkene stretching vibration. However, the isocyanate group band disappeared in the methacrylated wood, indicating the successful reaction of the isocyanate group and hydroxyl group in the wood cell walls. This conclusion is confirmed by the appearance of the alkene stretching vibration at 1634 cm^{-1} and N-H bending at 770 cm^{-1} and the enhancement of the carbonyl at 1708 cm^{-1} in methacrylated wood. In addition, the band of the hydroxyl group ($3433\text{--}3325 \text{ cm}^{-1}$) was decreased due to the methacrylation. For the copolymerized wood, the incorporation of PMMA resulted in the

Figure 2: ATR-FTIR spectra of various wood samples, IEMA and PMMA.

The peak at 1634 cm^{-1} is related to the alkene stretching vibration. The increase of peaks at 1722 and 1146 cm^{-1} in the copolymerized wood related to the incorporation of PMMA.

increase of peaks at 1722 and 1146 cm^{-1} associated with the carbonyl and C-O-C stretching vibration in PMMA, respectively. In addition, the disappearance of alkene stretching vibration at 1634 cm^{-1} indicated that the MMA was successfully grafted onto the wood cell walls through free radical copolymerization. This grafting copolymerization could efficiently reduce the leaching rate of PMMA from the wood structure, which was confirmed by the WPG results after extraction. Figure 3 shows the XRD curves of reference and treated wood samples. The diffraction peaks of the reference at 15.8° , 21.8° and 34.5° are attributable to the cellulose crystal planes I_{101} , I_{002} and I_{040} , respectively. No remarkable change for the 2θ diffraction peak and intensity before and after methacrylation could be seen, indicating that the methacrylation might have no significant impact on the structure of the cellulose. The same result was also obtained by a previous study (Dong et al. 2016b). After copolymerization and MMA treatment, the intensity of the I_{101} peak was significantly increased, which could be due to the incorporation of an amount of amorphous PMMA. However, the intensity of the I_{002} peak

Figure 1: The double bond of IEMA is bonded on wood via isocyanation, then copolymerized with MMA. Chemical reaction routes of (a) methacrylation and (b) copolymerization.

Figure 3: XRD curves of the reference, methacrylated wood, copolymerized wood and MMA-treated wood.

in the copolymerized sample was remarkably reduced, indicating that the crystal size of cellulose was reduced.

Noticeable amounts of nitrogen were observed in the XPS spectra of the methacrylated and copolymerized wood, due to the grafting of IEMA onto the wood components (Supplementary Figure S2). The atomic ratios of carbon, oxygen and nitrogen in the wood samples are shown in Table 1. Remarkably, the percentage of nitrogen increased after methacrylation, due to the introduction of the isocyanate group. Compared to the methacrylated wood, the amount of carbon in the copolymerized wood increased to 62%, due to the polymerization of MMA. As a result, the relative amounts of oxygen and nitrogen in the copolymerized wood sample decreased, as can be seen by the decreased O/C ratio.

To evaluate the chemical structures of the treated wood samples, high-resolution XPS spectra of C1s levels were recorded. The high resolution of C1s was fitted with their decomposition into four components (Popescu et al. 2009; Bryne et al. 2010). The fitted peaks are shown in Figure 4 after curve fitting. The four peaks in the deconvoluted high-resolution XPS spectrum of the C1s peaks are expressed as C_{1-4} . These carbon bonds correspond to $-C-C/-C-H$ (C_1), $-C-O-$ (C_2), $-C=O/-C-O-C$ (C_3) and the ester $-O-C=O$ (C_4), respectively. The relative atomic compositions of carbon

with different oxidation levels in the reference, methacrylated and copolymerized wood were calculated and are presented in Table 2. Remarkably, the percentage of C_4 in methacrylated wood was higher than in the reference. The percentage of C_4 further increased after copolymerization, which was due to the introduction and formation of ester bonds in the wood structure. Additionally, C_1 also increased through the incorporation of alkyl chains from modifiers. Therefore, the percentages of C_2 and C_3 were reduced in relative terms. These results indicate that the wood sample was successfully methacrylated, and the polymerization of MMA was induced into the wood structure.

Polymer distribution in wood

The cross-sections of untreated and treated wood samples were observed by SEM and are displayed in Figure 5 and Supplementary Figure S3. The wood cell walls were partly damaged in the methacrylated wood, which could have resulted from the dryness of the sample which was then hard to cut with a microtome even in a wet state. In order to confirm the reaction of IEMA and the wood cell walls, the mapping of the carbon and nitrogen distributions in methacrylated wood was performed using EDS (Figure 5e and f). Owing to the introduction of the isocyanate group, the nitrogen signal clearly appeared in the cell walls (Figure 5f), which coincided with the results of XPS. These results indicate that IEMA penetrated into the cell walls and reacted with the components. For the copolymerized sample (Figure 5c), the surfaces of the cell walls showed a brittle fracture surface (Figure 5d), but the cell lumens were not occupied by the polymer. This phenomenon could have resulted from the penetration of MMA into the wood cell walls as a result of methacrylation. PMMA is brittle and its composites always exhibit a brittle fracture surface (Shakeri et al. 2019). In addition, the image of the sample treated with MMA alone showed a lack of interfacial adhesion between the PMMA and the wood cell wall internal surface, and the clearance interface gaps between the polymer and the cell wall became visible due to the shrinkage of the PMMA after polymerization (Mattos et al. 2015).

The distribution of components in the reference and treated wood samples was observed by Raman spectroscopy, as shown in Figure 6. For all samples, integration of the lignin signal clearly illustrated that the cell corners and compound middle lamella contain considerable amounts of lignin ($1580-1620\text{ cm}^{-1}$, orange-colored zones), while the integration of cellulose ($345-398\text{ cm}^{-1}$) shows an opposite trend. However, there

Table 1: Experimental atomic composition and the O/C ratio obtained by XPS analysis.

Sample	% C	% O	% N	O/C
Reference	56.7	41.5	1.8	0.7
Methacrylated	53.4	38.9	7.7	0.7
Copolymerized	61.7	34.3	4.0	0.6

Figure 4: C1s peaks of untreated and treated wood samples. (a) reference, (b) methacrylated wood and (c) copolymerized wood. The carbon peaks correspond to $-C-C/-C-H$ (C_1), $-C-O-$ (C_2), $-C=O/-C-O-C$ (C_3) and the ester $-O-C=O$ (C_4), respectively.

Table 2: Relative atomic compositions of carbon with different oxidation levels for untreated and treated wood sample.

Sample	Relative content (%)			
	C_1	C_2	C_3	C_4
Reference	32.4	50.0	13.3	4.3
Methacrylated	37.2	43.2	7.0	12.5
Copolymerized	48.4	33.4	1.4	16.8

was a remarkable overlap of signals from cellulose and the polymers filled in the cell lumen of the copolymerized sample. Though the band from 795 cm^{-1} to 825 cm^{-1} is mainly the signal of the methylene of PMMA (Choi et al. 2001), which was pronounced in the copolymerized

sample, it was difficult to observe the distribution of PMMA in the wood cell wall. Figure 7 displays the Raman images of the methacrylated and copolymerized wood. The intensity profiles of the alkene in the methacrylated wood ($1624\text{--}1648\text{ cm}^{-1}$) and of the methylene of PMMA in the copolymerized wood ($795\text{--}825\text{ cm}^{-1}$) were compared to the intensity of cellulose ($1075\text{--}1170\text{ cm}^{-1}$) and lignin ($1580\text{--}1620\text{ cm}^{-1}$) along a line across the cell wall. In Figure 7a, the intensity profile of the alkene clearly showed a similar trend with the cellulose in the cell wall regions, indicating that the IEMA penetrated into the wood cell walls and reacted with the carbohydrates, which also was supported by the EDS results (Figure 5). The same results have also been found for wood treated with methacryloyl chloride and *p*-toluenesulfonyl

Figure 5: Copolymerized sample shows brittle fracture surface of cell wall. MMA-treated sample shows interface gaps between PMMA and cell wall.

SEM imagines of samples in (a) the reference, (b) methacrylated wood, (c) copolymerized wood and (d) MMA-treated wood; EDS imagines of (e) carbon distribution and (f) nitrogen distribution of the sample in methacrylated wood.

Figure 6: Raman images of lignin ($1580\text{--}1620\text{ cm}^{-1}$), cellulose ($1075\text{--}1170\text{ cm}^{-1}$) and methylene ($795\text{--}825\text{ cm}^{-1}$) in wood samples. The images column from left to right: reference, methacrylated and copolymerized wood. The scale bar is $20\text{ }\mu\text{m}$.

Figure 7: The intensity profiles of cellulose ($1075\text{--}1170\text{ cm}^{-1}$), lignin ($1580\text{--}1620\text{ cm}^{-1}$), alkene ($1624\text{--}1648\text{ cm}^{-1}$) and methylene of PMMA ($795\text{--}825\text{ cm}^{-1}$) in the cell wall along the white line: (a) methacrylated wood and (b) copolymerized wood. The Raman images were from integration of the $1580\text{--}1620\text{ cm}^{-1}$ band of lignin.

chloride (Ermeydan et al. 2014; Keplinger et al. 2015). Along the PMMA profile in Figure 7b, the intensity was notably larger in the cell lumen than in the cell wall. However, the PMMA signal was larger near the surface

of the cell lumen compared to the signal at the center of the secondary cell wall, indicating some flow of PMMA chains into the cell wall. Therefore, the MMA was polymerized in the wood cell and formed a strong interaction

layer from the cell lumen to the cell wall. However, there was an overlap between the Raman signals of the PMMA and the wood polymers, which limited the suitability of univariate analysis for mapping the distribution of PMMA in the cell wall.

To further distinguish components of the treated wood sample and to fully understand the penetration of PMMA, PCA was applied to analyze the Raman data set of the individual samples. PCA summarizes information from a large number of spectral variables into a few uncorrelated latent variables generally called PCs. For each PC, the score images describe differences between individual pixels, while the loadings illustrate the respective changes in the spectra. The variation in the Raman intensity for the methacrylated and copolymerized wood within the wood cell wall was described by the first three PCs (Figure 8). In total, PCs 1–3 explained 86% of the variation in the image data. Pixels representing the water in the cell lumen from the reference and methacrylated wood sample were also removed, as they did not provide relevant information and made it easier to separate the changes in the wood cell walls.

PC1 explained 67% of variation in the data and mainly separated the reference from the treated wood cell walls and the filled lumens from the copolymerized wood.

Several negative bands could be assigned to wood components (e.g. lignin at 1592 cm^{-1}), while positive bands at 599 , 811 , 1724 and 2997 cm^{-1} were attributed to the groups from methacrylated wood and copolymerized wood. The largest PC1 scores were found in the cell lumens of the copolymerized wood, due to the presence of PMMA. However, increased PC1 scores were also present in the cell walls near the interface to the cell lumen. This showed a clear diffused layer of PMMA, indicating a strong interfacial interaction between the PMMA and the cell wall.

In the reference sample, PC2 (12%) and PC3 (7%) mainly separated the lignin-rich areas in the middle lamella and the cell corners (negative band at 1592 cm^{-1}) from the carbohydrate-rich wood cell walls (peak at 379 cm^{-1}). Additionally, PC2 and PC3 provided a clear separation between the cell walls of the methacrylated and the copolymerized wood. The bands at 1289 and 1635 cm^{-1} were related to C=C and N-H groups from methacrylation (positive bands in PC2 and PC3 loadings), respectively, while the peak at 808 cm^{-1} was related to the C-O-C group from PMMA (negative band in PC2 and PC3 loadings). Increased PC2 and PC3 scores of the methacrylated wood highlighted the capability of IEMA to evenly penetrate the cell wall and to react with the wood polymers.

Figure 8: Raman images of wood samples created using scores collected from PCs 1–3 and the associated loading plots. The images column from left to right: reference, methacrylated and copolymerized wood. PC1 separates the reference from treated wood cell walls and the filled lumens from copolymerized wood, while PC2 and PC3 mainly separate the lignin-rich areas in the middle lamella and cell corners from the carbohydrate-rich wood cell walls. Bright field images indicate the high intensity of positive peaks.

Water uptake, dimensional stability and mechanical properties

Figure 9a displays the WU capacity of the reference and treated wood samples. Obviously, after 24 h of water immersion, the reference sample showed a WU of 140%, in contrast to the methacrylated samples which exhibited less than 60% water absorption, the MMA treated samples with 30% and the copolymerized sample with less than 20% water absorption. After a further 144-h immersion, the WU of the reference, methacrylated wood, wood treated with MMA alone and the copolymerized wood was 180%, 110%, 58% and 37%, respectively. The reduction in WU of the methacrylated sample was due to the IEMA reactions with numerous hydroxyl groups contained in the wood components. After copolymerization, the WU was further reduced due to the reduction in the space available for water in the interior of the wood cell lumens and the cell walls by the polymer (Ermeýdan et al. 2014).

After copolymerization, the surface properties of the wood were also significantly changed. Figure 9b shows the experimental data and the model fit line of the contact angle as a function of time for deionized water on the surfaces of the different samples. Obviously, the contact angle decreased more rapidly during the initial 10 s compared with the succeeding measurements, and eventually stabilized to a relative equilibrium state. The initial contact angles of all samples were similar. The surfaces of treated wood samples showed higher equilibrium contact angles than those of the reference, especially for the copolymerized wood sample. The reaction of IEMA with the wood cell wall increased the hydrophobicity of the wood, while the penetration of water was not distinctly reduced by

this reaction, because the wood's macropores remained open for water transport. These results also coincide with those for acetylated wood reported by Petrić et al. (2007). The high equilibrium contact angle of the copolymerized sample suggests that this sample had the lowest penetration due to blocking of the polymer in the wood structure, coupled with the hydrophobicity of PMMA. Similar results were also observed by Mattos et al. in composites prepared by treatment of pine wood with MMA and glycidyl methacrylate (Mattos et al. 2015).

The ASE indices were determined to evaluate the dimensional stability of the treated wood samples. Figure 10a shows the ASE values of the treated samples. As indicated, the copolymerized wood samples exhibited a significant improvement in ASE compared with the methacrylated samples. The grafting of MMA onto the wood cell walls could have contributed to this increment. The wood samples treated with MMA alone exhibited only 19% ASE after 48 h of immersion. Such limited ASE values were reported by many authors who claimed that MMA only filled the cell lumens and were not in tight contact with the wood cell walls (Zhang et al. 2005; Li et al. 2012). The high ASE of the copolymerized wood sample indicated that IEMA could improve the interfacial interaction between wood cell wall and PMMA.

Mechanical properties of the reference and copolymerized wood cell walls were investigated by nano-indentation, as shown in Figure 10b and c. MMA is the most commonly used monomer for hardening of wood in many reports (Yildiz et al. 2005; Ding et al. 2013). Clearly, the improvement in hardness for the copolymerized wood samples was significant compared to the reference (0.69 GPa vs. 0.53 GPa). A similar result was also reported by Ermeýdan et al. (2014). However, copolymerization

Figure 9: Water uptake capacity (a) and dynamic wettability (b) of reference and treated wood samples.

After a further 144 h of immersion, the water uptake of reference, methacrylated wood, wood treated with MMA alone and copolymerized wood was 181.5%, 110.6%, 58.1% and 37.4%, respectively. The surface properties of wood were also significantly changed by copolymerization.

Figure 10: Dimensional stability (a), hardness (b) and indentation modulus (c) of wood samples.

The copolymerized wood samples exhibited a significant improvement in ASE compared with the sample treated with MMA alone. The improvement of hardness for the copolymerized wood sample was significant compared with that for the reference.

had only a slight effect on the indentation modulus of the wood cell walls (14.6 GPa vs. 13.4 GPa). The penetration of “strange” molecules within the cell wall polymers could cause disturbance in the crystalline order of cellulose, which to a certain extent reduces the elastic properties of wood in general.

Conclusions

In this study, methacryl groups were successfully grafted onto the cell walls of wood via reaction between IEMA and hydroxyl groups, which resulted in a moderate ASE (36%). For wood samples treated with MMA alone, the polymer was located only in cell lumens and resulted only in a slight improvement in dimensional stability (ASE of 19%). However, copolymerization, causing a reaction between the grafted cell walls and MMA, resulted in the highest ASE (57%). This copolymerization, confirmed by FTIR and XPS, strengthened the wood cell wall. Methacrylation improved the penetration and copolymerization of MMA in the wood cell wall, thus forming a strong interfacial interaction layer from the cell lumen to the cell wall. The distribution of the components in modified wood and the interaction between the modifying agents and wood components were confirmed by Raman microscopy combined with PCA. As a result, wood properties, such as dimensional stability, water resistance and mechanical properties, were significantly improved by grafting copolymerization.

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