

EFFECTS OF NANOFILLERS ON WATER RESISTANCE AND DIMENSIONAL STABILITY OF SOLID WOOD MODIFIED BY MELAMINE-UREA-FORMALDEHYDE RESIN

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ABSTRACT

The water absorption and dimensional stability of wood impregnated with melamine-urea-formaldehyde (MUF) and wood impregnated with different nanofiller/MUF formulations were investigated. Three kinds of nanoparticles, Cloisite® 30B, Claytone® APA, and Cloisite® Na⁺, were selected and mixed with MUF resin, and subsequently impregnated into solid aspen wood through a vacuum and pressure process. The wood polymer nanocomposites were prepared by in situ condensation polymerization of the impregnated wood under specific conditions. Significant improvements in water repellency and better dimensional stabilities were obtained for the nanofiller/MUF-treated wood. The untreated wood absorbed around 63% of moisture after 24 h soaking in water, while water uptake was about 125% after 1 week immersion in water. The MUF resin-impregnated wood absorbed about 8.3% and 38.5% of moisture after 24 h and 1 week immersion in water, respectively. For the organophilic nanoclay/MUF resin-impregnated wood, much lower water absorption in the amounts of around 5% water uptake in 24 h and 22% after 1 week was observed. The antiswelling efficiency (ASE) was also improved from 63.3% to 125.6% for the nanofiller/MUF-treated wood. The significant improvement in water resistance and dimensional stability of the resulting wood polymer nanocomposites can be attributed to the introduction of MUF and nanofillers into the wood. X-ray fluorescence shows that some nanoparticles have migrated into the wood cell wall. Wood treatments with MUF and nanofiller/MUF showed no significant influence on the color of the wood, which is important for practical application of the treated wood in some specific areas such as flooring.

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INTRODUCTION

Wood is a three-dimensional polymeric material, made up mainly of cellulose, hemicellulose, and lignin. These constituents are responsible for most of the physical and chemical properties of wood. Because of its strong physical strength, aesthetically pleasant characteristics, and low processing cost, wood is an important building and industrial raw material. But wood has some drawbacks such as high moisture uptake, biodegradation, and dimensional change with environmental variations (Kumar 1994; Galperin et al. 1995), which limit its use. These defects have primarily been ascribed to the presence of numerous hydroxyl groups in the three major wood components (cellulose, hemicellulose, and lignin) and its various cavities. The hydroxyl groups attract water molecules through hydrogen bonding from the surrounding environment, causing swelling, and the cell cavities and lumens are major paths for moisture movement. This process being reversible, wood shrinks as it loses moisture upon drying.

The dimensional changes of wood due to atmospheric moisture can be minimized by appropriate chemical treatments such as the formation of wood polymer composites (WPC), which is a promising way to improve wood properties (Schneider et al. 1991; Hartley and Schneider 1993; Rowell 1983). Attempts to reinforce solid wood with polymers have been extensive in the past decades. Both thermoplastic and thermosetting systems have been used and have achieved certain improvements in wood properties, but both showed limitations (Kumar 1994; Deka and Saikia 2000; Schneider 2001; Ayer et al. 2003). Thermoplastic-related monomers such as acrylates or methacrylates, for instance, do not improve the dimensional stability because these monomers do not penetrate the cell wall or do not react with the wood. Many polymers, even though formed in situ, only filled the empty lumens in the wood, which leads to a mixture of two materials rather than a real composite. Ac-

cordingly, the resulting products were still subject to dimensional changes with water uptake.

Nanocomposite technology with organophilic layered silicates as in situ nano-reinforcement offers new opportunities for the modification of polymeric material properties and has been intensively investigated in recent years (Schadler 2003). Polymer/layered silicate nanocomposites were first developed based on the thermoplastic polyamide 6 (Kojima et al. 1993). Since then, a great deal of research has been carried out in the field of polymer nanocomposites using various thermoplastic and thermoset polymers over the past decade (Schadler 2003; Ray and Okamoto 2003). Essential improvements of physical and mechanical properties including tensile modulus and strength, flexural modulus and strength, thermal stability, flame resistance, and barrier resistance have been observed for various polymer nanocomposites of low silicate content (Byun et al. 2001; Qutubouddin and Fu 2002; Schadler 2003). Barrier properties, fire resistance, and mechanical properties are of great importance for the successful application of selected wood products. Nanotechnological preparation of WPCs could be a promising new approach to obtain better products. Little work, however, has been devoted to the preparation of a wood polymer composite using nanotechnology. This led us to investigate the feasibility of preparing a wood polymer nanocomposite through impregnation of nanoparticles into the wood. In our previous work (Cai et al. 2007), we reported on a procedure to prepare wood polymer nanocomposites from solid aspen wood with impregnation of a MUF resin and different layered aluminosilicate nanofillers. Significant improvements in various physical and mechanical properties of the resulting nanocomposites such as surface hardness and modulus of elasticity were found. In this paper, we investigate the location of MUF resin and nanofillers in the wood and the effects of nanofillers on water ab-

sorption, dimensional stability, and color of the resulting wood polymer nanocomposites.

EXPERIMENTAL

Materials and sample preparation

Trembling aspen (*Populus tremuloides*, an abundant, low density, and fast-growing wood) logs, used in this work were provided by a local forest farmer at Ste-Foy (Québec, Canada). The green log was cut into lumber and low temperature kiln-dried for 2 weeks. Wood samples were chosen from defect-free boards. End-matched samples with dimensions in longitudinal, tangential, and radial of $7.5 \times 5 \times 1.25$ cm were prepared. The urea, formaldehyde, and melamine used for MUF resin cooking were industrial samples. Low viscosity MUF resins, with a solid MUF content of around 50%, were used as prepolymers to impregnate into the wood samples and were prepared as described in the literature (Cai et al. 2006; Kim 2001). The layered aluminosilicate nanofillers (NF), specifically Cloisite® 30B (NF1, organophilic, density, 1.98 g/cm^3), Claytone® APA (NF2, organophilic, density, 1.70 g/cm^3), and Cloisite® Na⁺ (NF3, a pristine nanoclay, hydrophilic, density, 2.86 g/cm^3) were obtained from Southern Clay Products, Inc. (USA), and were used as received. The average particle size of the clay powder received is $8 \text{ }\mu\text{m}$, and each nanoparticle contains at least 3,000 platelets. The impregnation solutions were prepared by adding 1% (wt/wt) nanoclay into the low viscosity MUF resin at a mixing speed of 3050 rpm for 20 min to form suspensions that were subsequently used to impregnate the solid aspen wood samples under specific conditions. A minimum of 20 specimens was used for the impregnation of each combination. The wood polymer composites and nanocomposites were prepared with the procedure described in our previous work (Cai et al. 2007). In short, a low viscosity MUF solution containing 1% nanoparticules, these being of mean 100 nm in length and 10 nm in thickness, was impregnated in the wood and cured in situ at 140°C for 20 min in a compression mold press.

Moisture absorption

The controls and treated wood samples were oven-dried at 103°C for 24 h. They were then placed in a conditioning chamber at a temperature of 21°C and a relative humidity of 65% for approximately 6 weeks. After stabilization, the weight of each sample was measured. The moisture content (MC) at equilibrium (Eq.) was calculated as follows:

$$\text{MC}(\%) = (M_2 - M_1) / M_1 \times 100 \quad (1)$$

where M_2 is the mass of the aspen block at moisture adsorption equilibrium, and M_1 is the oven-dried mass of the control or treated aspen block sample.

Water absorption and dimensional stability measurements

Water absorption and dimensional stability for both the treated wood specimens and the control samples were measured according to ASTM-1037 (1999). All the samples were conditioned as described above. The mass gain and dimensional changes of each sample were measured and recorded (denoted as the dry data). After that, the conditioned specimens were immersed in distilled water at a temperature of $20 \pm 1^\circ\text{C}$ for either 24 h or 1 week, when the specified samples were taken out. The excess water on the soaked samples was wiped off, and the weight and dimensional changes of the wood were recorded (the wet data). The dimensional swelling and water absorption of the samples were calculated using the dry and the wet data obtained. The swelling coefficient and anti-swelling efficiencies in the longitudinal, radial, and tangential directions were also calculated using data obtained for the wood polymer nanocomposites and corresponding data for the control samples. For each combination, there were at least 20 values for the swelling coefficient and anti-swelling efficiency at each direction (longitudinal, radial, or tangential), which allows analyzing the results obtained statistically by SAS.

The water repellency efficiency was calculated by Eq. (2):

$$WRE(\%) = (W_c - W_t)/W_c \times 100 \quad (2)$$

where W_c is the water absorption of a wood control sample and W_t is the water absorption of a treated sample, which was calculated by Eq. (3):

$$W(wt\%) = (w_i - w_0)/w_0 \times 100 \quad (3)$$

where w_0 is the initial weight of an oven-dried sample, and w_i is the weight after water immersion for 1 day and 7 days at 21°C, respectively.

Anti-swelling-efficiency measurements

The anti-swelling efficiency (ASE) was determined after test samples being soaked in water at 21°C at a water flow rate of 20 ml/s for 7 days. The volumetric swelling coefficients were calculated according to the formula:

$$S(\%) = (V_2 - V_1)/V_1 \times 100 \quad (4)$$

where V_2 is the volume of the water-saturated wood and V_1 is the sample volume of the dry untreated or treated wood.

The percentage of swelling was calculated for the wet and oven-dried volumes of the treated and untreated blocks according to:

$$ASE(\%) = (S_c - S_t)/S_t \times 100 \quad (5)$$

where S_c is the volumetric swelling coefficient of the control samples and S_t is the volumetric swelling coefficient of the treated samples.

Scanning electron microscopy (SEM) measurement

The morphologies of the treated and untreated wood samples in transverse surface were observed and analyzed using a Jeol JSM-840A scanning electron microscope (SEM). The pure wood, MUF- and nanofiller/MUF-treated wood blocks were prepared with a razor blade mounted onto a microtome by carefully cutting one of the end-grain surfaces to a depth of about 3 mm. All blocks were desiccated with phosphorus pentoxide for 2 weeks. A gold/palladium al-

loy was sputtered on the cutting surfaces prior to the investigation.

Electron probe micro-analysis (EPMA)

Electron microprobe technique is one of the most precise and accurate methods for surface elemental analysis. The distribution of nanofillers in the wood for the nanofiller/MUF-treated wood samples was further investigated using an Electron Microprobe Analyzer (CAMECA S×100, France). The samples used for the EPMA analysis were prepared using a way similar to the SEM samples before coating. The cross-section of the wood samples was coated with carbon (25 nm) prior to the measurements in order to make it conductive and to protect the surface from beam damage to some extent. Electron microprobe analysis was performed in a mapping mode with an accelerating voltage of 15 kV and 10 nA. The images of elements Al and Si, which are mainly from aluminosilicate nanofillers for the nanofiller/MUF-impregnated wood, were captured digitally to allow for enhanced analysis of the samples.

Color measurement

The colors of the control, MUF- and nanoclay/MUF-treated wood samples were measured using a Color-guide BYK-Gardner GmbH equipment (Germany), according to the procedure of the Color-guide 45°/0°, Kat. Nr./Cat. No.6805. The color change of each sample was calculated by Eq. (6):

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (6)$$

where L^* is the lightness, $a^* = + \text{red} / - \text{green}$, $b^* = + \text{yellow} / - \text{blue}$, $\Delta = \text{sample} - \text{standard}$. ΔE^* defines the total color difference between sample and standard.

RESULTS AND DISCUSSION

Microscopy investigations

Figure 1 shows micrographs of the untreated wood (Fig. 1(a)) and treated wood samples (Fig.

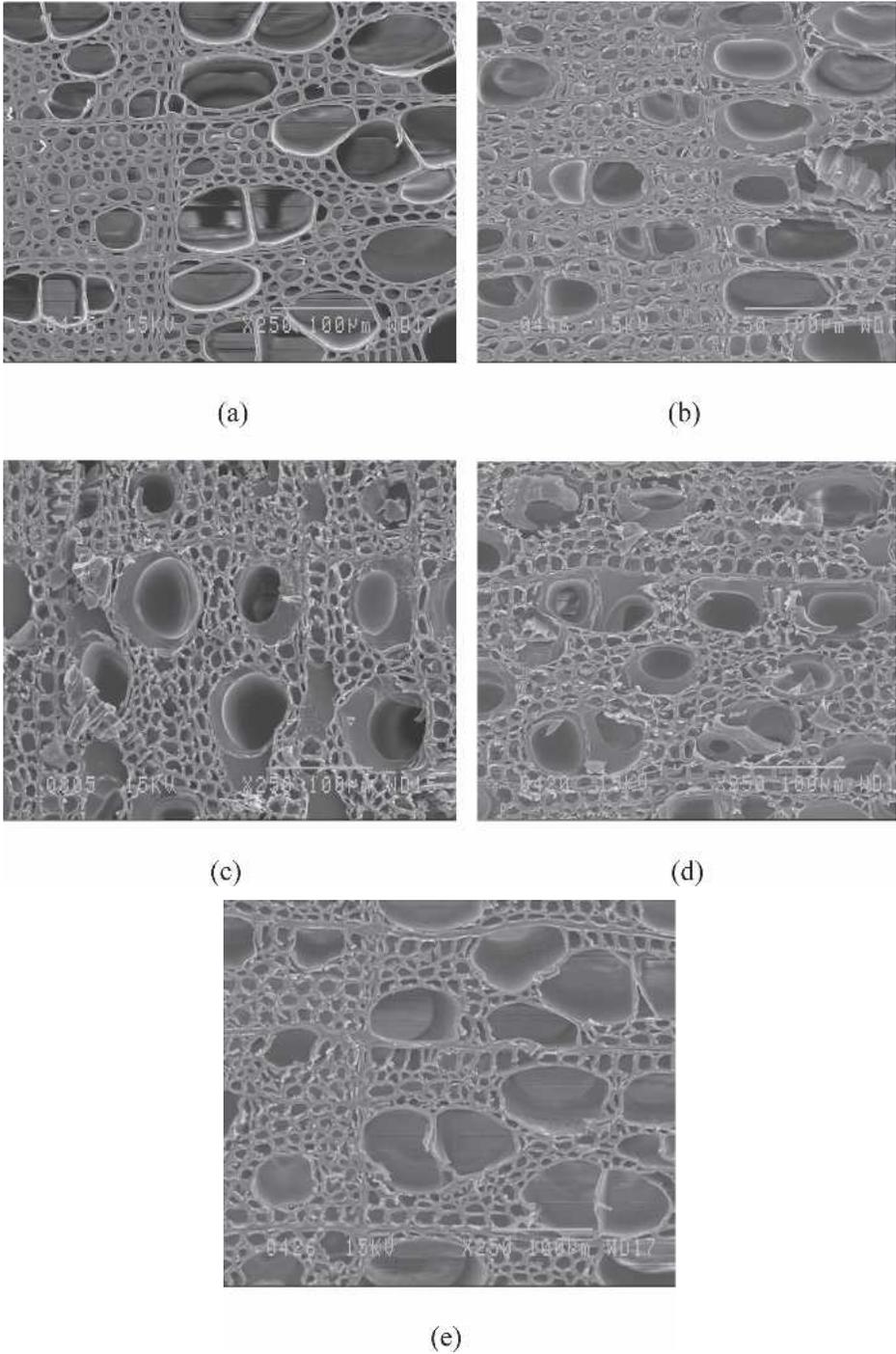


FIG. 1. Scanning electron microscopy photographs of (a) control pure wood, (b) MUF-treated wood sample, containing 42.1% polymer, (c) NF1/MUF-treated wood sample, NF1/MUF content 40.9%, (d) NF2/MUF-treated wood sample, containing 40.6% NF2/MUF, and (e) NF3/MUF-treated wood sample, containing 35.6% NF3/MUF.

1(b), (c), (d), and (e)) in a typical transversal section. It is clear that good penetration and adhesion of the MUF resin to the cell wall were observed for the treated wood. For the NF3/MUF-treated wood, relatively lower polymer loading (nanofiller/polymer content, 35.6% by weight) was obtained, and the impregnated materials seem to be located mainly in the cell wall (Fig. 1 (e)). Higher weight gains were achieved for other treatments with MUF (polymer content, 42.1%) or the organophilic nanoclay/MUF formulations (NF1/MUF, 40.9% and NF2/MUF, 40.6%), and the impregnated materials were found in both the cell wall and vessels of the wood. Figure 2 illustrates the electron microprobe analysis results of the nanofiller/MUF-treated wood samples. Figure 2(a) shows, as an example, the cross-section morphology for the NF2/MUF-treated wood, and Fig. 2 (b) shows the captured Al and its distribution in the corresponding section of the sample. Similar results were also observed for other aluminosilicate nanofiller/MUF-treated wood samples. From Fig. 2(b), it is seen that the middle lamella and cell wall have the highest concentration of Al, implying that the aluminosilicate nanofillers diffuse in the lamella and the cell wall. Further work has also been done through transmission electron microscopy (TEM) analysis of the cell

wall of both the control and nanofiller/MUF-treated samples, confirming that nanoparticles have been impregnated into the cell wall. Thus for the nanofiller/MUF-treated wood, we may say that both MUF resin and the nanofillers were successfully impregnated into the wood, and into the cell wall. This could not only result in enhanced mechanical properties of the wood, but contribute to decrease in water absorption and increase in dimensional stability of the treated wood as well. In a previous paper (Cai et al. 2007), it has been shown that mechanical properties of such composites were much better than untreated wood, but diffusion of nanoparticles in the cell wall had not been discussed.

Moisture absorption

The moisture absorption (MA) values for the control and treated samples at equilibrium (21°C, 65% RH) were measured and are summarized in Table 1. From Table 1, it is seen that MUF and different nanofiller/MUF-treated wood samples exhibited much lower MAs than did control samples. For untreated wood, around 8.5% water adsorption was observed, while less than half as much water adsorption occurred in

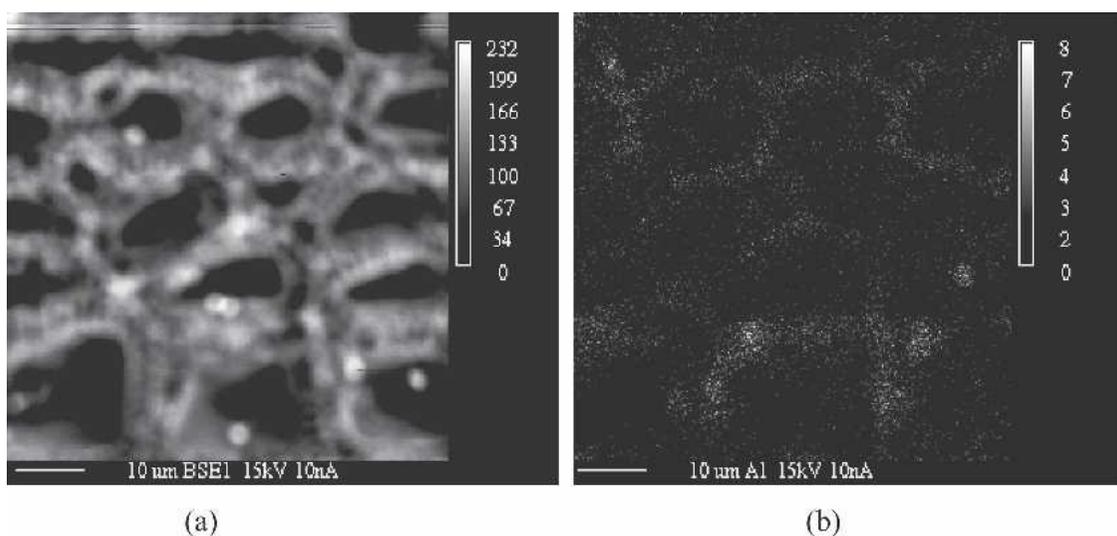


Fig. 2. Electron microprobe analysis of NF2/MUF treated wood, (a) transversal face, and (b) Al elemental distribution.

TABLE 1. Moisture absorption and moisture content at Eq (at 21°C, 65% MC for 6 weeks) of MUF and nanoclay/MUF-treated and untreated aspen.¹

Treatment	Moisture adsorption, at Eq, %	t-test grouping ²
Untreated	8.52 ± 0.97	A
MUF	2.83 ± 1.11	C D
NF1/MUF	3.10 ± 0.86	C
NF2/MUF	3.88 ± 0.87	B
NF3/MUF	2.55 ± 0.70	D

¹ Each value is the average of 10 specimens.

² The same letters are not significantly different at $\alpha = 5\%$.

the wood containing MUF or nanofiller/MUF, i.e. 2.8% for the MUF-treated wood, and about 3.1%, 3.9%, and 2.5%, for the NF1/MUF-, NF2/MUF-, and NF3/MUF-treated wood samples, respectively. The reduction in moisture absorption for the treated wood could be attributed to the impregnated polymer MUF and/or the nanofiller/MUF, which may block sorption sites on interior of wood cell lumens and in the cell walls (Gindl and Gupta 2002).

From Table 1, it is also apparent that different combinations of nanofiller/MUF-treatment provide different levels of protection from moisture absorption. It is interesting to see that the hydrophilic nanoclay NF3/MUF-treated wood showed relatively lower moisture absorption. The nanofiller NF3 is hydrophilic, which makes it compatible with the MUF prepolymer during the preparation process of the impregnation solution. However, this makes it incompatible with the cured MUF matrix, because the polarity of the MUF resin is changed from hydrophilic to hydrophobic during the curing process. This could result in poor interphase interactions of the hydrophilic nanofiller and the cured hydropho-

bic polymer matrix, causing poor mechanical properties of the resulting WPC composites. This has been evidenced from our previous work that lower surface hardness and MOE were observed for the hydrophilic nanofiller/MUF-treated wood samples than those of the organophilic nanoclay/MUF-modified wood (Cai et al. 2007). Poor dispersion of NF3 into the wood was also observed as shown by large amounts of NF3 nanoclay, as aggregates, left on the surface of the NF3/MUF-treated wood samples. Even though poorly dispersed nanoclays could result in poor mechanical properties of the resulting WPC composites, the higher concentration of the accumulated nanoclays on the top skin of the sample may inhibit moisture absorption on the surface and delay the moisture diffusion in and through the wood. Thus better moisture repellency would be expected. For the organophilic nanofillers (NF1 and NF2), better dispersion behavior was observed, and better interphase interactions of the organophilic nanofillers with the polymer matrix were expected and achieved as observed in our previous work [Cai et al. 2006], and in Fig. 1 and Fig. 2. The difference in the effect of different nanofillers on moisture absorption, however, was not obvious as compared to the MUF treated samples.

Water absorption

The water absorption of the treated and untreated wood samples in water at 21°C after 1 day and 7 days was measured and results are given in Table 2. As one can see, the untreated wood absorbed around 63% of its weight water after a 24-h soak and about 125% after 1 week

TABLE 2. Water absorption in 1 day and 1 week of MUF and nanoclay/MUF-treated and untreated aspen.¹

Treatment	Water absorption 1 day, %	Tukey grouping ²	Water absorption 1 week, %	Tukey grouping ²
Untreated	63.44 ± 15.06	A	125.52 ± 8.04	A
MUF	8.27 ± 2.25	B	38.46 ± 9.88	B
NF1/MUF	7.32 ± 1.75	B	35.24 ± 8.85	B
NF2/MUF	5.12 ± 0.45	B	22.18 ± 1.43	C
NF3/MUF	6.32 ± 2.23	B	26.73 ± 4.46	C

¹ Each value is the average of 10 specimens.

² The same letters are not significantly different at $\alpha = 5\%$.

immersion. The MUF-impregnated wood absorbed about 8.3% and 38.5% after 24 h and 1 week immersion, respectively. Thus, MUF treatment significantly reduces water absorption by the wood. For the nanofiller/MUF-impregnated wood, much lower water absorption was observed, e.g. around 5% in 24 h and 22% in 1 week for the NF2/MUF-impregnated wood. Similar water absorption behaviors could also be observed for wood composites made with other nanofillers (both organophilic and hydrophilic: Table 2).

Figure 3 illustrates the water repellency efficiencies (WREs) of MUF and nanofillers/MUF-treated wood samples. The WREs of MUF-treated wood samples were 63.8% and 59.6% for 24 h and 1 week immersions, respectively. The WREs of nanofillers/MUF-treated wood samples were between 90%–92% for 24 h and between 78%–83% for 1 week water immersion, respectively. The WREs of nanofillers/MUF-

treated wood samples were much higher than that of pure MUF-treated wood samples for both 24 h and 1 week water immersions. A significant improvement in water repellency was achieved for the nanofiller/MUF-impregnated wood. The WRE, however, was not significantly different between the hydrophilic (NF3) and the organophilic (NF1 and NF2) nanofiller/MUF treatments. Several reasons could be ascribed to the decrease in water absorption for the treated wood. First, the cured hydrophobic polymer MUF shields the wood surfaces and remains in the cell wall and lumen, resulting in less water penetration into the wood. Secondly, the MUF resin may react with the numerous hydroxyl groups contained in wood components (Gindl and Gupta 2002); thus fewer water absorption sites would remain, which would also contribute to the reduction in water uptake by the treated wood. For the nanoclay/MUF-impregnated wood, since the nanolayers themselves are im-

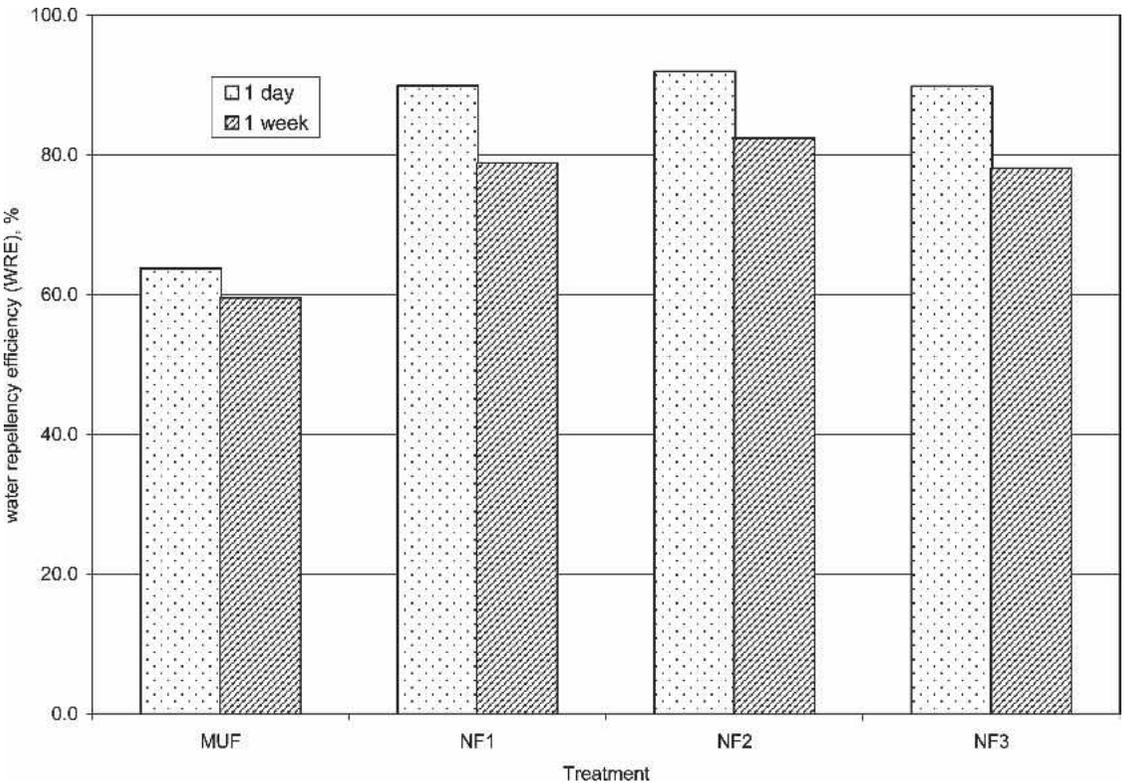


FIG. 3. Water repellency efficiency.

permeable, the impregnated nanolayers could generate a tortuous pathway for a permeant, e.g. the water molecules, to diffuse through the nanocomposite. The hindered diffusion of a permeant in the wood could lead to enhanced barrier properties, reduced swelling behavior, and probably improvement in chemical stability and flame retardance as well (Gilman 1999).

Dimensional stability

The results of thickness swelling (in radial direction) of MUF- and nanofillers/MUF-treated wood are given in Table 3. From Table 3, all treatments significantly decreased the swelling in thickness of the wood. The untreated wood showed a swelling in thickness of 3.83% and 4.13% after 24 h and 1 week soaking in water, respectively. For the MUF-treated wood, a thickness swelling of 2.13% for 24 h and 3.03% for 1 week was obtained. Compared to the pure MUF-treated wood samples, much lower swelling in thickness for nanofiller/MUF-treated wood was observed, e.g. 0.75% in 24 h and 1.81% in 7 days for the NF3/MUF-treated wood. Thus the addition of nanofillers into MUF sig-

nificantly decreased thickness swelling. The lowest swelling in thickness of 0.54% for 24 h and 1.50% for 1 week immersion, respectively, was achieved with the combination of NF2/MUF.

Table 4 gives the results for tangential swelling for the control, MUF- and three formulations of nanofiller/MUF-treated wood samples. Similar swelling behavior was seen in the radial direction. For the untreated wood, the highest values for swelling in the tangential direction of 5.29% for 24 h and 6.37% for 1 week immersion in water were observed. Much lower swelling was achieved for both MUF- and nanofillers/MUF-treated wood samples, e.g. 1.05% for NF3/MUF-treated wood samples after 24 h soaking (Table 4). Comparing the pure MUF- and nanofiller/MUF-treated wood samples, better results were achieved for the formulations containing nanofillers. For instance, NF2/MUF gave the lowest swelling in the tangential direction of 2.84% after 1 week water immersion, which was significantly lower than the 6.37% for the control samples and 5.06% for pure MUF-treated wood.

TABLE 3. Thickness swelling (radial) after 1 day and 1 week in water of MUF and nanoclay/MUF-treated and untreated aspen¹ samples.

Treatment	Thickness swelling (%, 1 day)	Tukey grouping ²	Thickness swelling (%, 1 week)	Tukey grouping ²
Untreated	3.83 ± 0.70	A	4.13 ± 1.10	A
MUF	2.13 ± 0.84	B	3.03 ± 1.80	B
NF1/MUF	1.87 ± 0.50	B	2.70 ± 0.78	B C
NF2/MUF	0.54 ± 0.14	C	1.50 ± 0.20	C
NF3/MUF	0.75 ± 0.59	C	1.81 ± 0.27	B C

¹ Each value is the average of 10 specimens.

² The same letters are not significantly different at $\alpha = 5\%$.

TABLE 4. Swelling in width (tangential) (1 day and 1 week) for MUF and nanoclay/MUF-treated and untreated aspen¹ samples.

Treatment	Width swelling (%, 1 day)	Tukey grouping ²	Width swelling (%, 1 week)	Tukey grouping ²
Untreated	5.29 ± 0.53	A	6.37 ± 0.23	A
MUF	3.97 ± 0.35	B	5.06 ± 0.31	B
NF1/MUF	1.29 ± 0.21	C	2.92 ± 0.23	C
NF2/MUF	1.28 ± 0.17	C	2.84 ± 0.22	C
NF3/MUF	1.05 ± 0.66	C	3.16 ± 0.67	C

¹ Each value is the average of 10 specimens.

² The same letters are not significantly different at $\alpha = 5\%$.

TABLE 5. Swelling in length (1 day and 1 week) for MUF and nanoclay/MUF-treated and untreated aspen¹ samples.

Treatment	Length swelling (%; 1 day)	Tukey grouping ²	Length swelling (%; 1 week)	Tukey grouping ²
Untreated	0.2407 ± 0.0516	A	0.2649 ± 0.0504	A
MUF	0.1569 ± 0.0626	A	0.1627 ± 0.0734	A
NF1/MUF	0.0586 ± 0.0291	B	0.0391 ± 0.0222	C
NF2/MUF	0.1377 ± 0.1870	A B	0.1365 ± 0.1277	B
NF3/MUF	0.0823 ± 0.0431	B	0.0816 ± 0.0671	B C

¹ Each value is the average of 10 specimens.

² The same letters are not significantly different at α = 5%.

Table 5 gives the results of swelling in the longitudinal direction. Although minimal, the swelling of the control samples was still significantly higher than those of MUF- and nanofiller/MUF-treated wood samples. The difference in the longitudinal swelling between the pure MUF resin-treated and the nanofiller/MUF-treated wood samples is not significant for 24 h water immersion, but significant for 1 week water immersion, which indicates that nanofillers decreased the swelling in the longitudinal direction as well.

Figure 4 (a) gives ASEs in tangential and radial directions for both pure MUF and nanofillers/MUF-treated wood samples. Compared to the pure MUF-treated wood, all the nanofiller/MUF-treated wood samples have increased ASE, both in tangential and radial directions. The improvement in ASE, in both tangential and radial directions of nanofillers/MUF-treated wood samples, is significant compared to pure MUF resin-treated wood samples. The effect of different nanofillers/MUF combinations on

ASE, both in tangential and radial directions, were not significantly different from each other, even though the ASE for NF2/MUF-treated wood was slightly higher than that of NF1/MUF- and NF3/MUF-treated wood samples. The results of ASE in volume are given in Fig. 4(b). The ASE of the MUF-treated wood samples was 63.3%, while the ASEs of NF1/MUF-, NF2/MUF- and NF3/MUF-treated wood samples were 102.9%, 125.6%, and 94.2%, respectively. All the nanofillers/MUF treatments improved ASE significantly as compared to the pure MUF resin, which means that better dimensional stability could be obtained using nanofiller/MUF-impregnated wood.

Color variations

The color change of each sample after wood treatment with MUF and/or nanofiller/MUF was investigated. Table 6 gives differences in color change of above samples as compared to the

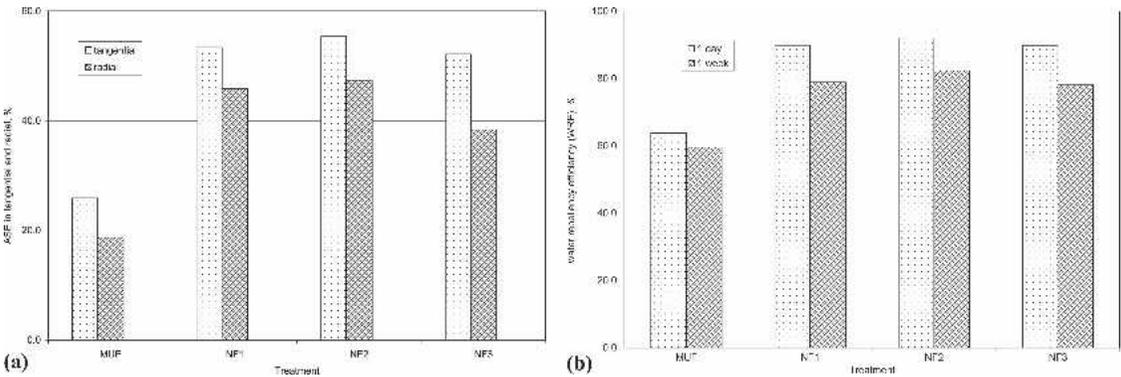


FIG. 4. Antiswelling efficiency, (a) tangential direction and radial direction, (b) ASE in volume.

TABLE 6. Color variation values of the MUF- and nanofiller/MUF-treated wood samples as compared to the controls

Treatment	MUF	NF1/MUF	NF2/MUF	NF3/MUF
ΔE^* value	1.88	3.88	0.83	2.32

controls. As one can see all the color variation values are less than 5. This means that wood treatments with MUF and nanofiller/MUF showed no significant influence on the color of the wood, which is important for practical application of the treated wood in some specific areas such as flooring.

CONCLUSIONS

Wood polymer composites and nanocomposites were prepared through impregnation of melamine-urea-formaldehyde (MUF) and different nanofiller/MUF formulations into aspen. Significant improvements in water repellency and better dimensional stabilities were obtained for the nanofiller/MUF-treated wood samples. The untreated wood absorbed around 63% of its weight in water after 24 h of soaking and about 125% after 1 week immersion. The MUF resin-impregnated wood absorbed about 8.3% and 38.5% after 24 h and 1 week immersion, respectively. For the nanofiller/MUF resin-impregnated wood samples, much lower water absorption was observed, e.g. around 5% water uptake in 24 h and 22% in 1 week for the organophilic nanoclay/MUF-impregnated samples. Anti-swelling efficiency was also improved from 63.3% to 125.6% for the nanofiller/MUF-treated wood. The significant improvement in water resistance and dimensional stability of the resulting wood polymer nanocomposites could be attributed to the introduction of MUF and nanofillers into the wood. Wood treatments with MUF and nanofiller/MUF showed no significant influence on the color of the wood, which is important for practical application of the treated wood in some specific area such as flooring. Finally, with high resolution elemental mapping and our further TEM observation, some nano-

particules used in MUF formulations have been shown to diffuse into the wood cell wall.

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REFERENCES

- AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). 1999. Standard Test Methods for Evaluating Properties of Wood-Base Fiber and Particle Panel Materials. D 1037-99, American Society for Testing and Materials, West Conshohocken, PA.
- AYER, S. W., D. FELL, AND H. WAN. 2003. Hardening of solid wood: Market opportunities and review of existing technologies. Forintek Canada Corp., Québec, Canada.
- BYUN H. Y., M. H. CHOI, AND I. J. CHUNG. 2001. Synthesis and characterization of resol type phenolic resin/layered silicate nanocomposite. *Chem. Mater.* 13:4221–4226.
- CAI X., B. RIEDL, S. Y. ZHANG AND H. WAN. 2007. Formation and properties of nanocomposites made up from solid aspen wood, melamine-urea-formaldehyde, and clay. *Holzforschung.* 61:148–154.
- _____, _____, AND _____ 2006. Effect of Nanofiller on the Performance of Wood/Melamine-Urea-Formaldehyde Nanocomposites, BioPlastics Montreal, September 27–29, 2006, Montreal, Canada.
- DEKA M., AND C. N. SAIKIA. 2000. Chemical modification of wood with thermosetting resin: Effect on dimensional stability and strength property. *Bioresource Technol.* 73:179–181.
- GALPERIN A. S., G. G. KULESHOV, V. I. TARASHKEVICH, AND G. M. SHUTOV. 1995. Manufacturing and properties of modified wood: A review of 25 years work. *Holzforschung* 49:45–50.
- GILMAN, J. W. 1999. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Appl. Clay Sci.* 15:31–49.
- GINDL W., AND H. S. GUPTA. 2002. Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. *Composites Part A* 33:1141–1145.
- HARTLEY I. D., AND M. H. SCHNEIDER. 1993. Water vapour diffusion and adsorption characteristics of sugar maple (*Acer saccharum*, Marsh.) wood polymer composites. *Wood Sci. Technol.* 27:421–427.
- KIM, M. G. 2001. Examination of selected synthesis

- parameters for wood adhesive-type urea-formaldehyde resins by ^{13}C NMR spectroscopy. III. *J. Appl. Polym. Sci.* 80:2800–2814.
- KOJIMA, Y., A. USUKI, M. KAWASUMI, A. OKADA, T. KURAUCHI, AND O. KAMIGAITO. 1993. Sorption of water in nylon 6-clay hybrid. *J. Appl. Polym. Sci.* 49:1259–1264.
- KUMAR, S. 1994. Chemical modification of wood. *Wood Fiber Sci.* 26(2):270–280.
- QUTUBUDDIN, S., AND X. FU. 2002. Polymer-clay nanocomposites: Synthesis and properties. Pages 653–673 in M. ROSOFF, ed. *Nano-Surface Chemistry*. Marcel Dekker Inc., New York, NY.
- RAY, S. S. AND M. OKAMOTO. 2003. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog. Polym. Sci.* 28:1539–1641.
- ROWELL, R. M. 1983. Chemical modification of wood. *For. Prod. Abstr.* 6(12):363–382.
- SCHADLER, L. S. 2003. Polymer-based and polymer-filled nanocomposites. Pages 77–154 in: P. M. AJAYAN, L. S. SCHADLER, AND P. V. BRAUN eds. *Nanocomposite Science and Technology*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- SCHNEIDER, M. H. 2001. Wood-polymer composites. Pages 9764–9766 in K. H. J. BUSCHOW, R. C. FLEMINGS, B. ILSCHNER, E. J. KRAMER, AND S. MAHAJAN, eds. *The Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd., New York, NY.
- , K. I. BREBNER, AND I. D. HARTLEY. 1991 Swelling of a cell lumen filled and a cell-wall bulked wood polymer composite in water. *Wood Fiber Sci.* 23(2):165–172.