Surface Properties of Methyl Methacrylate Hardened Hybrid Poplar Wood

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ABSTRACT: The surface properties of fast-growing poplar clones and their methyl methacrylate (MMA)-hardened wood related to potential end uses were investigated. Samples from 24 trees of six hybrid poplar clones in one plantation in Quebec were hardened with MMA. The effects of MMA hardening on the density and surface properties were studied. Scanning electron microscopy and Fourier transform infrared analysis showed that filling the voids in the wood structure was the main hardening mechanism. The incorporation of the polymer increased the density of all of the poplar clones by 120–160%. The Janka hardness was found to be 2.5–4 times higher in the treated poplar wood than in the untreated poplar wood. The treated wood also exhibited superior abrasion resistance compared to the controls. The results indicate that hardening with MMA improved the surface properties and that the MMA-hardened wood was comparable to natural hardwoods. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1428–1436, 2012

Key words: composites; density; hardness; surfaces; surface modification

INTRODUCTION

Hybrid poplar has been planted throughout North America because of its fast growth rate and easy hybridization.[1] The fast growth of hybrid poplar is associated with a low specific gravity and high moisture content. The average specific gravity of hybrid polar in North America ranges from 0.30 to 0.39.[2] Standing poplar trees have a high moisture content, typically around 100%, with only minor differences between sapwood and heartwood.[2] Poplar wood is bright and light in color, with a straight grain and uniform texture.[3] Its low extractive content makes it liable to discoloration and decay.[2] Because of these intrinsic properties, hybrid poplar wood is not well suited for products requiring a high strength or surface hardness or for load-bearing applications. Currently, poplar wood is primarily used for pulp and paper production and engineered wood products, such as oriented strand board, laminated veneer lumber, and structural composite lumber.[2]

To generate high values from hybrid poplar wood, properties such as density, dimensional stability, hardness, and durability need to be improved. Of the available technologies, wood hardening through chemical impregnation by various polymers significantly improves the surface properties and dimensional stability of the wood. The most commonly used monomer for wood impregnation is methyl methacrylate (MMA), a low-viscosity, relatively cheap, and readily available monomer. Many other polymers and resins have been used for wood hardening, including acrylate-based polymers and melamine-based resins.[4–6]

Acrylic-based polymers and MMA treatment generally enhance the physical and mechanical properties of wood, especially for low-density woods such as poplar.[6–15] The MMA treatment of yellow poplar (*Loriodendron tulipifera* L.) reduced moisture adsorption and swelling rates by 60–90%.[14] Poplar (*Populus x. euramerican*) after MMA treatment showed a higher compression strength and static bending strength and better decay resistance than untreated wood.[15] The tangential and radial hardness values of MMA-treated aspen (*Populus sp.*) were approximately four times higher than those of solid wood.[13]

Wood hardening offers the possibility of tailoring wood product properties to meet end-use requirements, especially wood flooring. For such applications, the surface properties, including hardness and abrasion resistance, are of prime importance.

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TABLE I
General Information on the Investigated Hybrid Poplar Clones

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

Previous studies have focused on the impact of the hardening process on the wood density, hardness, and dimensional stability. However, poly(methyl methacrylate) (PMMA) hardening renders the wood more brittle.[16] It has been reported that the inherent brittleness of hardened wood can be overcome by the combination of isocyanate and monomers because the isocyanate compound crosslinks the copolymer.[16] Other additives have been used to improve the mechanical performance of hardened wood, including clay and metallic-based nanoparticles.[5,6,17]

Information on other properties, including abrasion resistance, is lacking for not only hardened wood but for wood in general. This property determines the suitability of the wood for various high-value applications, such as flooring, furniture table tops, and other uses, where the wood is subject to traffic and mechanical friction and abrasion.

In a few studies, researchers have investigated the wood properties of hybrid poplar woods[18–22] and their suitability for different end uses.[22] Only a few publications have addressed the suitability of hybrid poplar woods for chemical impregnation.[14] Thus, the objectives of this study were (1) to understand the interaction between the hybrid poplar wood structure and the MMA monomer, (2) to evaluate the effect of MMA hardening on the density and surface properties of hybrid poplar wood, (3) to study the interclonal variations in the density and surface properties of hardened and nonhardened wood, and (4) to investigate the potential of impregnated hybrid polar wood for high-value products.

EXPERIMENTAL

Materials and methods

A total of 24 hybrid poplar trees were chosen randomly from a 6-year-old experimental plantation near Montreal, Quebec, Canada (Table I). From each tree, a log was taken at between 0.5 m and breast height, and samples were extracted to measure the physical and mechanical properties. From each log, four standard specimens were prepared for each investigated property, according to standard test methods, to evaluate the wood density, hardness, and abrasion resistance. Each specimen was labeled with a specific code to identify the source clone and tree. The four specimens from each tree for each test were divided into two equally sized groups: a control group and a treated group. The controls were kept in an air-conditioned room at 21°C and 40% relative humidity for 60 days to reach a moisture content of 9% before testing. The treated group was designated for the hardening treatment. Northern white cedar (*Thuja occidentalis*), white ash (*Fraxinus americana*), red oak (*Quercus alba*), quacking aspen (*Populus tremiloides* Michx), and silver maple (*Acer saccharinum*) were also impregnated with MMA to establish relationships between the polymer retention (PR), species density, and hardness.[18]

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 % Vazo 52 [2,2′-azobis-2,4-dimethylvaleronitrile, $(CH_3)_2CHCH_2(CH_3)(CN)CN{=}NC(CN)(CH_3)CH_2CH(CH_3)_2$], a low-temperature polymerization initiator from DuPont Canada, Inc. (Mississauga, Ontario, Canada). The 0.5 wt % Vazo 52 was based on the weight of the monomer. The monomer solution was prepared immediately before the impregnation process to prevent self-assembly into PMMA polymer.

The wood specimens of hybrid poplar clones and reference species were conditioned at room temperature (21°C) and 45% relative humidity for 1 week before impregnation 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. The initial dimensions of the samples for density testing were determined in all three principle directions to the nearest 0.01 mm. The specimens were placed in an impregnation autoclave. A vacuum of approximate 75 mmHg was applied for 20 min. 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 min to ensure maximum impregnation. After pressure release, impregnated samples were removed from the autoclave, and excess

monomer was wiped from the surface. Specimens were weighed and placed in the reactor for polymerization at 690 kPa (100 psi) nitrogen pressure and cured for 4 h at 158°F (70°C). After curing, the reactor was depressurized, and samples were removed and placed in a ventilated area to evaporate the nonpolymerized monomer. Excess polymer was removed from the surface of some samples. Composite weights were measured again to the nearest 0.01 g, and the dimension of the samples for density testing were to the nearest 0.01 mm. PR in the composites was calculated with the following equation:

$$\mathrm{PR}\ (\%) = (w_{\mathrm{HW}} - w_s)/w_s \times 100 \qquad (1)$$

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

Density profiles of the hardened and nonhardened wood samples were measured with an X-ray densitometer on samples 2.5 cm in width. Scanning electron microscopy (SEM) micrographs of diamond polished hardened and nonhardened wood samples were taken on platinum coated transverse sections perpendicular to the grain direction. The SEM measurements of the hybrid poplar wood were done with a Hitachi S-3500N (Tokyo, Japan) microscope. Surface images were scanned by secondary electrons (20KeV, 100 μA, Working Distance (WD) = 6 mm) operating at high vacuum.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on both the hardened and nonhardened wood samples to (1) provide detailed information on the functional groups present on the surface of PMMA and the hardened and nonhardened wood samples and (2) examine the possibility of bond formation between the MMA functional groups and wood functional groups. DRIFTS was conducted on a Tensor 27 Fourier transform infrared (FTIR) system (Bruker Optics, Ettlingen, Germany) equipped with a deuterated triglycine sulfate detector. For each sample, spectra were recorded by the collection of 164 scans in the range 4000–400 cm^{-1} at 4-cm^{-1} resolution. Pure powdered potassium bromide (KBr) was used as a reference substance. Samples for DRIFTS 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 agathe 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.

Samples with nominal dimensions of 100 × 20 × 20 mm^3 (Longitudinal × Radial × Tangential directions) were used to determine the oven-dried density (ρ_o). The samples were oven-dried for more than 24 h at 103 ± 2°C to achieve a constant weight. The sample dimensions were then determined in all three principle directions to the nearest 0.01 mm, and the weight was recorded to the nearest 0.01 g. ρ_o was calculated with the following equations:

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

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

Hardness tests were performed on a wide surface measuring 75 × 150 mm^2 (Tangential × Longitudinal directions) according to ASTM D 143–94 and with a Zwick/Roell Z020 universal testing machine (Ulm, Germany). Five penetrations were made into each specimen, with penetration points set 30 mm apart to prevent interference between the penetrations points. The specimen hardness was recorded as the average of the five hardness values measured.

The abrasion resistance was determined with a CS-17 Taber Abrader (North Tonawanda, New York, USA) according to ASTM D 4060 and was expressed as wear index, which is the weight loss in milligrams per specified number of cycles under a specified load (1000 g). The sample dimensions were 100 × 100 × 10 mm^3 (Length × Width × Thickness), and the weight losses after 500, 1000, 1500, 2000, and 2500 cycles were recorded. The weight was measured with a digital scale to 0.0001 g of precision. Both the control and MMA-treated composites were tested without further finishing processes.

Statistical data analyses were performed with Statistical Analysis System (SAS) software.[23] Analysis of variance was performed with the general linear model (GLM) and the (Least Squares Means (LSMEANS)/P-values for differences (PDIFF)) test on the combined data (control and treated) to determine the differences between the mean values for the treated sample in the hybrid crosses. The residual normal distribution for each trait was verified by both Shapiro–Wilks's *W* test and a normal probability plot with 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 the homogeneity of variances for the density and hardness variables.

RESULTS AND DISCUSSION

Hardening mechanism and microstructure of the wood–polymer composites

We formed the hardened wood impregnating the wood with MMA monomer and curing the monomer via a catalyst and a heating procedure. The

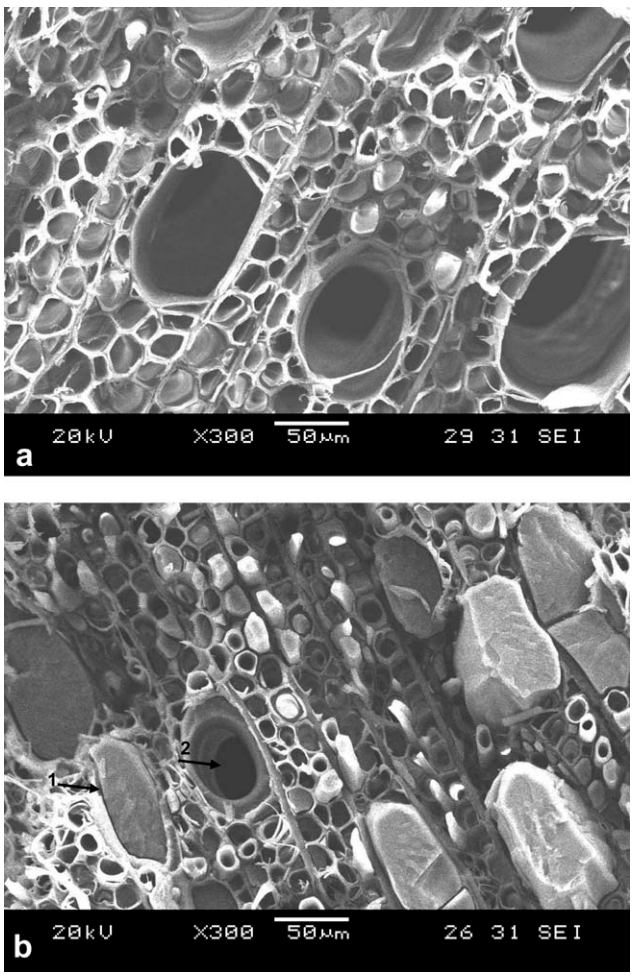

Figure 1 SEM of (a) untreated hybrid poplar wood and (b) PMMA-hardened hybrid poplar wood. Arrows indicate 1) absence of attachement of PMMA to wood tissue, and 2) unfilled cells.

reactions of MMA polymerization during the hardening process are given as follows:[4,10]

1. One molecule of Vazo 52 generated two molecules of free radicals and nitrogen gas:

$$\text{Vazo } 52 \xrightarrow{\text{Heat}} 2\text{R} \bullet + \text{N}_2$$

2. The free radicals reacted with the MMA monomer:

$$\text{R} \bullet + \text{CH}_2 = \text{CR}_1\text{R}_2 \xrightarrow{\text{Heat}} \text{RCH}_2(\text{R}_1\text{R}_2)\text{C} \bullet$$

3. The short chemical chains propagated to long-chain PMMA:

$$\text{RCH}_2(\text{R}_1\text{R}_2)\text{C} \bullet + (n-1)\text{CH}_2 = \text{CR}_1\text{R}_2 \rightarrow \text{R} - [\text{CH}_2 - \text{C}(\text{R}_1\text{R}_2)]_n - \text{PMMA} \quad (\text{n} = 2, 3, 4, \ldots)$$

where R is $C(CN)(CH_3)CH_2CH(CH_3)$, R_1 is CH_3, and R_2 is $COOCH_3$.

Little interaction was found between the nonpolar MMA monomer and the functional groups on the wood surface.[4,9,10] Previous findings have suggested that the hardening process is accomplished by the filling of the void structures, such as the vessels and lumen, in the wood,.[4–7,9] SEM images of the treated hybrid poplar wood (Fig. 1) also showed that PMMA filled the vessels, lumen, and other void spaces in the wood structure. However, the SEM images clearly showed, in some vessels and other wood tissues, cracks between the wood cell walls and PMMA. The presence of such voids supported the theory that a low degree of interaction occurred between the functional groups of the MMA monomer and the wood surface.

The results of the FTIR analysis of the hardened and nonhardened hybrid poplar are presented in Figure 2. The spectra of the untreated wood particles showed the presence of a typical band observed in wood.[24–26] A broad stretching band for intermolecular bonded hydroxyl groups (OH) was observed at 3400 cm^{-1}.[19–21] The methylene/methyl bands appeared at 2905 cm^{-1}. A broad, medium intensity ester carbonyl vibration appearing at 1735 cm^{-1} was presumed to emanate from the carbonyl (C=O) stretching of acetyl groups in hemicelluloses and carbonyl aldehyde in lignin and extractives.[24,26,27] The bands around 1605 and 1510 cm^{-1} were associated with the aromatic C=C skeletal vibrations associated with the lignin.[26,28,29] The medium intensity bands around 1457, 1424, and 1373 cm^{-1} were associated with methylene deformation and methyl asymmetric and methyl symmetrical vibrations.[24–26] The bands appearing at 1271 cm^{-1} were due to either a carbon single-bonded oxygen stretching vibration or an interaction vibration

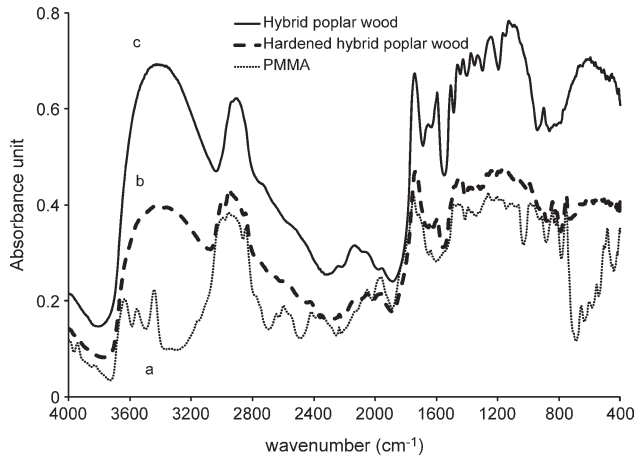

Figure 2 FTIR spectra of (a) PMMA, (b) PMMA-treated hybrid poplar wood and (c) untreated hybrid poplar wood.

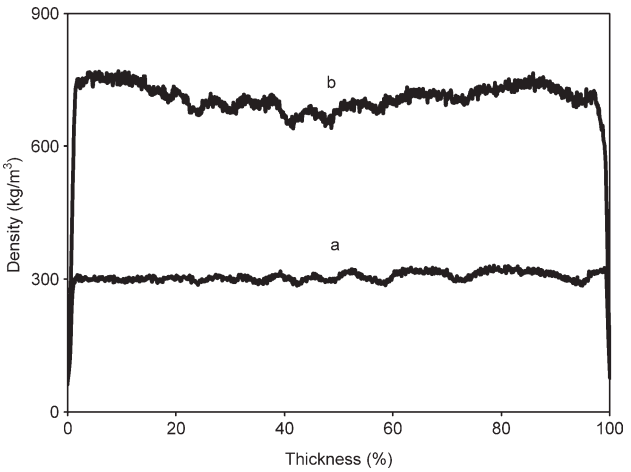

Figure 3 Density profile of (a) hybrid poplar wood and (b) hardened hybrid poplar wood.

between carbon single-bonded oxygen stretching and in-plane carbon single-bonded hydroxyl bending in carboxylic acids.[30] The band at 1158 cm^{-1} may have arisen from the asymmetric stretching of C—O—C in the cellulose and hemicelluloses[26,31] or from saturated fatty acid ester carbon single-bonded oxygen stretching in association with the ester carbonyl.[26,31] Strong-intensity bands at 1059 and 1036 cm^{-1} were essentially in the positions corresponding to those observed in the IR spectra of single cotton fibers.[32] The vibrations appearing further down the field at 896 and 810 cm^{-1} may have arisen from disubstituted ring stretching and out-of-plane carbon single-bonded hydrogen.[26,30]

The FTIR spectrum of PMMA in the frequency range 4000–400 cm^{-1} (Fig. 2) showed two distinct bands at 2978.4 and 2877.8 cm^{-1}. The first band arose from the asymmetrical stretching mode in which two C—H bonds of the methyl group were extended.[33–35] The second band arose from symmetrical stretching (CH_3). At 1731 cm^{-1}, a sharp intense peak appeared; this peak was attributed to the presence of ester carbonyl group stretching vibrations (C=O). A broad peak ranging form 1260–1000 cm^{-1} was attributed to the C—O (ester bond) stretching vibrations. The broad band from 950 to 650 cm^{-1} was due to the bending of C—H.[33–35]

The FTIR spectrum of the treated hybrid poplar showed the same functional peaks observed in the untreated wood spectra but at a much lower absorbance unit. This lower absorbance of wood functional peaks was simply due to the lower concentration of the wood fibers in the reference matrix (KBr). The bands appearing at 2995 and 2845 cm^{-1} were attributed to the asymmetrical (C—H) and symmetrical stretching reported for PMMA. The band at 750 cm^{-1} was attributed to the bending of C—H reported in PMMA.

From the FTIR spectra, there was little evidence of bond formation between the wood and PMMA. The presence of a peak around 1730 cm^{-1} might have suggested the eventual formation of C=O bond between the wood fibers and PMMA. The change in the intensity of the peak near 1730 cm^{-1} was attributed to the possible formation of C=O bonds after the MMA reaction with wood.[31] However, because C=O bonds are also present in wood lignin, it was not evident whether these bonds were the result of a possible chemical reaction. The shift of the wood —OH peak from 3425 cm^{-1} in the untreated wood sample to 3445 cm^{-1} was attributed to the possible bond formation between the —OH on the wood surface and MMA. Previous reports attributed the shift of —OH in treated wood samples to bond formation between the hydroxyl groups and MMA.[17,36]

Density and PR

The hardening treatment had a significant effect on the density (Table II), with density improving from 2.2 to 2.6 times, depending on the clone. The density of the hardened hybrid poplar wood was similar to or higher than that of commercial hardwood species, including silver maple (667 kg/m^3), red oak (665 kg/m^3), and white ash (719 kg/m^3). Figure 3 illustrates an example of the density profile of a hybrid poplar sample before and after hardening. This profile shows that the wood sample was impregnated through its thickness. The density of the hardened sample was much higher than that of the nonhardened wood sample.

The final density of the treated wood varied with PR, which varied among the clones. PR decreased with increasing initial wood density [Fig. 4(a)] in the studied hybrid poplar clones ($R^2 = 0.84$). This tendency was confirmed by the close relationship ($R^2 = 0.97$) between PR and the initial wood density of the six wood species [Fig. 4(b)]. The highest PR rates (159 and 162%) were obtained for eastern white cedar and hybrid poplar wood, respectively. White ash (48%), red oak (39%), and silver maple (44%) showed the lowest PR rates, and the rate for aspen was in the middle, at 113%.[37] This pattern of variation was attributed to the porosity of the wood species.[38] Woods with higher porosities generally had a lower density and a higher PR rate.[38] This result was also in good agreement with those of previous reports, where aspen wood showed a higher PR rate than silver maple[11] and it was by differences in the wood permeability.[39] A linear relationship was also reported between the wood density and PR in sugar maple.[40] However, the reported coefficient of determination ($R^2 = 0.52$) between the initial density and retention rate was lower than that found in this study.

TABLE II
Density (kg/m^3), Janka Hardness (N), Wear Index (%), and PR (%) for the Hybrid Poplar Clones

						Wear index (%)					
		ρ_o (kg/m^3)		Hardness (N)		After 500 cycles		After 2000 cycles		PR (%)	
Treatment	Clone	Mean	CV[b]	Mean	CV	Mean	CV	Mean	CV	Mean	CV
Control	915313M × D	305 E[a]	5.8	1647 F	8.2	0.279 AB	13.9	0.719 A	12.1	—	—
	915508M × D	320 DE	5.5	1738 EF	4.8	0.242 BC	23.3	0.617 AB	16.7	—	—
	3729N × M	336 D	3.4	2007 DE	12	0.243 ABC	27.6	0.609 AB	12.2	—	—
	915303M × D	284 F	5.4	1334 G	18.1	0.301 AB	9.0	0.661 AB	10.1	—	—
	915311M × D	305 E	4.3	1637 F	12.6	0.318 A	11.5	0.696 AB	11.2	—	—
	3531D × N	317 DE	6.2	2178 D	13	0.187 CD	39.4	0.468 C	31.8	—	—
Treated	915313M × D	735 BC	3.1	5118 B	10.9	0.143 D	14.1	0.571 BC	7.2	168 BA	7.8
	915508M × D	743 B	1.6	5290 AB	9.6	0.136 D	9.6	0.558 BC	4.1	145 B	13.2
	3729N × M	749 B	1.6	5072 B	16.1	0.162 D	14.2	0.576 BC	3.2	142 B	5.9
	915303M × D	687 C	2	3776 C	10.3	0.223 BCD	—	0.746 A	—	180 A	13.4
	915311M × D	798 A	4.7	6400 A	14.8	0.124 D	—	0.496 BC	—	175 A	17.6
	3531D × N	805 A	3.6	6033 BA	12.1	0.103 D	—	0.406 C	—	161 BA	12.2

[a] Numbers followed by the same letter within a column are not significantly different at $p > 0.05$ (Least Squares Means (LSMEAN)/P-values for differences (PDIFF)).
[b] CV = coefficient of variation (%). — denotes that value was not available for this clone because of insufficient observations.

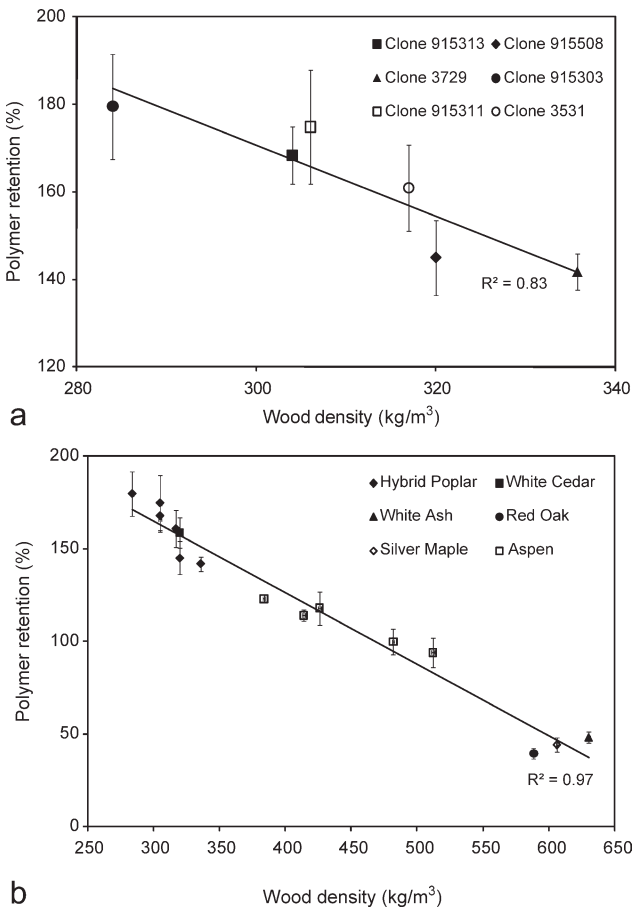

Figure 4 Relationship between the polymer retention (PR) and density in (a) hybrid poplar clones and (b) different wood species.

Hardness

The incorporation of the polymer (PMMA) in the wood resulted in substantial increases in the Janka hardness for all of the tested samples (Table II). Hardening increased the hardness of virgin wood by 1.5 to 2.9 times. Two of the investigated clones fell in the range 6.0–6.4 kN; this was comparable to or even better than that of many commercial species used for flooring,[41] such as silver maple and red oak, and even their oil-finished wood (Table III). The Janka hardness test is most commonly used to determine whether a species is suitable for applications such as flooring, and it is the industry standard for determining the ability to tolerate denting. Therefore, MMA-hardened poplar wood could potentially be used in the wood flooring industry; this would substantially increase the commercial potential of hybrid poplar.

The hardness varied among the studied clones (Table II). The highest value was observed for clone

TABLE III
Comparison of the Janka Hardnesses Between Some Poplar Clones and Commercial Wood Flooring Species[a]

	Hardness (N)		
Species	Solid wood	MMA-treated	Oil-finished
Hybrid poplar clones	1637–2178	3776–6400	—
Aspen	1700–3200	5600–7800	
Silver maple[b]	4500	—	5800
Red oak[b]	6300	>16,000	6700

[a] All hardness measurements were made according to the same ASTM standard method (ASTM D 1037).
[b] Hardness values obtained from Koubaa[41] and Chabot.[37]

TABLE IV
Results of General Linear Model (GLM) Analysis of the Variance of Density, Hardness, and Abrasion for the Hybrid Poplars

Source of variation	Degree of freedom (df)	Density[a]	Hardness[a]	Abrasion (wear index) 500 cycles	Abrasion (wear index) 2000 cycles
Constant	1	1980.3**	3171.5**	443.8**	1031.2**
Clone	5	9.2**	15.6**	3.13*	3.65**
Treatment	1	10.5**	15.0**	41.53**	6.40*
Tree	3	1.66	1.56	0.82	0.92
Clone × Treatment	5	3.0*	3.26*	—[b]	—[b]

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
[a] Logarithmic transformation was applied to the variable.
[b] This interaction was not significant and was not considered in the model for abrasion results.

915311. Clone 3531 was in second place. The treatment, the clone, and their interaction significantly affected the hardness of the studied clones (Table IV). The relationships between the density and hardness were also investigated for several species: northern white cedar, aspen, red oak, white ash, silver maple [Fig. 5(a)], and poplar wood and its MMA-hardened wood [Fig. 5(b)]. The average hardness showed a close relationship with the density for the investigated species ($R^2 = 0.89$) and for the hardened ($R^2 = 0.84$) and unhardened poplar wood ($R^2 = 0.93$). The variation in hardness among species could, therefore, be explained by variations in the wood density. The relationship (not shown) between the PR rate and hardness for the treated hybrid poplar was not significant ($R^2 = 0.10$). In good agreement with previous findings,[11] this result indicates that the clone and the density had greater impacts on the hardness than the impregnation rate. Moreover, a high impregnation rate increased not only the sample density but also the risk of brittle failure and decreased the hardness value. Indeed, the hardening process increased the risks of splitting the sample during the hardness test, although no splits were observed in the control group. As discussed previously, splitting is expected in hardened samples because PMMA hardening renders the samples more brittle.[16]

Abrasion resistance

Abrasion resistance is the ability of a material to maintain its surface appearance and structure when it is subjected to mechanical actions such as rubbing or scratching. The lower the wear index is, the better the abrasive resistance should be. The wear index

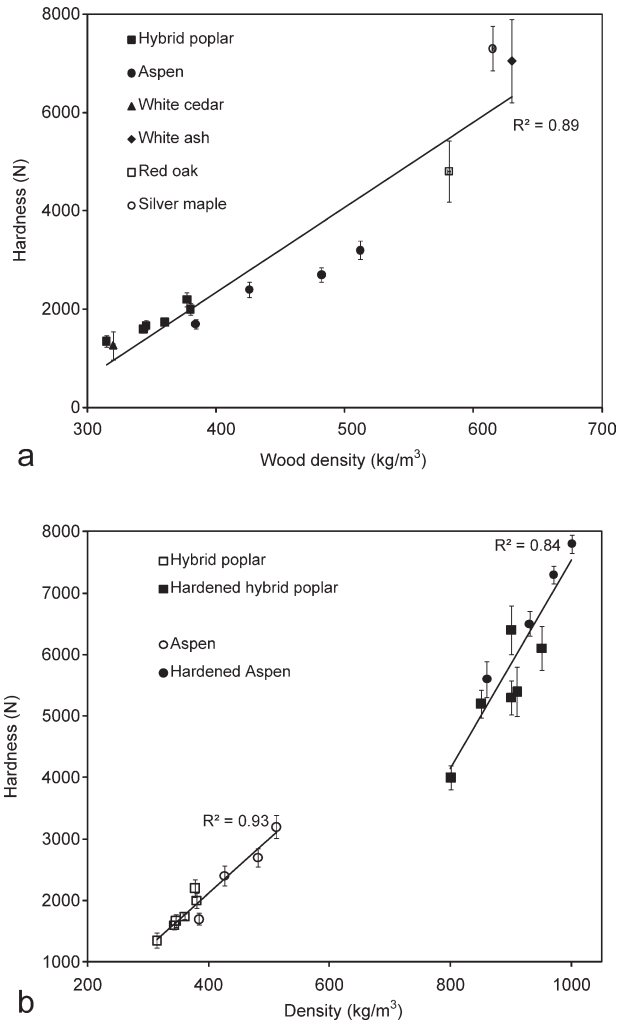

Figure 5 Relationship between the wood density and hardness for (a) different wood species and (b) hardened (filled symbols) and unhardened (open symbols) wood from aspen (*Populus tremuloides* Michx) and hybrid poplar clones. (All hardness and density measurements were made according to the same standard).

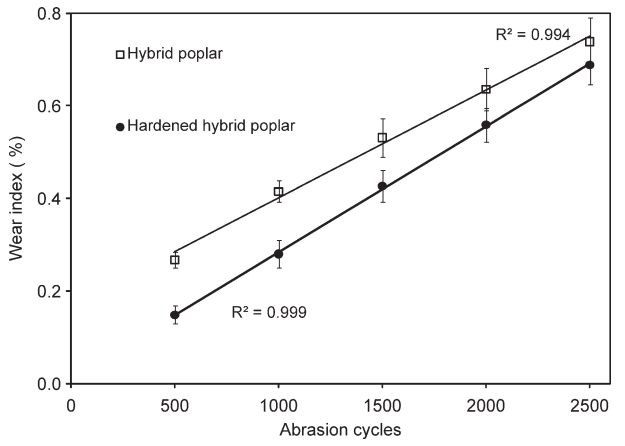

Figure 6 Variation in the abrasion wear index for the hardened and unhardened wood of hybrid poplar.

increased with abrasion cycles, and hardening had a positive effect on the wear index (Fig. 6). Wood hardening substantially reduced the wear index of the samples by nearly 50% after 500 cycles. However, the effect became slightly weaker with increasing abrasion cycles. At 2500 cycles, the effect nearly decreased (Fig. 6). This result could be explained by the higher impregnation rate at the wood surface. Moving toward the core, the impregnation rate decreased slightly (Fig. 3); this explained the decrease in the abrasion resistance with increasing abrasion cycles.

The wear index varied among the clones after 500 and 2000 cycles (Table II). This implied that hybrid poplars should be appropriately selected for desired surface properties. The hardened wood produced from clones 915311 and 3531 showed the lowest wear indices at 0.50 and 0.41 after 2000 cycles, respectively. These wear indices were, nonetheless, high compared to some commercial flooring species, such as silver maple (0.35) and red oak (0.16),[41] despite the high densities of the previous two poplar composites. These relatively high wear indices may have resulted from the surface morphology and roughness, which did not change significantly after the MMA treatment. The densities of the control samples and the hardnesses of the treated wood played important roles in the wear index determination. Koubaa[41] also reported that abrasion resistance was correlated to both the surface hardness and the material density. Rodriguez et al.[42] found that the surface properties were related not only to polymer type but also to the additives that chemically bound to the wood substrate. Thus, the crosslinking surface structure is liable to improve the abrasive resistance, for example, by the addition of silica nanoparticles. Furthermore, surface coating, which is usually applied over a material, offers an alternative method for reducing friction, obtaining better surface properties, and allowing more high-value applications.

CONCLUSIONS

The hardening of hybrid poplar wood through MMA impregnation improved its density and surface properties, as demonstrated by the SEM images and FTIR analysis. The hardening mechanism was due to PMMA filling of the void spaces in the wood structure. The density of the hardened poplar wood was over two times that of the untreated wood, and PR was found to be inversely proportional to the initial wood density. The hardness of the poplar wood was improved by 1.5–2.9 times, and the resistance ability to abrasion also increased. Compared to commercially available flooring species, some of the MMA-hardened hybrid poplar clones wood appeared to be good possible alternatives to natural hardwoods.

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