

MONTMORILLONITE NANOPARTICLE DISTRIBUTION AND MORPHOLOGY IN MELAMINE–UREA–FORMALDEHYDE RESIN-IMPREGNATED WOOD NANOCOMPOSITES

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(Received September 2009)

Abstract. Attempts were made to investigate nanoparticle distribution in aspen by using electron probe microanalysis (EPMA) and Wincell software analysis to detect and analyze aluminum elements of impregnated montmorillonite (MMT) nanoclays. The cross-section morphologies of both untreated and nanoclay/melamine–urea–formaldehyde (MUF)-treated wood samples were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). With the combination of EPMA and TEM, it was demonstrated that nanoparticles were distributed through the wood cell wall structure. Wood cell walls functioned as filters or sieves to capture nanoparticles, especially in the compound middle lamella and the external layer of the secondary wall (S1) to form a nanoparticle distribution network. The interphase interaction and adhesion between MMT and MUF resin was characterized by AFM observation. Organophilic montmorillonites showed better interphase interactions than the pristine untreated hydrophilic MMT nanoparticles. It was confirmed that the functional groups on the surface of MMT play an important role in the compatibility between MMT nanoclay and MUF resin, which have a strong influence on the physical/mechanical properties of the resulting nanoclay/MUF wood nanocomposites.

Keywords: Wood nanocomposites, nanoparticle distribution, interphase morphology, impregnation, atom force microscope (AFM).

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INTRODUCTION

Many efforts have been made to improve wood properties to meet specific end-use requirements through impregnation with a monomer or a prepolymer to form wood polymer composites (WPCs) in the past decades (Kumar 1994; Schneider 1994, 2000; Schneider et al 1991; Deka and Saikia 2000; Ayer et al 2003). Both thermoplastic and thermosetting systems have been used and have achieved certain improvements in the properties of the composites, but both have limitations (Kumar 1994; Schneider 1994, 2000). Nanotechnology using montmorillonite (MMT) as in situ nano reinforcement offers new opportunities for the modification of thermoplastic and thermoset properties (Wang and Pinnavaia 1998a, 1998b; Byun et al 2001; Qutubuddin and Fu 2002; Ray and Okamoto 2003). Combinations of nanocomposite technology and wood chemical impregnation might be a promising way to modify and improve certain wood properties.

In our previous work, three types of MMT nanoclay/melamine-urea-formaldehyde (MUF) resin impregnations were reported that resulted in comprehensive wood properties improvement, eg surface hardness, abrasion resistance, modulus of rupture, modulus of elasticity, water repellence, and dimensional stability (Cai et al 2007a, 2007b, 2008). Approaches were successfully used for electron probe microanalysis (EPMA) to detect the distribution of aluminum in MMT nanoclay and scanning electron microscopy and transmission electron microscopy (TEM) to characterize interphase interactions, morphology, and their effects on the performance of the resulting WPC nanocomposites (Cai et al 2007b, 2008, 2010). Incorporation of MMT nanoclay into MUF resin was found to be an efficient way to improve low-quality wood properties through impregnation. It was also observed that different types of MMT nanoclays displayed different effects on the properties of the modified wood products. The factors that cause such differences are very interesting topics. It was expected that the interaction between nanoclay/MUF resin and the wood chemical components might be a key player for the improvement of mechanical/

physical properties. Furthermore, the compatibility of layered aluminum silicate nanoclays and MUF resin as well as compatibility of the mixture of MUF/nanoclay with wood components was critical in the properties improvement of modified wood products.

The main objective of this study was to verify if wood ultrastructure having different chemical components has different capacities to capture the MMT nanoparticles. MMT contains typical elements such as aluminum (Al), magnesium, silicon (Si), and oxygen as well as hydroxyl groups. Wincell software analysis of the images of Al distribution was performed to determine the coverage rate of nanoparticles on the transverse section of wood ultrastructure. Atomic force microscope (AFM) was used to characterize the nanometric details of the nanoclay/MUF aspen (*Populus tremuloides*) surface.

MATERIALS AND METHODS

Materials

The detailed procedures on wood impregnation with MMT nanoclay/MUF resin to make wood nanocomposites have been described elsewhere (Cai et al 2007a, 2007b). The low-viscosity MUF resins, with a solid MUF content of about 50%, were prepared in our laboratory using industrially available urea, formaldehyde, and melamine samples. The abbreviations used in this article followed our previous publications (Cai et al 2007a, 2007b, 2008), where NF1 is Cloisite[®] 30B (organic modifier is $\text{CH}_3[\text{CH}_2\text{CH}_2\text{OH}]_2\text{N}^+\text{T}$), NF2 Claytone[®] APA (organic modifier is $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{Cl}^-$), and NF3 Cloisite[®] Na (a pristine clay without organic modifier), all provided by Southern Clay Products, Inc. NF1 and NF2 are hydrophobic MMT, whereas NF3 is a hydrophilic MMT nanoclay.

Trembling aspen (*Populus tremuloides*) logs were provided by a local forest producer at Ste-Foy (Québec, Canada). The green log was cut into lumber and kiln-dried at low temperature (54–71°C) for 6–8 da. Wood samples were chosen from defect-free boards.

Electron Probe Microanalysis of Element Distribution

The distribution of nanofillers in the wood for the MUF/nanofiller-treated wood samples was investigated using EMPA (CAMECA S $\times$ 100), which is one of the most precise methods for surface elemental analysis. The cross-section of the wood samples was coated with carbon (25 nm) before the measurements to make it conducive and to protect the surface from beam damage. EMPA was performed in a mapping mode with an accelerating voltage of 15 kV and 10 nA. The images of Al and Si, which are largely from aluminosilicate nanofillers for the nanofiller/MUF-impregnated wood, were captured digitally to permit enhanced analysis of the samples. EPMA basically works by bombarding a microvolume of a sample with a focused electron beam (typical energy is 5–30 keV) and collecting the X-ray photons thereby induced and emitted by the various elemental species. Because the wavelengths of these X-rays are characteristic of the emitting species, the sample composition can be easily identified by recording Wavelength Dispersive Spectroscopy (WDS) spectra. WDS spectrometers are based on Bragg's law and use various moveable, shaped monocrystals as monochromators.

The coverage fraction of Al distribution on the wood surface was measured by tracing the pixels of EPMA images with Win/Mac Cell V. 5.6 D software (Regent Instrument Inc). To verify the parts of the wood ultrastructure that have greater capacity to capture MMT nanoparticles, micrographs of the Al distribution and the portion measured were duplicated by Photoshop software.

Transmission Electron Microscope Observation

A Jeol 200 kV TEM was used to obtain images of the ultrastructure of the same surfaces of untreated aspen wood. For TEM observation, ultrathin sections of both treated and untreated samples were microtomed to a thickness of about

50 nm at -80°C using a Leica Ultracut E cryoultramicrotome. The staining was done using OsO_4 in a water/formaldehyde mixture.

Atomic Force Microscope Observation

An AFM (Veeco Digital Instrument) was used to investigate the adhesion of the MMT platelets and MUF resin in the MUF/nanofiller-treated wood nanocomposites. For comparison, MUF-treated wood and untreated solid wood samples were also observed by AFM. The specimen for AFM experiments was ultramicrotomed with a diamond knife on a Reichert Ultracuts (Leica) microtome at -30°C to give a smooth surface. Trace mode was used to obtain phase images for the nanocomposites at ambient temperature. Resolution was set to 512 lines $\times$ 512 pixels for all scans on areas varying 2500 nm² to 100 μm^2 at a scan rate of about 1 Hz. The amplitude set point (± 1.7 V) and the drive amplitude (± 1.2 V) were adjusted to optimize the image quality.

RESULTS AND DISCUSSION

Montmorillonite Nanoparticle Coverage Rate on the Transverse Surface of Nano-Impregnated Aspen

EPMA was used to map the Al element distribution of MMT on the nanoclay/MUF-impregnated aspen nanocomposites. The nanoclay particle coverage rate on the MUF/nanofiller wood nanocomposite surface was further investigated using Wincell software to analyze the images of Al distribution on the treated wood surface (Fig 1). The colors from light blue to red indicate the concentration of Al. Light blue means the concentration of Al is low, which indicates the nanoclay was well exfoliated and dispersed in the modified wood, whereas colors from light blue to light green, green, light yellow to yellow, and orange to red indicate that the Al concentration increases with color change. The Al coverage area on the wood transverse section was thus estimated through calculation of the Al distribution pixels. The results are given in Table 1,

showing the Al coverage area (in percentage) on the cross-section of the WPC nanocomposites. Because the Al is largely from aluminosilicate nanofillers impregnated into the wood, based on the Al results, the distribution of MMT nanoclays on the investigated wood surface could be estimated. From Table 1, it is seen that the total surface area covered with Al is about 34%, of which 25% is light blue. The light blue part belongs to the fully exfoliated MMT. Because the average size of the received MMT microparticles is about 8 μm , each microparticle contains a minimum of 3000 platelets in sheet form. The result of such morphology is an extremely large surface area of about 800 m^2/g . It is thus estimated that 1 wt% of MMT could cover 34% of the surface area of wood if the nanoparticles

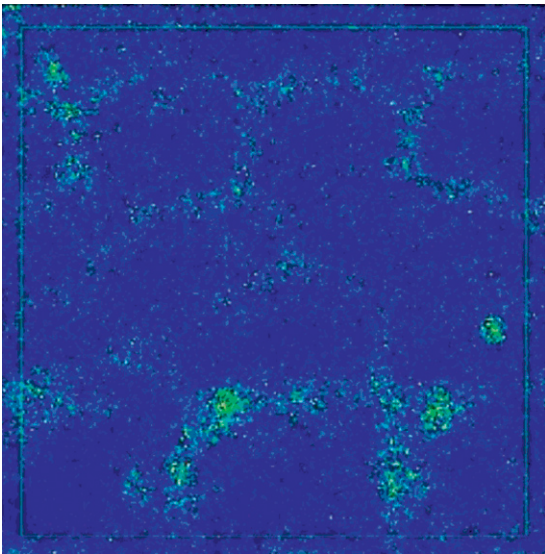


Figure 1. Images of aluminum distribution on the treated wood surface.

were efficiently exfoliated. Table 2 summarizes possible MMT nanoparticle distribution in the wood cross-section judging from the Al color changes and distribution on the wood surface. The light blue fraction was about 73%, light green 20%, and green 5%, meaning that 98% of the surface in which Al was detected contained exfoliated clay. The red color indicates high Al concentration, which means there might be localized nanoclay accumulation and the clay was not exfoliated very well in these areas.

Montmorillonite Nanoparticle Distribution on the Treated Wood Transverse Surface

The transverse section of untreated aspen wood was characterized by TEM and it provided the details of the aspen ultrastructure (Fig 2), which is a typical hardwood ultrastructure as we could find in the literature (Fengel and Wegener 1984. Figure 3 is the image of EPMA-detected Al distribution treated by Photoshop software. Combining the images of EPMA-detected nanoclay/MUF-impregnated aspen wood with those of the TEM analysis, the micrographs showed what part of aspen ultrastructure has the greater capacity to capture nanoclay. By superimposing both images (Fig 3), it was found that the distribution of MMT nanoclay appears as a network along the layers of the compound middle lamella (M) and external layer of the secondary wall (S1). For the nanoclay, the wood acts like a filter and the area included ML, M, P, and S1. These wood ultrastructures had greater capacity to capture the nanometric particles than the rest of wood microstructures such as the middle layer (S2) of the secondary wall. The ML is

Table 1. Calculation of surface area of aluminum distribution on the wood surface using Wincell software.

Total	Aluminum	Red	Orange	Yellow	Light yellow	Green	Light green	Light blue	Dark blue
Pixels	769,619	346	657	1799	9066	40,104	156,298	561,349	1,480,346
Area (%)	34	0.02	0.03	0.08	0.40	1.78	6.95	25	66

Table 2. Layered silicate distribution with the change of concentration of aluminum distribution.

Colors	Red	Orange	Yellow	Light yellow	Green	Light green	Light blue
Aluminum distribution (%)	0.04	0.09	0.23	1.18	5.21	20.31	72.94

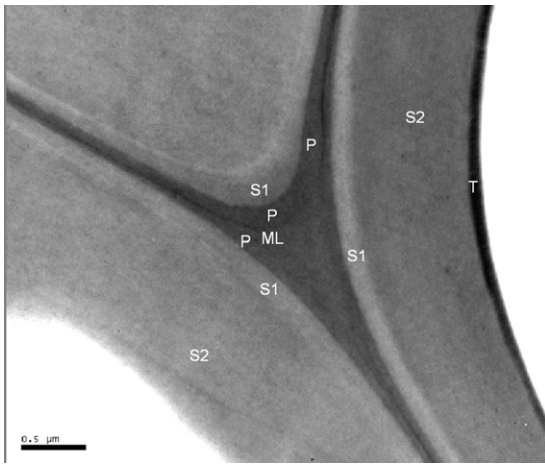


Figure 2. Ultrathin sections of the walls of aspen vessel with various wall layers: ML (middle lamella), M (compound middle lamella), P (primary wall), S1 (the external layer of the secondary wall), S2 (the median layer of the secondary wall), T (tertiary wall), and W (warts).

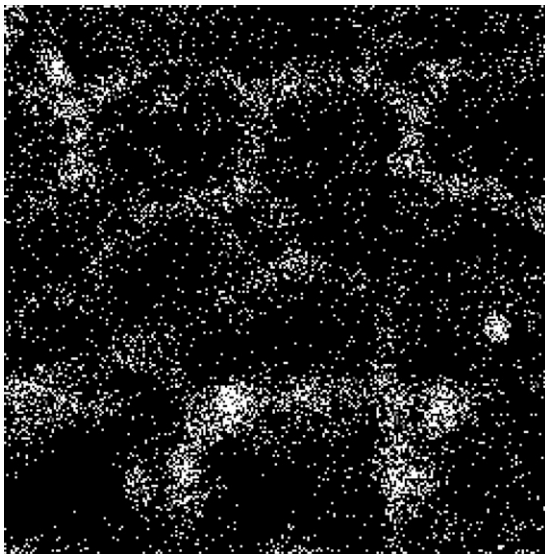


Figure 3. Distribution of montmorillonite nanoparticles along the cross-section ultrastructure of aspen-MUF nanocomposites; the bright color is the distribution of nanoparticles, and the intensity of the bright color represents the concentration of the nanoparticles. MUF, melamine-urea-formaldehyde.

basically free of cellulose and may be composed of entangled single fibrils. The main component of the M is rich in amorphous lignin substance, whereas the cellulose fibrils of the primary wall,

P, are arranged in thin interwoven layers with a gentle helical slope of the fibrils forming the external layer of the secondary wall (S1) (Fengel and Wegener 1984). These parts functioned like a sieve, which captured the MMT nanoparticles in the amorphous substance. Fewer nanoparticles were found on the middle layer of the secondary wall (S2) than the outer layers (P and S1) (Fig 3), which might be ascribed to lower lignin content in S2, because the dominant component in the S2 layer is partly crystallized cellulose.

Interaction Among Nanoparticles, Melamine-Formaldehyde Resin, and Wood

AFM was used to characterize the nanometric details of the nanoclay/MUF wood surface. The interphase interaction between MMT and MUF resin was observed by the AFM characterization. Figures 4a-b show AFM images of the pure aspen wood and MUF-impregnated aspen wood, respectively without nanoclay added. Figures 4c-f present the AFM images of aspen wood impregnated with different nanoclay/MUF formulations, which shows the interphase adhesion morphologies of nanoclay, MUF, and wood. The micrographs of pure aspen wood (Fig 4a) suggest surface morphology with some pores, whereas the MUF-impregnated aspen wood has a relatively smooth surface compared with the pure aspen. It might be from the MUF resin filling the pores of the wood structure. Comparing the micrographs of MUF-impregnated wood (Fig 4b) with the nanoclay/MUF resin impregnation wood (Fig 4c-d), differences in their surface morphologies could be observed. The texture of nanoclay/MUF wood composites is quite rough compared with the pure MUF-impregnated wood. The micrographs of hydrophobic NF1/MUF and NF2/MUF wood nanocomposites (Fig 4c-e) show the pulled-out layered Al silicate, which is MMT crystals that have a flat, thin sheet interphase adhesion morphology. In looking at Fig 4c, the sheet interphase adhesion morphology of the pulled-out nanoclay is uniquely on the surface. Usually the sheet morphology of MMT is irregular in overall

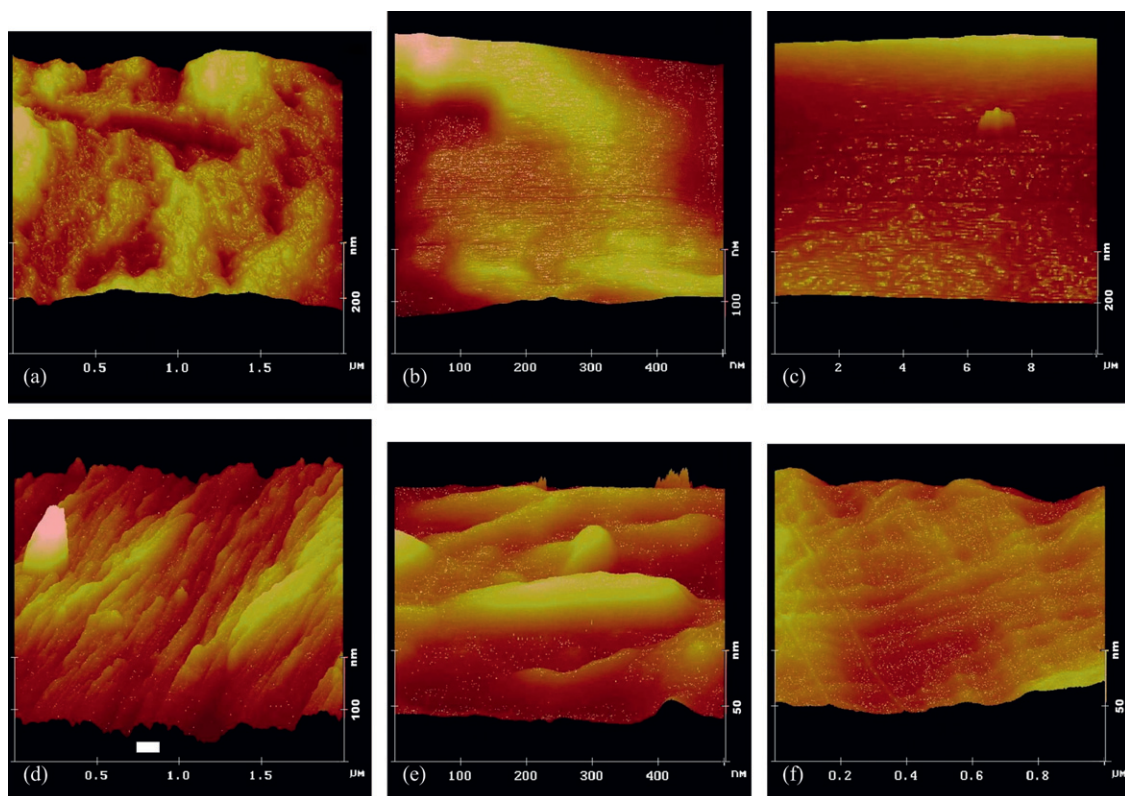


Figure 4. Atomic force microscopy images of the control and the nanoclay/MUF-treated wood samples: (a) aspen wood (resolution with axis X 0.5 $\mu\text{m}/\text{div}$ and axis Z 200 nm/div), (b) MUF-impregnated aspen wood (resolution with axis X 100 nm/div and axis Z 100 nm/div), (c) MUF/NF1/aspen wood (resolution axis X 2 $\mu\text{m}/\text{div}$ and axis Z 200 nm/div), (d) MUF/NF1/aspen wood (resolution with axis X 0.5 $\mu\text{m}/\text{div}$ and axis Z 100 nm/div), (e) MUF/NF2/aspen wood (resolution with axis X 100 nm/div and axis Z 50 nm/div), and (f) MUF/NF3/aspen wood (resolution with axis X 0.2 $\mu\text{m}/\text{div}$ and axis Z 50 nm/div). MUF, melamine–urea–formaldehyde.

shape and can be up to 1 μm in the largest dimension (Fig 4c). Comparing the images of NF1/MUF and NF2/MUF (Fig 4d-e, respectively), the pulled-out montmorillonites appear smooth and do not show adhered material for the NF1/MUF nanocomposite, whereas the appearance of the montmorillonites of the NF2/MUF nanocomposite is rough because they were covered by the MUF matrix adhering to their surfaces. This indicates better interphase interaction and adhesion between the MUF resin and the NF2 than NF1 nanofillers, which usually results in an improvement in mechanical properties of the resulting composites (Cai et al 2007a, 2007b). The AFM morphologies of NF1/MUF and NF2/MUF wood nanocomposites strongly

confirmed the hypothesis that the compatibility of the organophilic nanoclay NF2 is better than NF1 with MUF resin, because the functional groups $\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{N}^+\text{Cl}^-$ of NF2 are more compatible than the functional groups $\text{CH}_3(\text{CH}_2\text{CH}_2\text{OH})_2\text{N}^+\text{T}$ of NF1. This proves that the functional groups of the organophilic MMT play an important role in the compatibility between MMT nanoclay and MUF resin, which have a strong impact on the physical/mechanical properties of the resulting nanoclay/MUF wood nanocomposites as observed in our previous work (Cai et al 2007a, 2007b, 2008). Better interphase adhesion gives better physical/mechanical properties such as surface hardness, abrasion resistance, and dimensional stability for the

nanoclay/MUF-impregnated wood composites (Cai et al 2007a, 2007b).

CONCLUSIONS

This study investigated nanoparticle distribution in the wood structure of nanoclay/MUF-impregnated aspen wood. The characterizations of EPMA combined with the TEM demonstrated that the nanoparticles were distributed along the wood cell wall structure, where the cell wall functioned as a sieve to capture the nanoparticles in the cell wall area, especially along the layers of ML, M, P, and S1 to form a nanoparticle distribution network. The interphase interaction and adhesion between MMT and MUF resin was observed by the AFM characterization. This study confirmed that the functional groups on the surface of the MMT play an important role in the compatibility between MMT nanoclay and MUF resin, which have a strong influence on the physical/mechanical properties of the resulting nanoclay/MUF wood nanocomposites. The organic surfactant agent-treated organophilic montmorillonites showed better interphase interactions than the pristine untreated hydrophilic MMT nanoparticles. Better interphase adhesion gives better physical/mechanical properties such as surface hardness, abrasion resistance, and dimensional stability for the nanoclay/MUF-impregnated wood composites as observed in our previous work (Cai et al 2007a, 2007b, 2008).

ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds Québécois pour la Recherche en Sciences et en Technologie (FQRST), for this project is gratefully acknowledged. We thank Mr. Perre-Louis Cyr, PhD candidate at Centre de recherche sur le bois (CRB) of Université Laval, for the AFM measurement at USDA Forest Service, Alexandria Forestry Center.

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