DIMENSIONAL STABILITY OF METHYL METHACRYLATE HARDENED HYBRID POPLAR WOOD

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This study examines the dimensional stability of fast-growing poplar clones wood after treatment by impregnation with methyl methacrylate (MMA). Six hybrid poplar clones from one plantation in Quebec were sampled. The effects of hardening with MMA on density as well as longitudinal, radial, tangential, and volumetric swelling properties (*S*), water uptake capacity (*D*), anti-swelling efficiency (*ASE*), and water repellent efficiency (*WRE*) after soaking were investigated. Hardening treatment increased the density of all poplar woods by 1.2 to 1.6 and decreased the inner water migration rate during soaking. *S* and *D* values of hardened woods were significantly lower than those of controls, depending on the clone type. *ASE* and *WRE* values suggested that incorporating MMA effectively improved the dimensional stability of poplar wood at the early soaking stage, but was less effective in the long term.

Keywords: Hybrid poplar; MMA; Hardening; Dimensional stability; Water uptake; Swelling properties; Anti-swelling efficiency; Water repellent efficiency

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INTRODUCTION

Wood has been used for furniture, construction materials, and sports and recreational equipment for thousands of years thanks to its structural and thermal insulation properties, acoustic performance, and aesthetic characteristics. Moreover, it constitutes a renewable natural resource. Furthermore, according to life-cycle assessment, it outperforms many other materials, including steel, concrete, and synthetic plastics (Glover et al. 2002). However, it has some disadvantages, including poor dimensional stability, susceptibility to damage and deterioration, and frequent, costly maintenance. Most of these drawbacks can be attributed to the hygroscopic characteristics of wood. It swells differently in each of the three principal directions when absorbing water, and high moisture content (*MC*) further affects wood's mechanical properties and decay-resistance. Wood contains two kinds of water: free water and bound water. Free water is confined mainly in the cell lumens and other cavities, and can be easily removed by drying. Bound water, on the other hand, is held in the cell walls by the hydrogen bonding force between cellulose hydroxyl groups, and can be removed only after the free water has been completely removed. The difference in water vapor pressure between wood cell walls and the surrounding atmosphere is the driving force that removes bound water.

Below fiber saturation (around 30% *MC*), wood contains only bound water, and with further drying, the wood starts to shrink, with most wood strength properties increasing as a consequence (Kretschmann 2010). In service, the practical moisture content of wood is generally kept close to the equilibrium moisture content (*EMC*). Therefore, the dimensional stability of wood can be improved by controlling the moisture content of final wood products.

An effective way to reduce the amount of moisture that is absorbed is to modify the wood by impregnating it with chemicals and subsequently cure the chemicals in place using gamma radiation or a heat-activated catalyst. Various polymers and resins have been used for such treatment, including methyl methacrylate (Zhang et al. 2006a,b; Yildiz et al. 2005; Elvy et al. 1995; Ellis 1994; Schaudy and Proksch 1982; Rosen 1976), styrene (Devi and Maji 2007; Yildiz et al. 2005), polyurethane resin (Gao and Li 2007), phenol-formaldehyde resin (Deka and Saikia 2000), melamine urea formaldehyde resin (Cai et al. 2008; Deka and Saikia 2000), and maleic anhydride (Li et al. 2011a,b). After treatment, the dimensional stability of the treated wood is improved, either because the void spaces in the wood are filled (Zhang et al. 2006b; Ellis 1994; Schaudy and Proksch 1982; Rosen 1976) or because the number of free hydroxyl groups is reduced by chemical reactions (Deka and Saikia 2000; Zhang et al. 2006b; Ely et al. 1995; Ellis 1994, Li et al. 2011a,b). In addition, mechanical strength, decay resistance, and flammability resistance are also improved (Gao and Li 2007; Zhang et al. 2006a,b; Yildiz et al. 2005; Koubaa et al. 2012; Ely et al. 1995; Schaudy and Proksch 1982; Rodriguez et al. 2006; Li et al. 2011c). Therefore, wood modification offers the potential to tailor wood product properties to meet end-use requirements, especially for low-grade wood (Yildiz et al. 2005; Koubaa et al. 2012). Moreover, compared to wood-polymer composites manufactured by extrusion, impregnated wood retains a natural appearance.

In the present study, low-grade woods from hybrid polar species were selected as the base material for hardening. Due to their rapid growth and ease of reproduction, hybrid poplar woods have been widely planted in North America to provide an alternative wood source. The average specific gravity of hybrid polar in North America ranges from 0.30 to 0.39 (Balatinecz and Kretschmann 2001). Standing poplar trees have high moisture content, typically almost 100%, with only minor differences between sapwood and heartwood (Balatinecz and Kretschmann 2001). Although hybrid poplar wood is currently used primarily for pulp and paper production and engineered wood products (Balatinecz and Kretschmann 2001), modified wood materials could be another potential use.

Only few studies investigated the dimensional stability of hybrid poplar wood composites. However, either solvent, which is not desirable in the industrial-scale production, was involved in the preparation of the composites (Li et al. 2011a,b) or the properties related to dimensional stability were not studied systematically (Yildiz et al. 2005; Li et al. 2011a,b). Therefore, methyl methacrylate (MMA), a low-viscosity, relatively cheap, and readily available monomer, was used to fill the void spaces of poplar wood. The purpose of this study was to investigate the effect of MMA impregnation on the dimensional stability of hybrid poplar woods and to examine interclonal variations in their dimensional stability.

EXPERIMENTAL

Materials

Twenty-four hybrid poplar trees were chosen randomly from a six-year-old experimental plantation near Montreal, Quebec, Canada (Table 1). A log was taken from each tree at between 0.5 m and breast height, and samples were extracted to measure the physical properties. Four standard samples from each log were cut for each investigated property. Wood density and dimensional stability were determined according to standard test methods. Each sample was then labeled with a unique code to identify the source clone and tree. The four samples from each tree were divided into two equally sized groups for each test: a control group and a treated group. Controls were kept in an air-conditioned room at 21 °C and 40% relative humidity (*RH*) for 60 days to reach a moisture content of 9% before testing. The treated group underwent the impregnation treatment.

An impregnating solution was formulated from a hydroquinone-inhibited monomer [MMA, $H_2C=C(CH_3)COOCH_3$], provided by Univar Canada Ltd. (Richmond, British Columbia, Canada), and mixed with 0.5 wt.% of Vazo 52 (2,2'-azobis-2,4-dimethylvaleronitrile $(CH_3)_2C(CN)N=NC(CH_3)_2(CN)$), a low-temperature polymerization initiator obtained from DuPont Canada Inc. (Mississauga, Ontario, Canada). The 0.5 wt.% of Vazo 52 was based on the weight of the polymeric monomer mixture. The monomer solution was prepared immediately before the impregnation process to prevent self-assembling into polymethyl methacrylate (PMMA) polymer.

Table 1. General Information on the Investigated Hybrid Poplar Clones

Clones	Coding	Common name	Species cross	Number of trees
1	915313	M×B	*P.maximowiczii* × *balsamifera*	4
2	915508	M×B	*P.maximowiczii* × *balsamifera*	4
3	3729	N×M	*P.nigra* × *maximowiczii*	4
4	915303	M×B	*P.maximowiczii* × *balsamifera*	4
5	915311	M×B	*P.maximowiczii* × *balsamifera*	4
6	3531	D×N	*P.deltoides* × *nigra*	4

Preparation of Hardened Wood

Wood samples of the hybrid poplar clones to be treated were conditioned at room temperature (21 ºC) and 45% relative humidity (*RH*) for five weeks to reach an equilibrium moisture content of 9%. After conditioning and before impregnation, the initial weight of each sample was recorded to the nearest 0.01 g. Initial dimensions of the samples used for dimensional stability and density testing were measured in the three principal directions to the nearest 0.01 mm using a digital micrometer. The samples were then placed in an impregnation autoclave. A vacuum of approximately 10 kPa (75 mm Hg) was applied for 20 minutes. Next, the impregnation solution was introduced into the autoclave to immerse the wood samples. A pressure of 1.38 MPa (200 psi) was applied and maintained at room temperature for 20 minutes to ensure maximum impregnation. After pressure release, the impregnated samples were removed from the autoclave, and

excess monomer was wiped from the surface. The samples were then weighed and placed in the reactor for polymerization at 690 kPa (100 psi) nitrogen pressure and cured for 4 hours at 70°C (158°F). After curing, the reactor was depressurized and the samples were removed and placed in a ventilated area to evaporate the non-polymerized monomer. Excess polymer was removed from the surface of some samples. Composite weights of the final samples were remeasured to the nearest 0.01 g, and the dimensions of the samples for dimensional stability and density testing were measured to the nearest 0.01 mm. Polymer retention (*PR*) in the composites was calculated according to the following equation,

$$PR(\%) = (w_{HW} - w_S) / w_S \times 100 \quad (1)$$

where w_{HW} is the weight of the hardened wood sample and w_S is the initial weight of the corresponding untreated sample.

Density

Samples with nominal dimensions 100×20×20 mm (longitudinal × radial × tangential) were used to determine oven-dried density (ρ_o). The samples were oven-dried for more than 24 hours at 103 ± 2°C to achieve a constant weight. The dimensions of the samples were then determined in the three principal directions to the nearest 0.01 mm, and weight was recorded to the nearest 0.01 g. ρ_o was calculated according to the following equation,

$$\rho_o = \frac{M_o}{V_o} \quad (2)$$

where, M_o and V_o are the mass and volume of the oven-dried sample, respectively.

Water Uptake and Dimensional Stability

Samples with dimensions 100×20×20 mm (longitudinal × radial × tangential) were used to determine water uptake capacity and swelling properties according to ASTM D 1037 standard procedure (1999). Water absorption and swelling after submersion in water for periods of 2, 24, 48, 168, 336, and 720 hours were measured. After each saturation period, dimensions were determined to the nearest 0.01 mm in the three principal directions and samples were weighed to the nearest 0.01 g. Samples were then oven-dried for more than 24 hours at 103 ± 2°C until constant weight was reached. The same measurements were then repeated on the oven-dried samples. Water repellent efficiency (*WRE*) and anti-swelling efficiency (*ASE*) were calculated according to the following equations,

$$WRE(\%) = (D_S - D_{HW}) / D_S \times 100 \quad (3)$$

$$ASE(\%) = (S_S - S_{HW}) / S_S \times 100 \quad (4)$$

where D_S and D_{HW} are the water uptake of solid wood and hardened wood, and S_S and S_{HW} are the volumetric swelling coefficient of solid wood and hardened wood, respectively. *D* and *S* were calculated as,

$$D(\%) = (w_{w+o} - w_o) / w_o \times 100 \quad (5)$$

$$S\ (\%) = (V_{w+o} - V_o) / V_o \times 100 \quad (6)$$

where w_o is the weight of the oven-dried sample, w_{w+o} is the weight after water submersion, V_o is the volume of the oven-dried sample, and V_{w+o} is the volume after water submersion.

The swelling coefficient in the three principal directions was also calculated as,

$$S_\alpha(\%) = (\alpha_{w+o} - \alpha_o) / \alpha_o \times 100 \quad (7)$$

where α_o is the single direction dimension (radial, tangential, or longitudinal) of the oven-dried sample and α_{w+o} is the single direction dimension after submersion.

Scanning Electron Microscopy

In order to observe the microstructure, the samples were fractured in a brittle manner after immersing them into liquid nitrogen. The fractured surface was coated with a thin layer of platinum using a sputter coater (SC7620, Quorum Technologies, West Sussex, UK), and the microstructure was examined using a scanning electron microscope (SEM) (JSM-6060, JEOL, Tokyo, Japan). Surface images were scanned with a high vacuum secondary electron microscope (20kv, working distance = 31 mm).

Fourier Transform Infrared Spectroscopy

The infrared spectra of the untreated hybrid poplar wood, MMA-hardened poplar wood, and PMMA samples were recorded on a Tensor 27 Fourier transform infrared (FTIR) system (Bruker Optics, Ettlingen, Germany) equipped with a deuterated triglycine sulfate detector. Spectra for each sample were recorded by collecting 164 scans in the range 4000 to 400 cm^{-1} at 4-cm^{-1} resolution. Pure powdered potassium bromide (KBr) was used as a reference substance. Samples for FTIR spectrum analysis were carefully prepared in microcups as follows: 1 mg of each wood flour (100 mesh) or PMMA was mixed with KBr in the proportion of 1/100 wt % in an agate mortar and then transferred to a cup 4 mm in diameter, where it was lightly compressed and leveled with a spatula. Tilted baselines of the original spectra were not altered.

Statistical Data Analysis

Statistical data analyses were performed with Statistical Analysis System (SAS) software (SAS Institute Inc., 2004). Analyses of variance were performed with the generalized linear model (GLM) and the (Least Squares Means (LSMEANS)/ P-values for differences (PDIFF)) test on the combined data (control and treated samples) to determine differences between the mean values for the treated sample in the hybrid

crosses. The residual normal distribution for each trait was verified by both the Shapiro–Wilk W test and a normal probability plot using SAS Plot and univariate procedures. The homogeneity of variance for each trait was verified graphically by scatterplots of studentized residuals versus predicted values. A logarithmical transformation was applied to the variance analysis to obtain a normal distribution of residuals and homogeneity of variances for the density variables.

RESULTS AND DISCUSSION

Density

The hardening treatment had a significant effect on density (Table 2), which varied from 687 to 805 kg/m^3, which is 2.2 to 2.6 times higher than that of unhardened wood, depending on the clone. The highest density of the treated samples was observed at around 800 kg/m^3 for clones 915311 and 3531, and the lowest density was 687 kg/m^3 for Clone 915303. Hardened poplar wood density was comparable to or higher than densities of some commercial hardwoods such as silver maple (623 kg/m^3), red oak (596 kg/m^3), and white ash (695 kg /m^3). In a previous report (Koubaa et al. 2012), it was shown that the final density of the treated wood varied with polymer retention (*PR*), which varied among clones. *PR* decreased with increasing initial wood density in the hybrid poplar clones (R^2=0.83, significant). *PR* variation was attributed to the individual porosity of each wood (Ding et al. 2008). The improvement in wood density led to an equivalent improvement in wood hardness (Koubaa et al. 2012).

Table 2. Density (kg/m^3), Water Uptake (%) and Volume Swelling for Hybrid Poplar Clones

Clone	Density (kg/m^3)		Water uptake (%)				Volume swelling coefficient (%)			
			After 24 hours		After 720 hours		After 24 hours		After 720 hours	
	Mean	CV[b]	Mean	CV	Mean	CV	Mean	CV	Mean	CV
Control										
1	305E[a]	5.8	95.8AB	5.8	253.1AB	9.3	9.2BC	4.3	11.5BC	8.9
2	320DE	5.5	81.8BC	11.8	228.7C	9.7	9.4B	2.8	12.0B	6.3
3	336D	3.4	76.8C	13.0	214.1D	10.7	10.5A	4.6	13.2A	5.0
4	284F	5.4	95.1AB	8.3	263.5A	5.3	8.4C	3.3	10.8C	4.9
5	305E	4.3	97.9A	11.0	257.5AB	4.9	8.9BC	6.3	12.2B	7.9
6	317DE	6.2	88.7ABC	11.9	243.2B	9.1	8.7BC	2.3	11.4BC	2.6
Treated										
1	735BC	3.1	22.3D	6.2	57.6EF	4.3	3.0F	9.3	7.2F	13.1
2	743B	1.6	25.3D	6.3	63.9E	6.2	3.9DE	15.7	8.4E	16.9
3	749B	1.6	24.7D	8.7	62.3EF	10.4	4.6D	9.0	9.0DE	8.7
4	687C	2.0	27.0D	7.1	71.5E	8.3	3.5DEF	15.2	7.3F	9.0
5	798A	4.7	12.6E	17.5	33.8G	11.2	1.4G	14.3	5.0G	7.1
6	805A	3.6	19.9D	13.4	48.0FG	11.1	3.2EF	4.2	7.5F	13.7

[a] Numbers followed by the same letter within a column are not significantly different at $p > 0.05$ (LSMEANS/PDIFF test); [b] CV: coefficient of variation (%).

Water Uptake and Water Repellent Efficiency

Average water uptake (*D*) for control and methyl methacrylate (MMA)-treated hybrid poplar wood samples with soaking time is shown in Fig. 1. Water uptake for hardened wood was much lower than for control samples. Water uptake for both control and treated samples increased rapidly from the start of soaking to approximately 200 soaking hours, after which the increase rate decreased significantly. The water uptake increase rate for treated wood was much lower than that for controls, throughout the soaking time. Water uptake varied among clones after soaking in water for 24 and 720 hours (Table 2). Clone 3729 showed the lowest water uptake of the control group, and Clone 915311 had the lowest of the treated group, although its corresponding control had the highest water uptake. Water uptake was largely related to sample density (Fig. 2). Water uptake after 24 and 720 hours' immersion is shown, and all relationships were significant.

Water repellent efficiency (*WRE*) for each clone after 24 and 720 hours' immersion in water are shown in Table 3. Samples with lower water uptake capacity obtained higher *WRE*, with Clone 915311 showing the highest. WRE remained nearly constant after 24 hours. This indicates that the control wood had much higher water uptake rates than the treated wood, especially at the start of immersion. This improvement is attributed to the MMA polymer-filled voids, which create a physical and mechanical barrier that hinders water movement. Scanning electron microscopy (SEM) micrographs of the treated hybrid poplar wood (Fig. 3) clearly show that polymethyl methacrylate (PMMA) polymer filled the vessels, lumen, and other void spaces in the wood structure. The analysis of variance (ANOVA) revealed that the density difference (Dendif) between hardened wood and solid wood, clone, soaking time, and the interaction between Dendif and clone all had significant effects on *WRE* (Table 4). The density difference is defined as the amount of polymer contained per unit volume of wood.

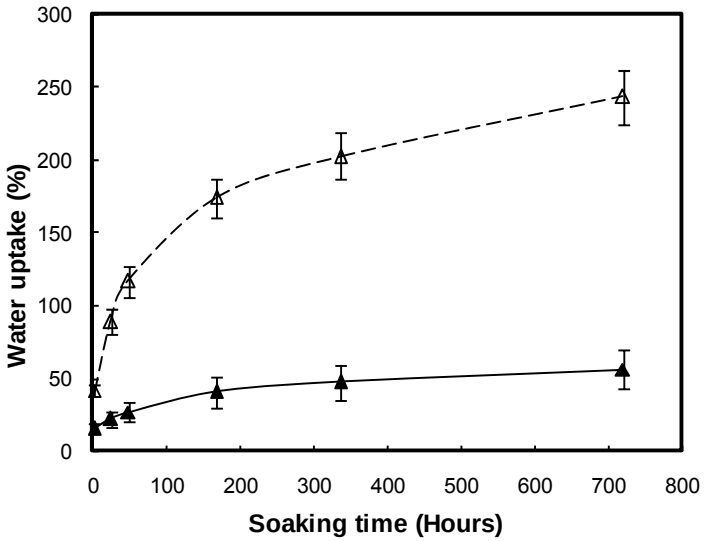

Fig. 1. Average water uptake (%) for control and treated hybrid poplar clones. △s denote control wood and ▲s denote treated wood

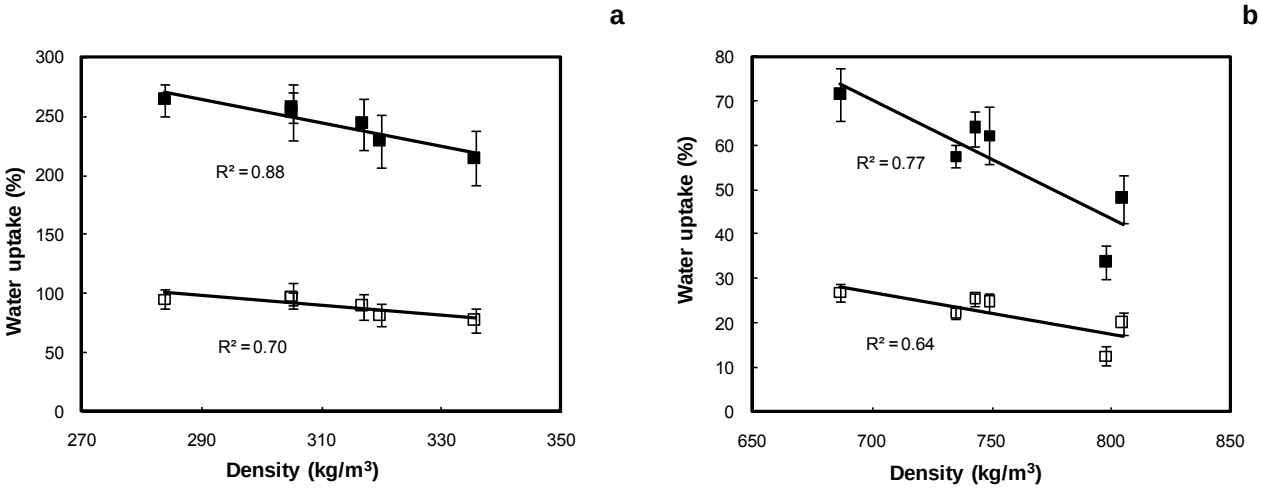

Fig. 2. Relationship between water uptake and density: a) control wood and b) treated wood; □s denote 24 hours and ■s denote 720 hours

Table 3. Water Repellent Efficiency (*WRE*, %) and Anti-Swelling Efficiency (*ASE*, %) after 24 hours and 720 Hours for Hybrid Poplar Clones

Clone	Water repellent efficiency (%)				Anti-swelling efficiency (%)			
	After 24 hours		After 720 hours		After 24 hours		After 720 hours	
	Mean	CV [b] (%)	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)
1	76.5 AB[a]	1.6	77.1 AB	1.9	67.0 B	2.4	37.6 B	9.7
2	68.6 B	3.1	71.9 BC	1.8	58.6 BC	10.1	30.4 B	24.3
3	67.6 B	3.0	70.9 BC	1.3	58.7 BC	4.5	31.4 B	10.7
4	69.2 B	4.9	72.9 BC	1.4	57.7 BC	10.9	32.1 B	11.5
5	86.8 A	3.0	86.7 A	2.0	84.2 A	2.0	59.3 A	1.9
6	77.3 AB	3.4	80.2 AB	1.0	63.9 B	3.3	34.2 B	34.9

[a] Numbers followed by the same letter within a column are not significantly different at $p > 0.05$ (LSMEANS/PDIFF test); [b] CV = Coefficient of variation (%).

Dimensional Stability

Swelling properties and anti-swelling efficiency

Figure 4 shows the variations in swelling (*D*) in the radial, tangential, and longitudinal directions for the control and treated hybrid poplar wood samples. Longitudinal swelling showed the lowest values, with an average of 0.6% for controls and less than 0.3% for treated samples after 720 hours' immersion in water. Swelling was mostly in the tangential direction at around 8.8% for control and 3.6% for treated samples. Radial swelling was in the medium range at an average of 3.5% for the control and 1.3% for treated samples. Overall, MMA-treated samples swelled less than half that of controls in all three principal directions. Longitudinal, radial, and tangential swelling of non-treated samples was in good agreement with previously reported data on hybrid poplar clones (Koubaa et al. 1998; Pliura et al. 2005).

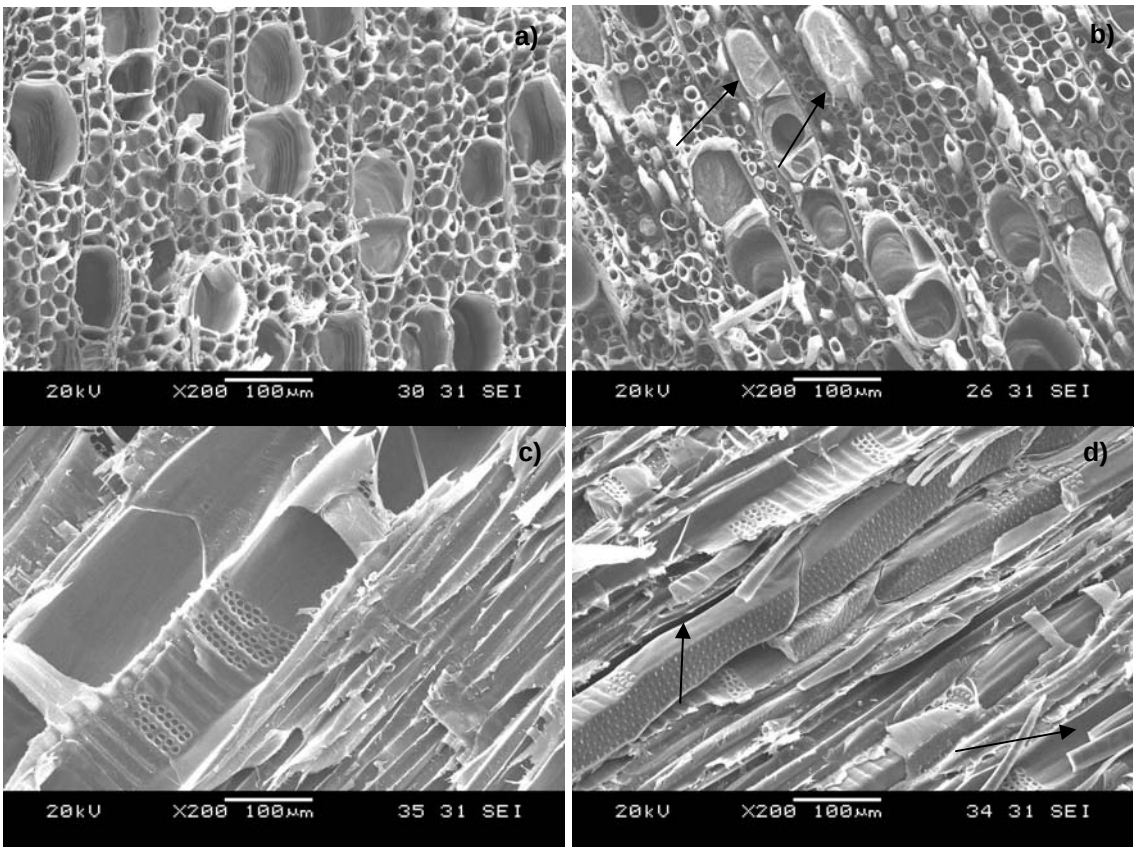

Fig. 3. Cross-section SEM of (a) untreated and (b) PMMA-hardened hybrid poplar wood; tangential section of (c) untreated and (d) PMMA-hardened hybrid poplar wood; arrows indicate microcracks between wood fiber cell walls and PMMA.

Table 4. Results of Analysis of Variance of Anti-Swelling Efficiency and Water Repellent Efficiency for Hybrid Poplar Clones

Source of variation		df	ASE *F*	WRE *F*
Fixed effects	Clone	5	5.50 **	2.44 *
	Time	5	2.99 *	0.13 n.s.
	Dendif	1	19.11 **	45.50 **
	Clone × Time	25	0.42 n.s.	0.63 n.s.
	Clone × Dendif	5	10.52 **	3.33 **
	Time × Dendif	5	2.87 *	1.80 n.s.
	Clone × Dendif × Time	25	0.41 n.s.	0.96 n.s.
Random effects			σ^2 ± SE	σ^2 ± SE
	Tree (Clone)		14.94±5.47	18.00±6.64
	Random error		18.16±1.78	23.61±2.31

df = degree of freedom; Dendif = density difference (treated – control); * Significant at the 0.05 probability level; ** Significant at the 0.01 probability level.

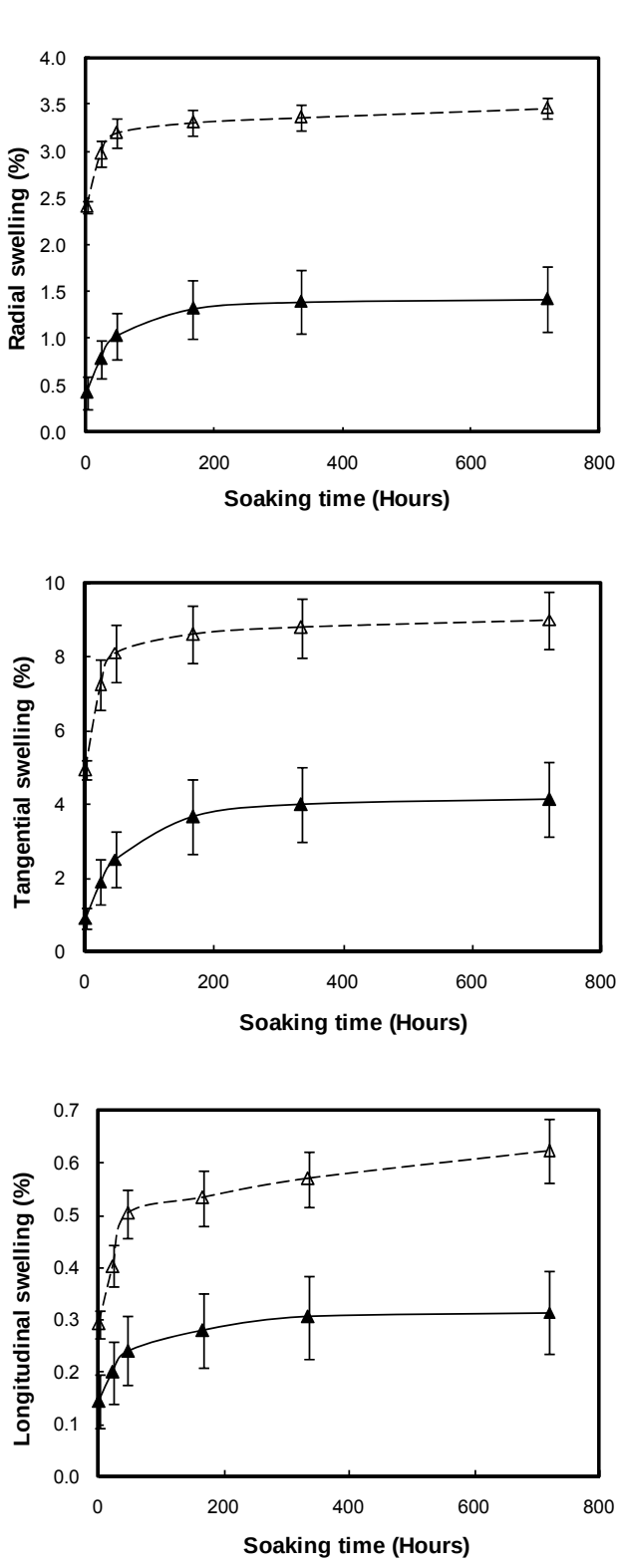

Fig. 1. Average swelling coefficient (%) in a) radial, b) tangential, and c) longitudinal direction for control and treated hybrid poplar clones; △s denote control wood and ▲s denote treated wood

The volumetric swelling coefficient varied among clones for both control and treated wood, depending on soaking time (Fig. 5 and Table 2). Wood hardening treatment significantly improved the dimensional stability of hybrid poplar wood, especially at the start of soaking. The average volumetric swelling coefficient of the controls increased dramatically in the first 48 hours, with the coefficient remaining nearly constant thereafter. In contrast, the treated samples took much longer (more than 1 week) to reach a relatively steady swelling coefficient, at around 6.8%, nearly 60% that of the controls. The average coefficient (11.8% after 720 hours) obtained for untreated wood was slightly lower than the average volumetric shrinkage of 12.8% in ten *P.* × *euramerricana* clones reported by Koubaa et al. (1998). The swelling coefficients of the hardened hybrid poplar samples were comparable to or lower than those of silver maple, red oak, and white ash, for which volumetric shrinkage was around 12.0%, 16.1%, and 13.3% (green to oven-dried), respectively (Alden, 1995). Control Clone 915303 showed the lowest coefficient after 720 hours at around 10.8%, more than twice that of treated Clone 915311. Density was significantly determinant for the volume swelling coefficient in controls (Fig. 6a). However, the relationship between the swelling coefficient and the density of the hardened wood was not significant (Fig. 6 b). This suggests that the density of the MMA-hardened wood was not determinant for the volume swelling coefficient. Cross-section SEM images of the treated hybrid poplar wood (Fig. 3) clearly show microcracks between the wood cell walls and PMMA. Water that passes through these microcracks into the wood cell therefore caused swelling. This indicates that impregnation with MMA does not significantly change the hygroscopic properties of wood. This finding is in agreement with other studies (Ellis 1994; Zhang et al. 2006b). Another explanation is that water may pass through and fill small pores that the MMA monomer cannot enter. Thus, the volume changes during the soaking period were likely due to the absorbed bound water, which contribute to wood swelling.

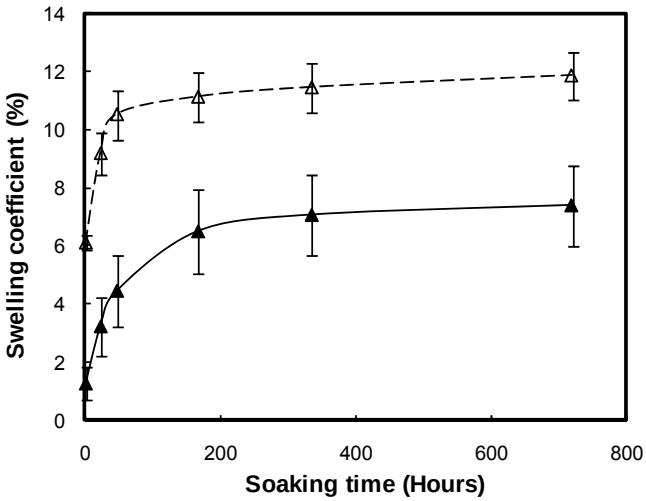

Fig. 5. Average volumetric swelling coefficient (%) for control and treated hybrid poplar clones; △s denote control wood and ▲s denote treated wood

Anti-swelling efficiency (*ASE*) was recorded after 24 and 720 hours' immersion in water (Table 3). Similar to the *WRE*, samples with low volumetric change showed high *ASE*. Clone 915311 showed the best anti-swelling capacity. However, Table 3 clearly shows that *ASE* decreased gradually with soaking time. This suggests that MMA monomer-treated poplar wood has effective water resistance in the short term only. The same explanation as for the swelling properties holds: the ANOVA of the *ASE* confirmed that soaking time was a significant factor (Table 4). In addition, clone type, density difference (Dendif), and interactions between Dendif and clone and Dendif and time had significant effects on *ASE*.

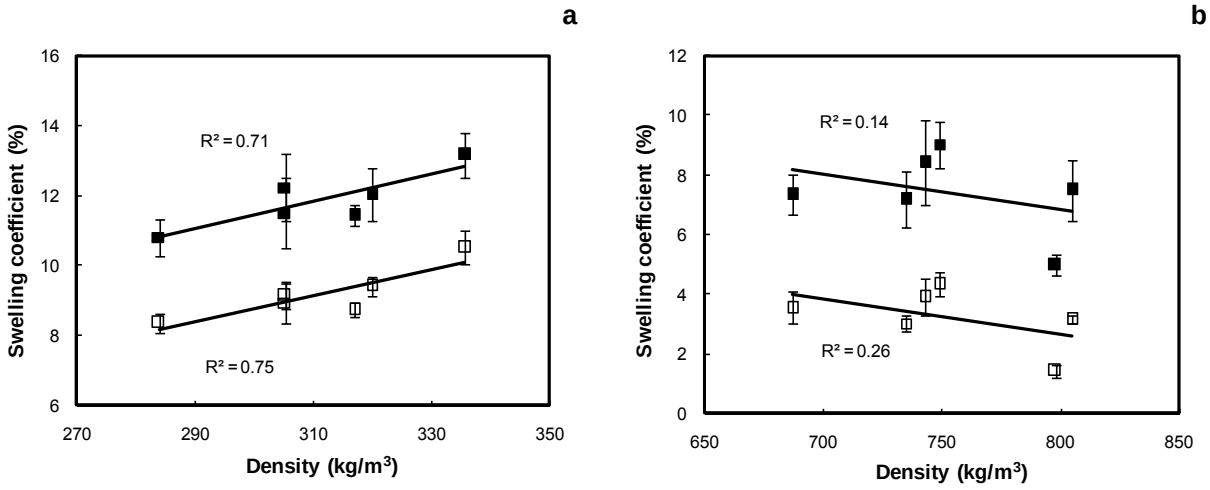

Fig. 6. Relationship between swelling properties and density: a) Control wood and b) Treated wood; □s denote 24 hours and ■s denote 720 hours

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Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Interaction between wood and MMA was confirmed by FTIR spectrum analysis of the untreated hybrid poplar wood, hardened wood, and PMMA, as shown in Fig. 7. The FTIR spectra for untreated samples show intensity bands in the regions 3400 cm^{-1}, 1735 cm^{-1}, 2905 cm^{-1}, 1510 and 1605 cm^{-1}, and 1158 cm^{-1} due to O–H stretching vibration, C═O stretching vibration, C–H stretching vibration, C═C stretching vibration, and C–O–C stretching vibration, respectively (Li et al. 2011b). These absorbance bands are due to hydroxyl groups in the cellulose, a carbonyl group of acetyl ester in the hemicellulose, and carbonyl aldehyde and aromatic compounds in the lignin. The

absorbance bands of PMMA at 3440 cm^{-1}, 2978 and 2878 cm^{-1}, 1731 cm^{-1}, and 1000–1260 cm^{-1} can be associated with –OH stretching of the lattice water, asymmetrical and symmetrical C–H stretching of CH_3, C=O stretching, and C–O stretching, respectively (Yang and Dan, 2003). The FTIR spectra of treated hybrid poplar show almost the same functional peaks as the untreated wood, but with much lower absorbance. This is probably attributable to the lower concentration of wood fibers in the reference matrix (KBr). However, the presence of an absorbance peak at around 1730 cm^{-1} may result from the formation of C=O bonds between the wood fibers and the MMA monomer (Hu et al. 2007; Xu et al. 2010). However, wood lignin also contains C=O bonds. The shift of the –OH peak from 3425 cm^{-1} in solid wood to 3445 cm^{-1} in hardened wood was possibly due to the reaction between the –OH of the fiber cell wall and MMA (Hu et al. 2007; Li et al. 2011d). Change in intensity of the C–H stretching of CH_3 was also reported due to the reaction between the –OH of the wood fiber at the surface and MMA (Hu et al. 2007). From the combined results of the FTIR spectra, the dimensional stability analysis, and the SEM micrographs, it can be concluded that there should be little or no interaction between the MMA monomer and the hydroxyl groups of the cellulose fibers.

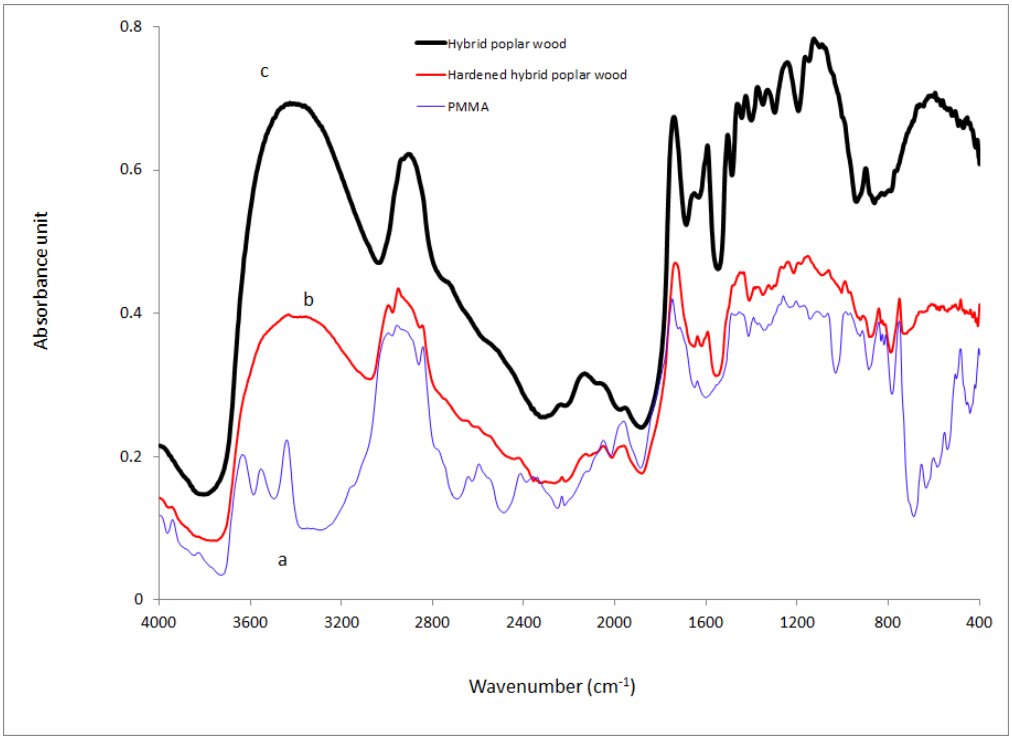

Fig. 7. FTIR spectra of a) PMMA; b) treated hybrid poplar wood; and c) untreated hybrid poplar wood (control)

Practical Implications

Hardening of hybrid poplar wood through MMA impregnation greatly improved its density, surface properties (Koubaa et al. 2012), and dimensional stability. The improvement in dimensional stability and surface properties of the hardened wood is an important indication of its suitability for end-uses where the untreated wood is not suitable. The potential applications include interior and exterior uses such as kitchen and

bathroom floorings and cabinets, deck flooring, etc. However, some issues could be raised such as the biodegradation, recycling, and environmental impacts of such products. For the biodegradation of hardened wood, He et al. (2011) reported important improvement in termite and fungus resistance of styrene and glycidyl methacrylate treated wood. According to these authors, the mass loss of hybrid poplar wood decreased from 25% when untreated to less than 5% when treated. The mass loss from fungus decay decreased from 30% for untreated wood to 14% 8% with styrene and glycidyl methacrylate, respectively, for treated wood. Similar results were reported in few other studies, for the biodegradation of hardened wood with several polymers including PMMA (Yildiz et al. 2005; Li et al. 2010). Despite its improvement in the biodegradation resistance, hardened hybrid poplar wood is still biodegradable in the compost environment, since microorganisms can consume the natural cellulose component (Bhat and Kumar 2006; Thakore et al. 2001) and the newly generated chemicals from hyrdrolysis and microbial attack will contribute to the scission of polymer chain into low-molecular-weight chains (Bhat and Kumar 2006; Seidenstücker and Fritz 1998).

There is no published information on recycling and environmental impacts of such products. Future research should address these issues to document any hazard or risk for humans and for the environment. However, it is believed that the polymerised methyl methacrylate (PMMA) is a safe product, and its use in wood composites should not present any risk. It has been used in several other applications including dentistry (Frazier et al. 2005; Guedes et al. 2006) and orthopaedics (McCaskie et al. 1998; Jaeblon 2010).

CONCLUSIONS

1. After low-density fast-growing hybrid poplar wood was hardened by impregnation with methyl methacrylate (MMA) monomer and cured with a thermal catalyst, the wood density, swelling properties, water repellent efficiency, and anti-swelling efficiency were significantly improved and water uptake was reduced.
2. This improvement was clone-dependent, and of the studied clones, Clone 915311 presented the best dimensional stability.
3. Although dimensional stability was remarkably improved, SEM and FTIR results suggested that PMMA is contained mainly in the void spaces of the wood, and there is little interaction between wood fiber and MMA.
4. Hardening treatment offers the potential for using hybrid poplar in value-added products, providing a good alternative to natural hardwood.

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