MODIFICATION OF RADIATA PINE WOOD WITH LOW MOLECULAR WEIGHT MODIFYING AGENTS AND LARGE MOLECULAR WEIGHT STYRENE/ACRYLIC ACID COPOLYMER DISPERSION

Wenbo Che, Zefang Xiao, Yanjun Xie
Northeast Forestry University
Harbin, P. R. China

ABSTRACT

Our previous study revealed that treatment with aqueous styrene/acrylic acid copolymer (SA) is a cell-lumen filling process, and the treated wood exhibited negative values for cell wall bulking efficiency (BE) and anti-swelling efficiency (ASE). In this study, three low-molecular-weight agents (LMWAs), 1, 3-dimethylol-4, 5-dihydroxyethyleneurea (DM, 10%), glutaraldehyde (GA, 10%), and n-methylol acrylamide (NMA, 10%), were separately combined with SA (5, 10, 15, or 20%) and used to modify radiata pine wood at the levels of cell walls and cell lumens. The combinative treatments caused positive BE and ASE values, indicating restrained wood deformation, likely due to the diffusion and reaction of LMWAs in the wood cell walls. Infrared spectroscopy and dynamic mechanical analysis showed that LMWAs exhibit little reaction with SA, and the SA copolymer retains thermoplasticity in the wood cell lumen. The combinative treatments resulted in considerable improvement in bending modulus, bending strength, and compression strength of wood of 36, 36, and 124%, respectively, but there was little effect on impact strength. These findings confirm that LMWAs can act as cell wall modifying agents to synergistically improve wood properties, especially the dimensionally stability, when used together with SA.

KEYWORDS: Wood modification, styrene/acrylic copolymer, low-molecular-weight agent, cell wall treatment, cell lumen filling, mechanical properties.

INTRODUCTION

Wood chemical modification is an effective way to improve the dimensional stability, mechanical properties, and durability of wood (Hill 2006, Rowell et al. 2005). Current

modification technologies target cell wall modification and/or cell lumen filling (Ormondroyd et al. 2015, Xie et al. 2013).

The utilization of a water-soluble copolymer for wood modification has the potential to decrease adverse environmental impacts. Based on our previous studies, the treatment of wood with an aqueous dispersion of styrene/acrylic acid copolymer (SA) dispersion can improve the mechanical property and water repellency of the treated wood because the copolymer fills in the wood cell lumens (Che et al. 2018). However, the bulking efficiency (BE) and anti-swelling efficiency (ASE) of treated wood may be notably decreased, because SA is a large molecule that is unable to effectively permeate the cell wall, resulting in an uneven distribution in the cell lumen. In addition, the alkaline environment of the SA dispersion can cause shrinkage of the wood cell wall due to the degradation of the hemicellulose.

To achieve permanently improved wood dimensional stability, cell wall modification is typically an effective strategy (Hill 2006). Some chemicals with small molecular sizes, such as low molecular weight urea formaldehyde and phenol formaldehyde resins, can effectively penetrate through wood micropores and grafting and/or crosslinking with wood cells to enhance the dimensional stability and other properties of wood (Furuno et al. 2004, Klüppel and Mai 2013, Yu et al. 2011), furfuryl alcohol (Baysal et al. 2004, Goldstein and Dreher 1960, Stamm 1977), and anhydrides (Hill et al. 1998, Himmel and Mai 2015, 2016). In particular, after 1, 3-dimethylol-4, 5-dihydroxyethyleneurea (DM), glutaraldehyde (GA) and n-methylol acrylamide (NMA) treatment, the ASE values of the treated wood increased by 70%, 70%, and 50%, respectively (Epmeier 2004, Krause et al. 2008, Xiao et al. 2010, Yasuda and Minato 1994).

Therefore, low-molecular-weight agents (LMWAs) were combined with the SA impregnation system to see if this would help to overcome the BE and ASE losses of wood after treatment. This study aimed to evaluate and compare the application of SA as a wood modification agent in combination with the different LMWAs: DM, GA and NMA. Theoretically, the permeability of the wood cell wall to LMWAs could compensate for the shrinkage of the wood cell wall that results from SA treatment, and meet the objectives of wood cell wall modification and cell lumen filling.

The reactivity of the different combination treatments was analyzed after curing via FT-IR spectroscopy and measuring the weight percent gains (WPG) of the treated wood. The dimensional stability of the treated wood was assessed by measuring BE and ASE. The mechanical properties of the treated wood were tested by using a universal mechanical testing machine and by dynamic thermomechanical analysis (DMA), and the fracture surface of the wood was observed by scanning electron microscope (SEM).

MATERIALS AND METHODS

Materials

Pinus radiata (D. Don) wood used in this study was imported from New Zealand, which is a fast-growing species with relatively low-quality. The wood has a density of 0.42 g·cm^3, average ring width of 5.3 mm, and sapwood/heartwood ratio of 1:5. Wood specimens measuring 15 × 25 × 25 mm (l × t × r) were cut from the sapwood of and used for the determination of WPG, BE, and ASE. The dimensions of other samples were (l × t × r): 180 × 10 × 10 mm (for measurements of bending), 125 × 13 × 13 mm (for measurements of impact strength), 30 × 20 × 20 mm (for measurements of compression strength), and 35 × 12 × 3 mm (for measurements of DMA). The aqueous SA copolymer dispersion (Thyosil IM76) was purchased from Diransa San Luis S.A (Buenos Aires, Argentina), and the average molecular mass of the SA copolymer

was 15000 g·mol^{-1}. The LMWAs used were aqueous solutions of DM (solid content 35%) and GA (solid content 50%) purchased from BASF (China) Co. Ltd (Shanghai, China) and NMA (solid) received from Wengjiang Reagent Company (Guangzhou, China). The chemicals *N*, *N*-dimethylethanolamine (DMEA), *p*-toluene sulfonic acid (PTSA), magnesium chloride hexahydrate (MgCl$_2$) and citric acid (CA) were of extra purity grade and were all purchased from Yongchang Chemical Company (Harbin, China).

Treatment of wood

There were three categories of impregnation solutions, DM/SA, GA/SA, and NMA/SA combinations. In those three categories, separate solutions of 10% DM, 10% GA, and 10% NMA were prepared plus SA solutions at 0%, 5%, 10%, 15%, and 20% concentrations. Treatment of wood with 10% DM (W_{10DM}) and 10% GA (W_{10GA}) included the addition of 1.5% MgCl$_2$ as a catalyst, and the 10% NMA (W_{10NMA}) treatment included 1.5% CA as a catalyst. For the other treatment groups, no catalyst was used, because these acidic catalysts can cause the SA to flocculate at low pH. Treatment with 10% SA (W_{10SA}) with added catalyst (a mixture of DMEA and PTSA at a weight ratio of 1:1) and wood treated with deionized water alone (W_{ctrl}) were prepared as controls. For each treatment totally 10 replicates were used. The different treatments of different chemicals and at different pH values are listed in Tab. 1.

Tab. 1: Test groups of wood with different treatments and the pH value.

Labels*	Treatment				Catalyst	pH
	SA (%)	DM (%)	GA (%)	NMA (%)		
Ctrl	0	0	0	0	-	7.1
10SA	10	0	0	0	0.04% PTSA	8.8
10DM	0	10	0	0	1.5% MgCl$_2$	3.7
10DM/5SA	5	10	0	0	-	8.4
10DM/10SA	10	10	0	0	-	8.5
10DM/15SA	15	10	0	0	-	8.7
10DM/20SA	20	10	0	0	-	9.1
10GA	0	0	10	0	1.5% MgCl$_2$	3.4
10GA/5SA	5	0	10	0	-	8.4
10GA/10SA	10	0	10	0	-	8.6
10GA/15SA	15	0	10	0	-	8.8
10GA/20SA	20	0	10	0	-	9.0
10NMA	0	0	0	10	1.5% CA	2.5
10NMA/5SA	5	0	0	10	-	8.7
10NMA/10SA	10	0	0	10	-	8.8
10NMA/15SA	15	0	0	10	-	8.8
10NMA/20SA	20	0	0	10	-	9.0

*Note: Ctrl shows wood treated with deionized water; the number in front of chemical abbreviation is the concentration of chemical (%).

The wood samples were treated with the different aqueous solutions under vacuum (0.01 MPa, 12 h) and pressure (0.6 MPa, 24 h). The specimens were then dried in air at room temperature (25°C) for one week prior to curing at 120°C for 24 h after impregnation, as described previously (Xiao et al. 2010a).

Weight percent gains, bulking efficiency, and anti-swelling efficiency

The weight percent gain (WPG) was calculated from the dry mass measurements of the wood samples before and after treatment and leaching. The leaching was performed by soaking wood in deionized water for 1 week and changed water every day, followed by air drying for 1 week and then oven drying at 103°C for 48 h. The oven-dry weights and dimensions of the specimens were determined. For each treatment, ten replicates were measured and the average values are presented. The BE and ASE of wood was calculated according to (Hill 2006).

FTIR analysis

The reactivity of the combination agents in wood was analyzed by FT-IR spectrometry (Magna-IR 560, Thermo Nicolet, Beijing, China) with a resolution of 4 cm^{-1}, and 40 scans were accumulated. The wood flour was measured by ATR technique and the measurements were three times for each treatment.

Mechanical test

Both the modulus of rupture (MOR) and the modulus of elasticity (MOE) in bending were determined at a test speed of 1.5 mm min^{-1} according to DIN52186 (1978) with a mechanical testing machine (Reger, Shenzhen, China). The compression strength (CS) was measured at speeds of 0.9 mm min^{-1} on the same machine according to DIN 52185 (1976). Impact strength (IS) was tested at a speed of 3.8 m s^{-1} with a 15 J pendulum using an impact tester (JJ-TEST, Chengde, China) according to the modified standard GB/T1940 (2009). Ten replicates were performed for each treatment, and the average values are presented. Prior to testing, the specimens were conditioned at 20°C and 65% RH for 15 days.

Dynamic thermomechanical analysis (DMA)

Dynamic mechanical analysis (DMA) of the untreated and treated wood samples was performed using a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, USA) in three-point bending mode with 10 Hz frequency and 10°C min^{-1} heating rate from 30°C temperature to 200°C. As the storage modulus (E') changed, the E' at a given temperature divided by the maximum modulus (E'_{max}) for the same data set yields a normalized storage modulus value (E'/E'_{max}). The normalized damping factor ($tan\delta/tan\delta_{min}$) was obtained by taking the ratio of $tan\delta$ at a given temperature to the minimum $tan\delta$ at low temperatures for the same data set (Ou et al. 2015).

SEM observations

The fractured specimens after the impact strength test were dried at 80°C overnight. The treated and untreated specimens were sputter coated with a layer of gold. The fractured surfaces were then observed by SEM (FEI Quanta 200, Hillsboro, USA, 2.5 kV). The observed was run in SEM under a vacuum mode with a working distance of 6 mm and the detector of the SEM was gaseous secondary electron.

Water uptake (WU) and moisture content (MC)

After being conditioned under 20°C/65% RH, all specimens were immersed in distilled water at 20°C for 2 weeks, with daily changing of the water. The weight of the specimens was measured according to GB/T 1934.1 (2009). The WU (%) of each specimen was expressed as the absorbed water weight divided by the dry weight of the specimen. Ten replicates were performed for each treatment, and the average values are presented.

The leached wood specimens were placed in a climate-controlled container at 20°C at RH 93%. When the weight of the samples changed less than 0.005 g within 24 hours, the samples were determined to have achieved the equilibrium state. After chemical modification, the oven dry weight of the modified wood increased. The equilibrium moisture content (EMC) value of modified wood was lower than that of the untreated wood when the adsorption water was the same. Therefore, in order to eliminate the influence of the modifier on the additional weight of wood, the EMC of wood was calculated by using the moisture content reduced (MC_R) of modified wood. The MC_R under the equilibrium state at RH 93% was calculated according to (Hill 2008) and (Xie et al. 2011).

RESULTS AND DISCUSSION

Weight percent gain, BE, and ASE

The WPG of treated wood in the presence of the LMWAs showed a linear increase with increasing SA concentration before leaching (Fig. 1a), and the WPG of the NMA treated wood was slightly lower than the other samples.

All specimens showed a reduction in WPG after leaching (Fig. 1b), due to the removal of unreacted chemical agents, water-soluble extractives, and degraded wood components. With increased SA, the WPG of LMWAs/SA-treated wood was lower than that the sum of values of wood treated separately (not shown). This is likely because the chemicals in wood are more easily washed without a catalyst, because the degree of reaction with wood was weakened, especially for the LMWAs. Additionally, the LMWAs may be prevented from entering the wood cell wall due to the increase in viscosity of the combination reagent solution. The WPG of the GA/SA treated wood was higher than the wood treated by either DM/SA or NMA/SA, indicating that GA is less influenced by the catalyst than DM and NMA chemicals. In general, the LMWAs/SA combination agent has high leaching resistance in wood after treatment.
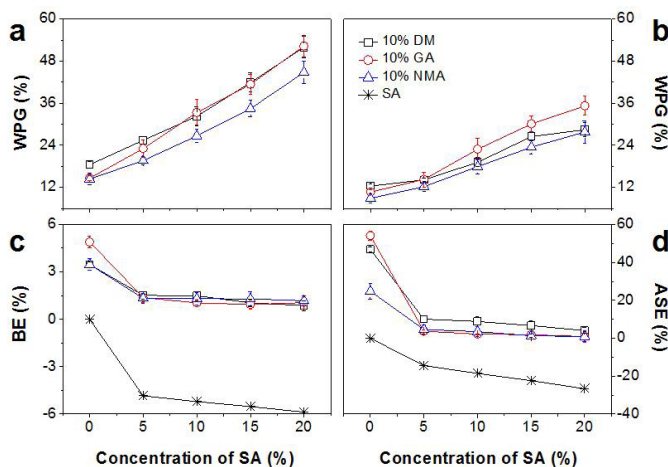

Fig. 1: Weight percent gains (WPG) of wood treated with 10% DM (Square), 10% GA (Circle), 10% NMA (Triangle) with different concentration of SA before (a) and after leaching (b), respectively. Bulking efficiency (BE) (c), and anti-shrink efficiency (ASE) (d) of wood treated with the same treatments as before; the asterisk represents the treated wood with SA alone and data adapted from (Che et al. 2018). Error bars are the standard deviation (StD) of 10 replicates per treatment.

The BE values of the wood samples treated with the combinations of agents were considerably promoted compared to treatment with SA alone (Fig. 1c). This indicates that the LMWAs penetrated into the wood cell wall and had a positive effect on BE. However, for the LMWAs/SA treatment groups, the wood cell bulking efficiency (after leaching) dropped to 1~2% with increasing SA concentration. This suggests the permeation into the cell walls of the LMWAs was inhibited due to the increased solution viscosity and the degradation of the cell wall in a hot alkaline environment (Kamdem et al. 2002, Seborg et al. 1953).

The ASE values were positive for the LMWAs/SA treated wood samples but decreased with increased SA concentration (Fig. 1d). This decrease in ASE was likely due to the degradation of the cell walls due to the high pH value (Tab. 1) of the treatment solution (Klüppel and Mai 2013). The reduction in the amount of LMWAs that enter the wood cell walls additionally contributes to the decreased ASE values, similarly to the effect on BE. In contrast to the negative BE and ASE values in wood treated with SA alone, the addition of LMWAs can effectively eliminate these negative effects and slightly improve the dimensional stability.

FT-IR analysis

The SA film formed after curing at 120°C and exhibited an infrared adsorption of carboxylate anions (-O=C-O-) composed of two characteristic bands due to the coupling effect of the polyelectron π bond: a band at 1550 cm^{-1} assigned to asymmetric stretching vibration and 1400 cm^{-1} to symmetrical stretching vibration (Fig. 2a).
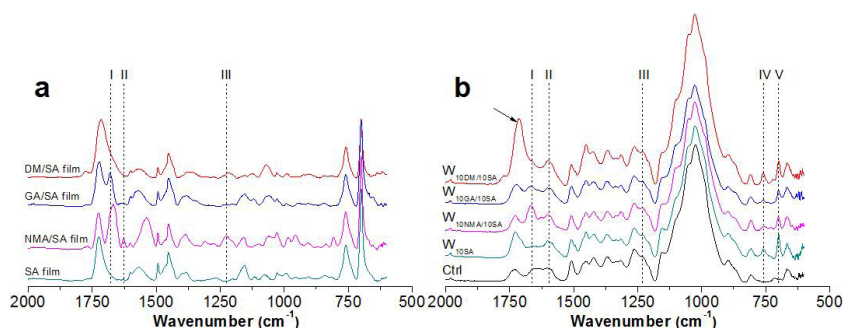

Fig. 2: FT-IR spectra of 10% SA, 10% DM/10% SA, 10% GA/10% SA, 10% NMA/10% SA combination film after curing (a), wood treatment with 10% SA (W_{10SA}), 10% DM/10% SA ($W_{10DM/10SA}$), 10% GA/10% SA ($W_{10GA/10SA}$), 10% NMA/10% SA ($W_{10NMA/10SA}$) and the W_{ctrl} is the wood without treatment (b). Band assignments: 1702 cm^{-1}(Arrow in b) and (aI, bI) 1674 cm^{-1}: C=O stretching vibration; (a_{II}, b_{II}) 1650–1550 cm^{-1}: N–H bending; (a_{III}, b_{III}) 1234–1257 cm^{-1}: C–O–C stretching vibration; (b_{IV}) 757 cm^{-1} and (b_V) 699 cm^{-1}: benzene ring substitution of SA.

The styrene can be recognized from the band of 1500 cm^{-1} assigned to the stretching of the benzene ring, and from two bands at 757 and 699 cm^{-1} assigned to the mono-substituted benzene in the copolymeric styrene (Zhang et al. 2008). The bands observed between 1234 and 1257 cm^{-1} are linked to the stretching -C-O-C- from ether bonds, which means that hydroxyl groups on DM or NMA can form ether bonds through self-polymerization. The spectra of GA/SA and NMA/SA showed new absorption bands at 1674 cm^{-1} that were not present for the SA only sample; the new band was assigned to stretching -C=O- from the GA and NMA (Alves et al. 2011, Baishya and Maji 2014). This peak was also reflected in the infrared spectrum of the treated wood (Fig. 2b), confirming the presence of GA and NMA in the wood. The peak at 1640 cm^{-1}

was attributed to N-H bending from the NMA. The SA and LMWA were simply superimposed under this condition because there were no obvious new functional groups.

Compared to the spectrum of the W_{ctrl} and the samples treated with a combination of agents, the peaks located at 1674 cm^{-1}, 757 cm^{-1}, and 699 cm^{-1} confirm the presence of SA in the wood. The peak observed at 1702 cm^{-1} (indicated by the arrow in Fig. 2b) corresponds to C=O from DM. The increase of peaks between 1234 cm^{-1} and 1257 cm^{-1} (-C-O-C-) in the DM/SA modified groups confirmed the DM crosslink with the wood cell wall. The spectra of wood treated with GA/SA and NMA/SA was the same as that for the SA samples, indicating that GA and NMA filled in the cell wall but did not react with them. This also corresponds to the improved ASE values for the wood treated with DM/SA compared to the samples treated with GA/SA or NMA/SA.

Mechanical properties

The LMWAs hardly affected the MOR and MOE of the wood samples (Fig. 3a, b), owing to the balance of increased compression strength on the top layer of wood and the loss of tensile strength on the bottom layer (Sun et al. 2016).
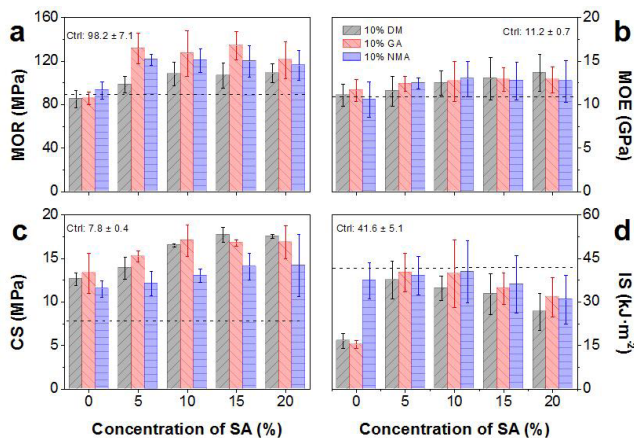

Fig. 3: Modulus of rupture (MOR) (a) and modulus of elasticity (MOE) (b) in bending, and compression strength (CS) (c) in the radial and impact strength (IS) (d) of wood treated with 10% DM (Left oblique strip), 10% GA (Right oblique strip), 10% NMA (Horizontal strip) plus various concentrations of SA, respectively. The horizontal dotted line is the value of untreated wood (Ctrl). Error bars are for StD for 10 replicates per treatment.

The MOR and MOE increased with increased SA, due to the strengthening effect of the SA copolymer located in the cell lumens, and the maximum improvement for both MOR and MOE was approximately 36% higher than these values for the W_{ctrl}. The MOR of the DM/SA treated wood samples was slightly lower than the MOR for the GA/SA and NMA/SA treated samples. This is because the DM treatment resulted in a slight decrease in the MOR of the wood (Xie et al. 2013). However, the increased SA concentration could not substantially increase the bending strength, which may be attributed to an offset of the reinforcement effect due to the increased cell wall degradation.

The compression strength of the treated wood was higher than that of the W_{ctrl}, and increased considerably with increasing SA concentration (Fig. 3c). This improvement can be

explained by the increased resistance to deformation due to the incorporation of the stiff SA inclusions in wood cell lumens (Gindl et al. 2004). The compression strength of the NMA/SA treated wood was lower than that of the wood treated with DM/SA or GA/SA due to the lower WPG of the NMA/SA treated wood.

More significant effects were seen on impact strength (Fig. 3d). A significant loss of about 62% occurs after either 10% GA or DM treatment in agreement with previous study (Xiao et al. 2010, Xie et al. 2007). This loss indicates the reduction of toughness due to the crosslinking of cell wall components by GA or DM. The impact strength of NMA treated wood did not decrease, which indicates NMA did not crosslink with wood, but instead only filled in or grafted with the cell wall. For the wood treated with the combination of chemicals at lower SA concentration, the impact strength did not decrease relative to the W_{ctrl} due to the lower degree of crosslinking by the LMWAs. Treatments with the combination of chemicals at higher SA concentration caused a slight reduction in the impact strength of wood, which was due to the hydrolysis of hemicellulose during treatment in an alkaline environment. In summary, LMWAs/SA impregnation increased the bending and compression properties without reducing the impact strength.

Dynamic thermomechanical analysis

The normalized storage modulus (E'/E'_{max}) of all wood samples showed a decrease in the tested temperature range (Fig. 4a, c, e), which can be attributed to the increased molecular mobility of wood cell wall polymers at elevated temperatures (Ou et al. 2014). The W_{ctrl} exhibited a considerable decrease in E'/E'_{max} above 100°C, consistent with the glass transition of amorphous wood polymers (Ou et al. 2015).
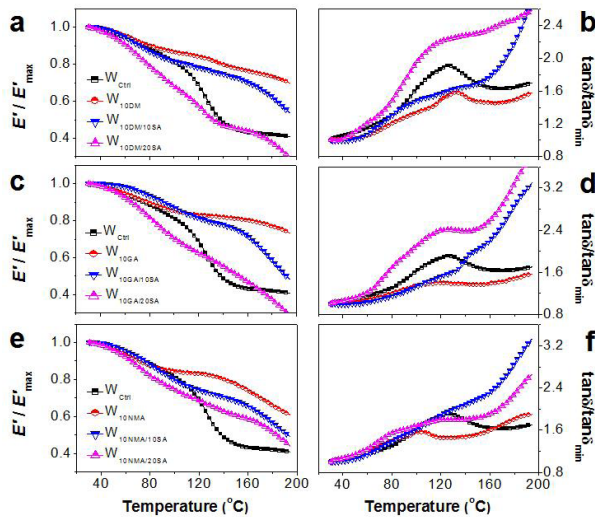

Fig. 4: E'/E'_{max} and tanδ/tanδ min of wood treatment with 10% DM (a, b), 10% GA (c, d), 10% NMA (e, f) plus various concentrations of SA, respectively. The W_{ctrl} is untreated wood.

The decrease in E'/E'_{max} of the wood treated with LMWAs was less than that for the untreated wood (Fig. 4a,c,e), suggesting an increased rigidity of wood due to the penetration of LMWAs into the wood cell wall and subsequent strengthening. However, the overall enhancement of wood decreased with the increase of SA: the LMWAs/SA treated wood showed

a lower E'/E'_{max} above 80°C that that of the W_{ctrl} when the concentration of SA increased to 20%. This showed that the SA copolymer in wood still presents thermoplasticity, and the softening point is about 80°C. Additionally, this suggests that LMWAs did not crosslink with SA in the wood cell lumens. The amplitude of the normalized damping factor (tanδ/tanδ$_{min}$) increased, and the relaxation peaks of the LMWAs/SA treated wood shifted to lower temperatures with increased SA content (Fig. 4b,d,f). This indicated that the combination treated wood softened during testing due to the mobility of thermoplastic SA copolymer in the cell lumen.

Morphological morphology

The cross section of the impact-fractured W_{ctrl} showed uneven breakage (Fig. 5a). After DM and GA treatment, the fracture profile became very smooth (not shown), suggesting fragile breakage.
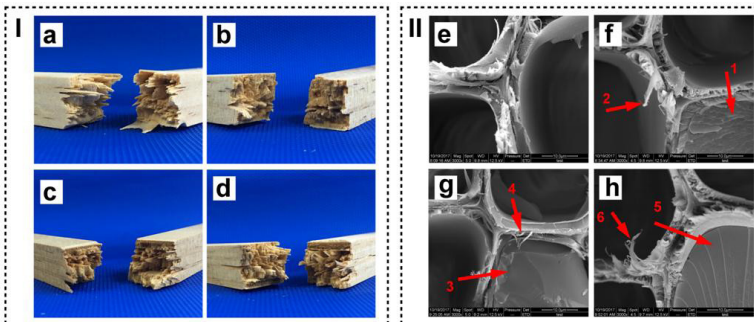

Fig. 5: Typical fracture modes (I) of wood after impact test: W_{ctrl} (a) and treated with 10% DM ($W_{10DM/10SA}$) (b), 10% GA ($W_{10GA/10SA}$)(c), 10% NMA ($W_{10NMA/10SA}$)(d) plus 10% SA. Micrographs (II) of the frozen impact–fractured cross section of W_{ctrl} (e, 3000×), $W_{10DM/10SA}$ (f, 3000×), $W_{10GA/10SA}$ (g, 3000×), and $W_{10NMA/10SA}$ (h, 3000×). The arrows 1, 3 and 5 point at inclusions precipitated in the cell lumens and the arrow 2, 4 and 6 points at the torn tough cell wall.

In contrast, there was no brittle fracture in the NMA-treated wood (not shown), which indicated that the NMA did not crosslink with the wood cell wall, a finding that was consistent with the results of mechanical tests. After addition of 10% SA, the fracture profiles of the specimens treated with DM (Fig. 5b) or with GA (Fig. 5c) became more stretched out in appearance compared with the samples treated with DM or GA alone. This indicated that the amount of LMWAs entering into the cell wall was reduced due to the presence of SA in the treatment solution. These morphological features confirm the results of the mechanical tests. Although NMA treatment did not decrease the impact strength of wood, the impact of wood after NMA/SA treatment was a little smoother than the control sample W_{ctrl} (Fig. 5d), due to the degradation of wood components in the alkaline aqueous solution.

The W_{ctrl} cell walls exhibited a tough fracture pattern, with the removal of some bundles of microfibrils (Fig. 5e). The combination treatments caused the full or partial filling of cell lumens by an incorporated LMWAs/SA polymer. The amount of incorporated inclusions in cell lumens increased with increased concentration of SA copolymer during the treatment (not shown). Bundles of microfibrils were still visible on the fractured surface of the wood samples treated with LMWAs/SA, implying good toughness of the wood (Fig. 5f, g, h), however, the samples treated with the combination of agents exhibited a smooth and brittle fractured surface (1, 3, 5 arrows in Fig. 5II). The combination of mixtures showed good contact with wood cell walls, suggesting that properly established interfacial adhesion leads to the improvement of other properties.

Reduced water uptake and MC

The treated wood exhibited a linear decrease in water uptake with increasing SA contents, and the maximum decrease was approximately 50% (Fig. 6a). The decreased water uptake can be attributed to the incorporation of treatments that slow the diffusion of water in wood. The reduction in moisture/water diffusion acts to dimensionally stabilize the wood.
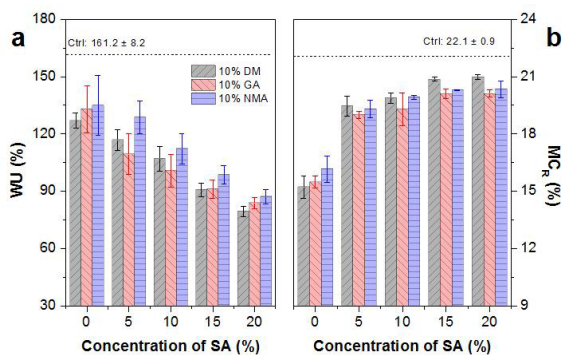

Fig. 6: The water uptake in water (WU) (a) and moisture content reduction (MC_R) at 93% relative humidity (b) of wood treated with 10% DM (Left oblique strip), 10% GA (Right oblique strip), 10% NMA (Horizontal strip) plus various concentrations of SA, respectively. Error bars are for StD for 10 replicates per treatment.

The EMC_R decreased in wood after treatment with LMWAs at 93% RH (Fig. 6b), due to the crosslinking or grafting reaction between the LMWAs and hydroxyl groups on the cell walls of wood. The EMC_R of the specimens treated with the mixtures increased linearly with increasing SA concentration. This indicated that a high concentration of SA prevents some of the LMWAs from entering the wood cell wall.

CONCLUSIONS

In this work, the combination of LMWAs (10% DM, 10% GA, 10% NMA) with the SA copolymer provided stable anti-leaching in the wood cell wall and lumens. The addition of LMWAs effectively eliminated the negative effects on cell wall BE and ASE that result from the treatment of wood by SA alone. In addition, the SA copolymer precipitation in cell lumens greatly improved the mechanical properties of wood. A synergistic effect of wood cell wall modification and cell lumen filling was achieved by LMWAs/SA treatment, suggesting that this treatment shows promise for the industrial application of wood modification. In spite of this, other important properties of the combination modified wood, such as weathering and decay resistance, need further investigation in the next work.

ACKNOWLEDGMENTS

REFERENCES

1. Alves, P.M.A., Carvalho, R.A., Moraes, I.C.F., Luciano, C.G., Bittante, A.M.Q.B., Sobral, P.J.A., 2011: Development of films based on blends of gelatin and poly(vinyl alcohol) cross linked with glutaraldehyde. Food Hydrocolloids 25(7): 1751-1757.

2. Baysal, E., Ozaki, S.K., Yalinkilic, M.K., 2004: Dimensional stabilization of wood treated with furfuryl alcohol catalysed by borates. Wood Science and Technology 38(6): 405-415.

3. Baishya, P., Maji, T.K., 2014: Studies on Effects of different cross-linkers on the properties of starch-based wood composites. ACS Sustainable Chemistry and Engineering 2(7): 1760-1768.

4. Che, W., Xiao, Z., Han, G., Zheng, Z., Xie, Y., 2018: Radiata pine wood treatment with a dispersion of aqueous styrene/acrylic acid copolymer. Holzforschung 72 (5): 387-396.

5. DIN 52185, 1976: Testing of wood. Wood-compression tests-parallel to grain.

6. DIN 52186, 1978: Testing of wood. Bending test.

7. Epmeier, H., 2004: Differently modified wood: comparison of some selected properties. Scandinavian Journal of Forest Research 19(5): 31-37.

8. 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 Science and Technology 37(5): 349-361.

9. GB/T 1934.1, 2009: Method for determination of the water aborption of wood.

10. GB/T 1940, 2009: Method of testing in toughness of wood.

11. Goldstein, I.S., Dreher, W.A., 1960: Stable furfuryl alcohol impregnating solutions. Journal of Industrial and Engineering Chemistry 52(1): 245-246.

12. Hill, C.A.S., 2006: Wood modification: chemical, thermal and other processes. John Wiley and Sons. Chichester, UK, 260 pp.

13. Hill, C.A.S., 2008: The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents: a reappraisal. Holzforschung 62(4): 423-428.

14. Hill, C.A.S, Khalil, H., H, M.D., 1998: A study of the potential of acetylation to improve the properties of plant fibres. Industrial Crops and Products 8(1): 53-63.

15. Himmel, S., Mai, C., 2015: Effects of acetylation and formalization on the dynamic water vapor sorption behavior of wood. Holzforschung 69(5): 633-643.

16. Himmel, S., Mai, C., 2016: Water vapour sorption of wood modified by acetylation and formalisation-analysed by a sorption kinetics model and thermodynamic considerations. Holzforschung 70(3): 203-213.

17. Kamdem, D.P., Pizzi, A., Jermannaud, A., 2002: Durability of heat-treated wood. European Journal of Wood and Wood Products 60(1): 1-6.

18. Klüppel, A., Mai, C., 2013: The influence of curing conditions on the chemical distribution in wood modified with thermosetting resins. Wood Science and Technology 47(3): 643-658.

19. Krause, A., Wepner, F., Xie, Y., Militz, H., 2008: Wood protection with dimethyloldihydroxy-ethyleneurea and its derivatives. American Chemical Society. Washington, Pp 356–371.

20. Ormondroyd, G., Spear, M., Curling, S., 2015: Modified wood: Review of efficacy and service life testing. Construction and Building Materials 168(4): 187–203.

21. Ou, R., Xie, Y., Wang, Q., Sui, S., Wolcott, M.P., 2014: Effects of ionic liquid on the rheological properties of wood flour/high density polyethylene composites. Composites Part A: Applied Science and Manufacturing 61: 134-140.

22. Ou, R., Xie, Y., Wang, Q., Sui, S., Wolcott, M.P., 2015: Material pocket dynamic mechanical analysis: a novel tool to study thermal transition in wood fibers plasticized by an ionic liquid (IL). Holzforschung 69 (2): 223-232.

23. Rowell, R.M., 2005: Handbook of wood chemistry and wood composites. Taylor and Francis Publisher, Second Edition, New York, USA, 703 pp.

24. Seborg, R. M., Tarkow, H., Stamm, A. J., 1953: Effect of heat upon the dimensional stabilisation of wood. Journal of Forestry Products Research Society 3(9): 59–67.

25. Stamm, A.J., 1977: Dimensional stabilization of wood with furfuryl alcohol. ACS symposium series, 43, Chapter 9, Americal Chemical Society. Washington, USA Pp 141-149.

26. Sun, W., Shen, H., Cao, J., 2016: Modification of wood by glutaraldehyde and poly (vinyl alcohol). Materials and Design 96(3): 92-400.

27. Xiao, Z., Xie, Y., Militz, H., Mai, C., 2010a: Effect of glutaraldehyde on water related properties of solid wood. Holzforschung 64 (4): 483-488.

28. Xiao, Z., Xie, Y., Militz, H., Mai, C., 2010b: Effects of modification with glutaraldehyde on the mechanical properties of wood. Holzforschung 64 (4): 475-482.

29. Xie, Y., Fu, Q., W, Q., X, Z., Militz, H., 2013: Effects of chemical modification on the mechanical properties of wood. European Journal of Wood and Wood Products 71(4): 401-416.

30. Xie, Y., Hill, C.A.S., Xiao, Z., Mai, C., Militz, H., 2011: Dynamic water vapour sorption properties of wood treated with glutaraldehyde. Wood Science and Technology 45(1): 49-61.

31. Xie, Y., Krause, A., Militz, H., Turkulin, H., Richter, K., Mai, C., 2007: Effect of treatments with 1,3-dimethylol-4,5-dihydroxy-ethyleneurea (DMDHEU) on the tensile properties of wood. Holzforschung 61(1): 43-50.

32. Yasuda, R., Minato, K., 1994: Chemical modification of wood by non-formaldehyde cross-linking reagents. Wood Science Technology 28(3): 209-218.

33. Yu, X., Sun, D., Li, X., 2011: Preparation and characterization of urea-formaldehyde resin-sodium montmorillonite intercalation-modified poplar. Journal of Wood Science 57(6): 501-506.

34. Zhang, P., He, J., Zhou, X., 2008: An FTIR standard addition method for quantification of bound styrene in its copolymers. Polymer Test 27(2): 153-157.

Wenbo Che, Zefang Xiao*, Yanjun Xie*
Northeast Forestry University
Key Laboratory of Bio-Based Material Science and Technology
(Ministry of Education)
26 Hexing Road
Harbin 150040
P. R. China
*Corresponding authors: zxiao@nefu.edu.cn, yxie@nefu.edu.cn