

PROPERTIES AND WOOD BONDING CAPACITY OF NANOCLAY-MODIFIED UREA AND MELAMINE FORMALDEHYDE RESINS

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Abstract. Urea formaldehyde (UF) and melamine formaldehyde (MF) thermosetting resins were substituted with up to 6% nanoclay (organic modified Cloisite®30B and unmodified Nanofil® 116; Southern Clay Ltd, Austin, TX) and assessed for mixing and curing compatibility using X-ray diffraction, differential scanning calorimetry, wood lap-shear tests, and particleboard strength tests. Cloisite® 30B exfoliated fully in both resin types, whereas Nanofil® 116 showed increased spacing between platelets (intercalation) but not exfoliation. Nanoclays improved bonding strength of MF more than UF resin, and 2% nanoclay with a coupling agent in MF significantly enhanced particleboard bonding strength. Also, thickness swelling of particleboard in water decreased with up to 6% nanoclay. To decrease costs, MF resin could potentially be substituted by up to 6% nanoclay with no detrimental effect on properties.

Keywords: Particleboard, nanoclay, bond strength, MOR, MOE, thermosetting resin, adhesion.

INTRODUCTION

Economic contraction affecting the construction industry and changing consumer preferences have decreased the demand and prices paid for particleboard (PB) during the past 5 yr (Clark 2011) accompanied by increased production costs during the same period (RISI 2011). As a result, PB manufacturers have struggled to remain profitable and several plants have closed

in recent years (Pepke 2010). Resins account for 20-25% of production costs. A 1% decrease in resin costs could generate savings of up to \$5 million US per year for a medium-sized panel board plant (Wang et al 2008). This has prompted interest in nanofillers, especially nanoclays, to supplement resin and enhance wood composite board properties (Wang et al 2008; Ashori and Nourbakhsh 2009).

Inorganic montmorillonite (MMT) nanoclays are naturally occurring Al-Mg-Si minerals whose particles are comprised of stacks of very

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fine platelets of nanometer-scale thickness. These platelets have a very high aspect ratio of between 10:1 and 1000:1 and provide very effective reinforcement of brittle polymer matrices (Ashori and Nourbakhsh 2009). They are therefore commonly used in the plastics industry as nucleating, reinforcing, and flame-retardant agents. Nanoclays have been shown to be excellent fillers and reinforcement for wood-plastic composite polymers and wood resins, significantly enhancing strength and toughness (Fu and Naguib 2006; Hetzer and De Kee 2008) and other properties such as material thermal stability (Labidi et al 2010). The majority of published research pertains to thermoplastic polymers (mainly high-density polyethylene [HDPE]). Adding small amounts (less than 10% w/w) MMT to wood-flour-filled extruded thermoplastic composites improves their strength, toughness, elastic modulus, flame and heat resistance, and water resistance (Zerda and Lesser 2001; Deka and Maji 2010).

Nanoclay platelets can also be separated and dispersed into a liquid matrix, such as thermosetting wood-bonding resins, which changes the curing and physical properties of the resin (Lin et al 2005; Lei et al 2008). Platelet separation is affected by resin chemistry and viscosity, the mixing method and time, clay type, and whether it has been pretreated with organic long-chain modifiers or polymer-philic coupling agents, which promote separation of platelet stacks and chemical affiliation with the surrounding polymer. There are three modes of platelet separation and dispersion into the host polymer (Alexandre and Dubois 2000; Pavlidou and Papispyrides 2008):

- 1) Exfoliated, ie the platelets are completely separated and evenly dispersed into the resin matrix at random angles,
- 2) Intercalated, whereby the distance is increased between the platelets by the intrusion of polymer but they remain grouped together in parallel stacks, and
- 3) Phase-separated, ie the nanoclay particles disperse into the polymer but each particle

remains as closely stacked platelets, ie resin cannot penetrate between the platelets.

For the nanoclay to interact with the resin and improve its fracture toughness and other properties, it must exfoliate or at the very least intercalate into the resin (Alexandre and Dubois 2000). The very fine particles and platelets of clay may also change resin viscosity, tack, and how it interacts with the wood surface whose natural roughness and tiny capillaries allow liquid resin to retreat away from the bonding interface, which can decrease bond strength between adjacent wood elements. There are very few studies on nanoclay-wood thermosetting resin mixes. Lei et al (2008) used X-ray diffraction (XRD) analysis showing MMT Na⁺ was exfoliated in the acid curing environment of urea formaldehyde (UF) resin. The Na⁺ ions counteracted the negative charge on the platelets, facilitating separation.

There are more studies that demonstrate how mixing nanoclays with wood resins prior to binding wood elements can improve bonding strength and strength and water resistance of the composites. Lin et al (2005) compared wood bonding strength of UF resin +1 or 1.5% nanosilica (not technically a nanoclay) with a UF-flour control mixture and found a 25% increase with the resin-nanosilica mix. Significant increases in the strength properties of plywood, PB, and medium-density fiberboard (MDF) bonded with UF resin doped with 1% nanosilica were reported. Similarly, bond strength of PB bonded with UF resin was increased by 25% with the addition of up to 10% Na⁺ MMT (Lei et al 2008). Their study also found significant increase in the resistance of UF binder in plywood to 25 min of boiling if 2% nanoclay Na⁺ was added to the resin prior to gluing and curing. Adding 6% nanoclay (Cloisite Na⁺) to UF resin increased modulus of rupture (MOR) by 20% and modulus of elasticity (MOE) by 35% for MDF (Ashori and Nourbakhsh 2009). A 12% increase in wood bonding strength of liquid PF and UF resins containing up to 2% replacement with nanoclay was reported by Becker et al (2003).

Pores and capillaries in wood elements of a composite also allow it to absorb water, resulting in unacceptable thickness swelling (TS) unless waxes and moisture-resistant resins are used. Ashori and Nourbakhsh (2009) reported that adding 8% nanoclay could decrease the 24-h TS of MDF containing no wax by 18%; it was thought that the nanoclay particles blocked interstitial spaces within the composite such as around and inside wood fibers; however, no visual evidence for this was available.

Several of the claims of previous studies regarding the ability of nanoclays to improve strength properties and moisture resistance in wood composites are remarkable. The objective of this study is to confirm if similar improvements are possible for PB. Adding nanoclay fillers to a costly wood resin such as melamine formaldehyde (MF) could not only decrease resin costs but may also alter its toughness and hence its bonding strength in PB. The main objectives were to 1) test and select the most appropriate method of dispersing MMT nanoclays into UF and MF wood resins; 2) assess how the clay affects the curing process of the resins; and 3) test the effects of resin–clay mixes on bonding wood, by lap-shear strength tests, and on the strength and moisture resistance properties of PB.

MATERIALS AND METHODS

Resins

UF resin is the most common adhesive used in PB manufacture because of its low cost, water solubility, fast curing, and good strength performance (Park and Kim 2008). Formaldehyde emissions and board moisture resistance properties can be enhanced through the use of MF, which is more expensive, reacts more completely with formaldehyde, and results in a more densely crosslinked polymer network when cured. These two resins (Casco C04SS UF [62% solids, 8.1–8.4 pH] and Casco HM707 MF [57% solids, 9.1–9.5 pH]) were obtained from Momentive Ltd (previously Hexion Ltd) in

Edmonton, Alberta, Canada. Resins were used as received with no catalyst added.

Nanoclays

Two platelet-based MMT clays, Cloisite[®] 30B and Nanofil[®] 116 (Southern Clay Ltd, Austin, TX) were used at 0, 2, 4, and 6% w/w resin. Ninety percent of Cloisite[®] 30B particles were <13 μm , and 50% were <6 μm . Median particle size for Nanofil[®] 116 is 12 μm . Each clay particle is comprised of thousands of individual platelets stacked together, which need to be separated and dispersed into the resin matrix prior to applying the clay–resin mix to wood element blending. Long-chain organic modifiers, such as alkyl ammonium, are commonly used to increase the distance between nanoclay platelets, therefore facilitating the exfoliation of clay into liquefied organic polymers (Labidi et al 2010). The Cloisite[®] 30B product comes modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium and is hereafter denoted as 30B. Nanofil[®] 116, denoted as 116, is a natural hydrophilic clay and was used in its pristine state without organic modifiers.

A coupling agent, 3-aminopropyltriethoxy silane (Alf Aescer, Ward Hill, MA), was used at either 0 or 10% of nanoclay weight and its presence is denoted by CA. Coupling agents are necessary to bond chemically incompatible surfaces such as wood powder and HDPE and also help with incorporating MMT nanoclays into this composite matrix (Zhao et al 2006). Nanoclays will also not disperse in certain resin systems such as epoxy without the aid of a primary amine “intercalant” (Ton-That et al 2004). A silane coupling agent facilitates the exfoliation of silicate nanoclay into polyurethane (Kim et al 2003), and coupling agents used in conjunction with organic modifiers can further assist in exfoliation of clay platelets (Han et al 2008).

Twelve different resin–clay mixes (not including pure resin samples) were prepared by first stirring the resin at 1000 rpm with a high-speed mechanical stirrer (Lightning Labmaster Model TS-2010; Cole-Parmer, Vernon Hills, IL) and then slowly

adding the nanoclay powder for a 1- to 2-min period with continued stirring for 30 min to maximize dispersion of the clay in the resin. For nanoclay–resin mixtures in which a coupling agent was used, this was first added to the resin and mixed as previously described for 5 min to allow for hydrolysis of the coupling agent into the resin. At 5 min, nanoclay powder was then added as before and the mixture stirred for another 30 min. Samples of each mixture were then immediately prepared for the following tests:

X-Ray Diffraction

For XRD, two 10- to 20-g samples of each nanoclay–resin mixture were poured into aluminum foil-lined petri dishes, which were then placed in a drying oven at 103°C to cure for 24 h. Afterward, they were removed and cooled to room temperature. Each cured sample was ground to powder which was poured into a sample holder and mounted in a D8 Focus X-ray diffractometer (Bruker ASX, Karlsruhe, Germany). The samples were scanned from 3–15° using a step size of 0.04° (0.8 s/step); X-ray radiation was generated with a 35-kV, 40-mA radiation source and Cobalt standard.

Differential Scanning Calorimetry

Enthalpy of curing of resin–clay mixes was detected using a TA Q1000 differential scanning calorimeter (DSC; TA Instruments, New Castle, DE) calibrated using an indium standard. Heating rate was set at 10°C/min, and gas purge was set at 50 mL/min flow rate. Samples of each resin–nanoclay mixture were prepared by taring a high volume pan on an analytical balance, pipetting 10 ± 5-mg samples into the pan, and recording the sample mass. The O-ring and lid were then placed to cover the pan and the assembly crimped shut using the sample encapsulating press provided with the DSC pan kit. A second reference pan containing no resin was also crimped closed, and both pans were then placed in the DSC. Prior to performing a DSC scan, the cell temperature was equilibrated at

20°C and the samples and reference pans were then heated from 20 to 200°C.

Lap-shear Bond Strength

Wood substrates for lap-shear bond testing were made by cutting 0.7-mm-thick sheets of sliced aspen (*Populus tremuloides*) veneer into strips 120 mm long × 20 mm wide using a pneumatic clipper. The long axis of the specimens was parallel to the fiber direction of the veneer, and veneer moisture content was 8%. Only sheets of veneer with straight grain and no defects were used. The automated bond evaluation system (ABES) was used to measure the lap-shear strength of different resin mixtures. The ABES test apparatus was set up with an overlap length (bonding zone) of 5 mm corresponding to a bond area of 5 × 20 mm. The resin or resin–clay mixes were applied to the bonding zone of each veneer specimen using a small paint brush until between 9 and 10 mg of resin had been spread on the bond area. The “open” time from the moment the resin was applied to each strand until it was placed in the ABES apparatus and tested to failure was approximately 1 min. Platen temperature was set at 140°C for UF resin and 160°C for MF resin based on the results of the DSC experiments; clamping pressure was 1 MPa. Initial tests of several hot pressing times (30, 40, 60, 120, and 480 s) on both resins showed 60 s to be sufficient to ensure full cure, and this was used for all the resin–clay mix tests. Eight replicate specimens of veneer assemblies were tested for each resin, resin–clay, or resin–clay–coupling agent treatment.

Particleboard Manufacture

PBs were manufactured only from those nanoclay treatments that resulted in increased average lap-shear strength (ie MF resin containing 116, 116 + coupling agent, or 30B + coupling agent). Surface and core PB furnish was supplied by the NewPro Particleboard Plant (Smithers, British Columbia, Canada) and consisted of spruce (*Picea glauca*) and yellow pine (*Pinus ponderosa*).

Table 1. Manufacturing parameters for particleboards.

Resin type	Melamine formaldehyde
Resin solids content	57 wt%
Board type	Three layers
Board length	635 mm
Board width	635 mm
Board thickness	15.9 mm
Board resin content	10 wt% odw for both face and core layers
Board wax content	1.5 wt% odw
Face furnish MC	7% odw
Core furnish MC	7% odw
Board MC	2% odw
Shipping density of board	720 kg/m ³
Ratio of face furnish	46% of total furnish mass
Blending time	10 min
Pressing time	10 min
Replicates	Three

odw, oven-dry weight.

Core particles of this furnish were mainly between 0.5 and 2 mm thick, whereas surface furnish mainly consisted of particles <0.5 mm thick (Sackey et al 2008). Three-layer PB boards, 635 mm long × 635 mm wide and 16 mm thick, were fabricated according to the parameters listed in Table 1. Mass of each component was calculated based on the oven-dried furnish mass. After blending the resin mix (Table 2) with furnish, a three-layer mat with core furnish in the middle was hot-pressed at 180°C for 10 min. The board was then removed from the press and allowed to cool to room temperature. PB physical and strength properties were tested according to ASTM (2006) and are listed in Table 2.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

XRD is used to evaluate the degree of clay platelet dispersion in polymer matrixes (Sinha Ray and Okamoto 2003). The result of an XRD test is a plot of X-ray intensity as a function of diffraction angle (θ). Example XRD plots for exfoliated 30B in UF and poorly dispersed 116 in MF resin are shown in Figs 1a and b, respectively. The angle at which these peaks occur is related to the spacing between the clay platelets according to Bragg's Law (Eq 1) (Bragg and Bragg 1913).

$$n\lambda = 2d\sin\theta \quad (1)$$

where n is the integer number for wavelength (in this case 1), λ = wavelength of the X-ray, d = platelet interlayer spacing in Å, and θ = X-ray maximum diffraction angle. Marked decrease in X-ray diffraction peak intensity and a peak shift to a lower θ denote separation and disordering of the crystalline, stacked structure of the platelets (Faruk and Matuana 2008).

Calculated d -spacings for each resin-clay mix are listed in Table 3. Average diffraction angles for pure clay at 2θ were 6.2° for 30B and 8.2° for 116. Platelet d -spacing of unmixed clay was an estimated 16.7 Å for 30B and 12.6 Å for 116; greater d -layer spacing of the 30B was caused by the presence of the organic modifier, which was expected to further facilitate separation during mixing with resin. After mixing 30B with UF and MF resin, there were no longer any

Table 2. Melamine-formaldehyde-bonded particleboard experimental factors and response variables.

Factors	Levels	
Clay type	Cloisite® 30B, Nanofil® 116	
Clay dose	0%, 2%, 4%, 6%	
Coupling agent	0%, 10%	
Responses variables	Number of samples per board	Number of samples per treatment
Internal bond	14	42
Screw withdrawal resistance	8	24
Thickness swell	2	6
Bending properties (modulus of rupture/modulus of elasticity)	2	6

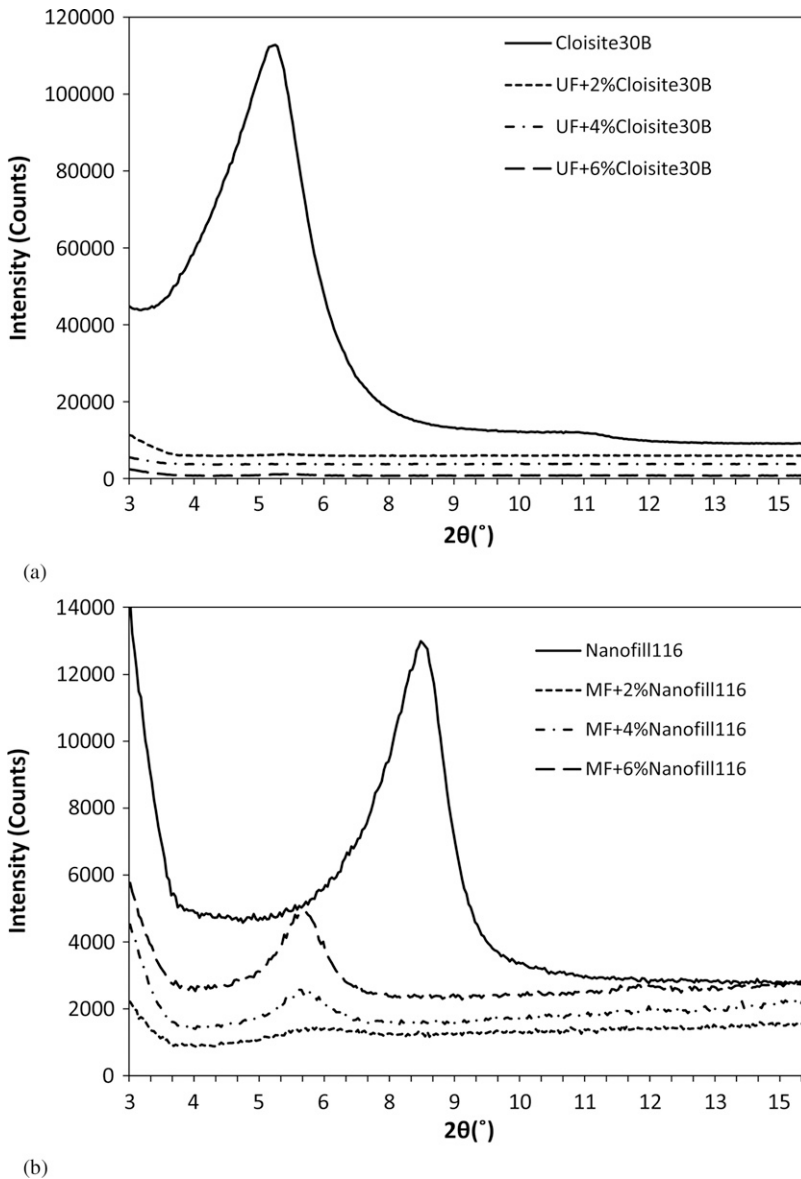


Figure 1. Example X-ray diffraction plots for (a) urea formaldehyde (UF) + Cloisite 30B; and (b) melamine formaldehyde (MF) + Nanofill 116.

detectable X-ray diffraction peaks, suggesting a complete disordering of the crystal structure of the clay that normally scatters X-rays, ie effective exfoliation of the clay platelets into both resins by the mixing technique used. This can be seen in Fig 1a with the complete loss of X-ray intensity peak for 30B + UF resin mixes.

For 116, there was a small but discernible shift downward in diffraction peak angle at 2θ between the pure 116 (8.15°) and this clay type mixed with UF (about 5.8°) or MF (about 6.2°) indicating a small degree of derangement (intercalation) of the crystal structure. The calculated d -spacing of 116 in the UF resin increased from

Table 3. Values for 2θ and estimated d -spacing between clay platelets for clay–resin–coupling agent mixes.^a

Resin type	Clay content	Coupling. agent	2θ (°)		d -space (Å)	
			30B	116	30B	116
—	0	0	6.226	8.155	16.663	12.579
UF	2	0	—	5.844	—	17.546
UF	4	0	—	5.799	—	17.682
UF	6	0	—	5.833	—	17.579
UF	2	10	—	5.869	—	17.489
UF	4	10	—	5.886	—	17.421
UF	6	10	—	5.702	—	17.983
MF	2	0	—	6.076	—	16.877
MF	4	0	—	6.101	—	16.809
MF	6	0	—	6.276	—	16.342
MF	2	10	—	6.152	—	16.668
MF	4	10	—	6.243	—	16.425
MF	6	10	—	6.188	—	16.342

^a No intensity peaks occurred for the Cloisite[®] 30B; this is indicated by a dash. UF, urea formaldehyde; MF, melamine formaldehyde.

12.6 Å to approximately 17.5 Å and to approximately 16.5 Å for MF resin. The slightly higher d -spacing in MF resin could have resulted from monomers of UF resin being smaller than those of MF resin and therefore being likely to more easily enter interstitial spaces within the clay particles. Clay loading or the use of coupling agent had no significant effect on diffraction angle or d -spacing for 116 resin mixes. An example of incomplete dispersion of 116 in MF resin is evident in Fig 1b with the presence of an X-ray intensity peak indicating some crystalline nanoclay existing in the resin mix. The higher the clay loading in the resin (6%), the greater the intensity peak.

The 30B may have dispersed more easily in resin because of its organic modifier, which was strongly hydrophilic and likely to interact with both the water in the resin liquid and the resin monomers facilitating platelet separation and exfoliation in both resin types (Giannelis et al 1999). Although it would appear that a coupling agent is not needed in this case, it may speed up the exfoliation process by decreasing the time needed for the resin to penetrate into the clay layers, because the coupling agent has one end compatible with the organic polymer and the other end designed to bond with the inorganic filler (Han et al 2008). If this had a beneficial effect on exfoliation of 30B, it was unable to be determined from our XRD results, because XRD

is unable to provide a full picture of platelet dispersion in a polymer without the aid of transmission electron microscopy or scanning electron microscopy imagery (Faruk and Matuana 2008).

Differential Scanning Calorimetry

Curing of thermosetting resins such as UF and MF is an irreversible exothermic reaction that shows up as an exothermic peak in the DSC curve and has been shown to be affected by the presence of nanoclay (Lei et al 2008). In this study, all liquid resins and resin–clay mixes were heated from B-stage monomers and fully cured. Resin solidification or vitrification was observed in all resin samples containing nanoclay, and even at the highest clay level of 6%, it did not appear to greatly affect the resin cure kinetics.

The means of three tests per treatment for T_{onset} , ΔH , and T_{peak} are given in Table 4. A selection of representative single DSC curves (ie those closest to the mean values) for UF resin with different percentages of Cloisite 30B is shown in Fig 2. Adding 30B (with or without a coupling agent) caused a slight delay in peak temperature and produced a higher curing temperature; however, these changes were not significantly different from the behavior of pure UF. In contrast, 116 increased both T_{onset} and T_{peak} of UF resin, with a delay in T_{peak} ,

Table 4. Mean values for T_{onset} , ΔH , and T_{peak} from three differential scanning calorimetry runs per treatment.

Resin treatment	Onset temperature T_{onset} ($^{\circ}\text{C}$)	ΔH (J/g)	Peak temperature T_{peak} ($^{\circ}\text{C}$)
UF	105.28	43.82	139.49
UF + 2%3OB	104.91	42.75	142.43
UF + 4%3OB	104.84	41.11	142.58
UF + 6%3OB	104.21	42.17	144.32
UF + 2%3OB coupling agent	105.73	41.06	142.49
UF + 4%3OB coupling agent	106.03	38.99	144.43
UF + 6%3OB coupling agent	106.33	38.57	144.13
UF + 2%116	114.06	36.29	150.40
UF + 4%116	116.07	34.68	148.27
UF + 6%116	115.13	33.83	147.70
UF + 2%116 coupling agent	112.68	28.72	150.73
UF + 4%116 coupling agent	115.18	28.12	154.99
UF + 6%116 coupling agent	119.44	19.28	154.43
MF	124.15	42.46	146.91
MF + 2%3OB	119.19	38.47	121.10
MF + 4%3OB	121.10	37.22	145.22
MF + 6%3OB	118.31	40.07	147.20
MF + 2%3OB coupling agent	119.52	34.86	148.74
MF + 4%3OB coupling agent	118.95	39.91	148.44
MF + 6%3OB coupling agent	119.38	33.18	147.75
MF + 2%116	130.53	36.57	154.35
MF + 4%116	134.27	35.75	157.51
MF + 6%116	137.92	32.39	159.61
MF + 2%116 coupling agent	130.05	37.55	153.62
MF + 4%116 coupling agent	137.17	30.90	159.23
MF + 6%116 coupling agent	134.82	26.43	158.07

UF, urea formaldehyde; MF, melamine formaldehyde.

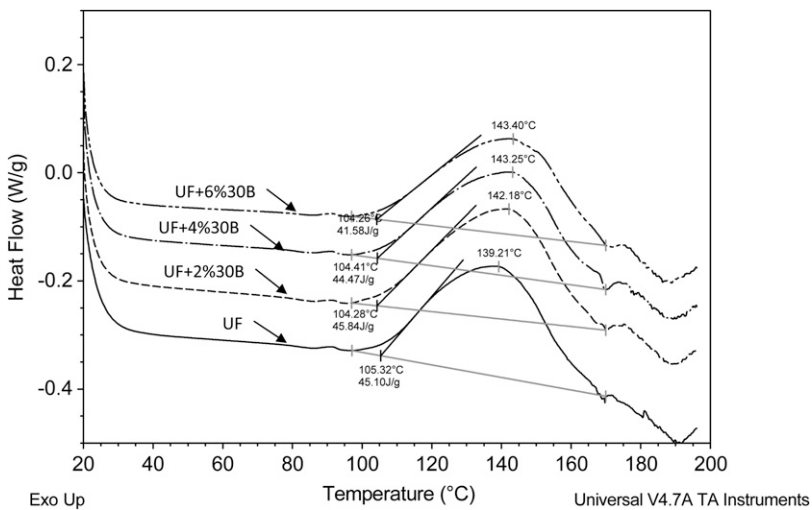


Figure 2. Typical heat flow curves of urea formaldehyde (UF) resin + Closiste[®] 30B nanoclay at different clay contents.

suggesting this clay type had a greater effect on curing. As clay loading increased, the area under the curing peak and ΔH decreased significantly (Table 4). This effect was further exacerbated when a coupling agent was added. These findings suggest that 116 may adversely affect curing and potentially decrease adhesive strength of the resin, which will be examined further using lap-shear and internal bond (IB) strength tests.

For pure MF resin, mean T_{onset} was about 125°C and T_{peak} approximately 147°C (Table 4). In contrast to UF resin, adding 30B at different loadings did not change the ΔH or the onset and peak temperatures. Coupling agent had a deleterious effect on curing of the clay–MF mixes. The ΔH of MF resin containing 30B and a coupling agent was decreased compared with pure MF or MF + clay, meaning that less heat was generated by this mix. As with UF resin, adding 116 also decreased the ΔH of MF resin and delayed its peak curing temperature. Increasing clay concentration decreased ΔH and increased T_{peak} , and the effect was further exacerbated by the addition of a coupling agent.

XRD showed how easily the hydrophilic organic modified 30B interacted with and exfoliated into liquid resin during mixing. This even dispersal of platelets appears to have had no significant effect on curing of the resin. In contrast, XRD analysis suggested that unmodified 116 did not exfoliate into the resin and therefore may have remained as large discrete particles throughout the resin matrix. Exactly how this affected resin curing is unclear without further diagnostic tests. Furthermore, the addition of coupling agent to the mix, which was intended to improve the compatibility of the nanoclay with the surrounding resin, appears to have adversely affected curing. It is possible that 10% coupling agent w/w nanoclay was too much (particularly with the higher dosages of nanoclay) and interfered with the optimum resin curing environment. Amino groups on the molecules of melamine are able to accept more formaldehyde molecules (up to six) than urea molecules, and therefore, MF reacts more completely with

the formaldehyde in the formulation to produce a more densely crosslinked polymer (Pizzi 1994; Kim and Kim 2006). Amino groups present in the added 3-aminopropyltriethoxy silane coupling agent also react with formaldehyde during curing (ie behaving as a formaldehyde scavenger), thereby competing for needed formaldehyde molecules and lowering the optimum formaldehyde to melamine mole ratio in the system. Decreasing the formaldehyde–melamine mole ratio is an effective way of reducing the very high crosslinking density of MF and enhancing matrix flexibility for laminating and postforming purposes (Doyle et al 2003); however, overly adjusting the mole ratio can adversely affect resin cure and performance (Meyers 1984, 1989; Pizzi 1994; Kim and Kim 2006).

Wood Bond Lap-shear Strength

Average lap-shear wood bond strengths of resin and resin–nanoclay mixes are shown in Fig 3. Average bond strengths for pure UF and MF resins were similar, between 4 and 5 MPa.

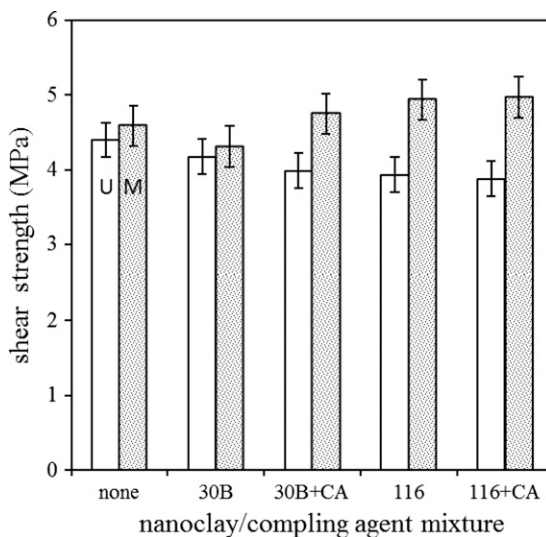


Figure 3. Lap-shear strength of urea formaldehyde (white) and melamine formaldehyde (gray) for neat resins and resin–clay mixtures with and without coupling agents at a 2% substitution; $n = 8$ for each mean, error bars in all figures represent 95% confidence intervals.

Lap-shear strength of UF–clay mixes were all slightly lower than pure UF resin and were further decreased with addition of coupling agent (Fig 3). It was also borderline significantly lower for the 116 + coupling agent mix. Any beneficial effect from nanoclay addition, which has been observed for UF resin previously (Lei et al 2008), may have been so marginal that it was counteracted by the decreased amount of resin on the specimens bonded with the resin–nanoclay mix. Based on this result, no UF–nanoclay particleboards were made.

Substituting MF resin with 2% nanoclay also had no significant effect on wood bonding strength, and most MF–nanoclay mixes resulted in slightly higher wood bond strengths. Surprisingly, the 116 and coupling agent mixes had higher bond strengths than the 30B mixes. This is in contrast to the adverse effect of coupling agent on MF resin curing kinetics from the DSC tests, and it is therefore possible that the reduced crosslink density and brittleness of pure MF enhanced its resistance to stress and/or the coupling agent facilitated stronger chemical bonding between the resin and the wood substrate.

Particleboard Properties

PB strength properties include IB strength (Fig 4), edge screw withdrawal resistance (SWR) (Fig 5), and bending properties, ie MOR and MOE (Fig 6). TS and WA properties for each treatment were also measured (Fig 7). During IB testing, some specimens failed at the glue line between the specimen surface and the metal grapple block. These were excluded from data analysis. All results were analyzed using the Tukey-Kramer pairwise means comparison test at the 5% significance level. Mean values are shown for the specified number of test specimens (n) in the upper right corner on Figs 3-6, and the error bars on these graphs indicate the 95% confidence interval.

Internal Bond. As anticipated from the ABES results, 2% 30B with a coupling agent and 2%

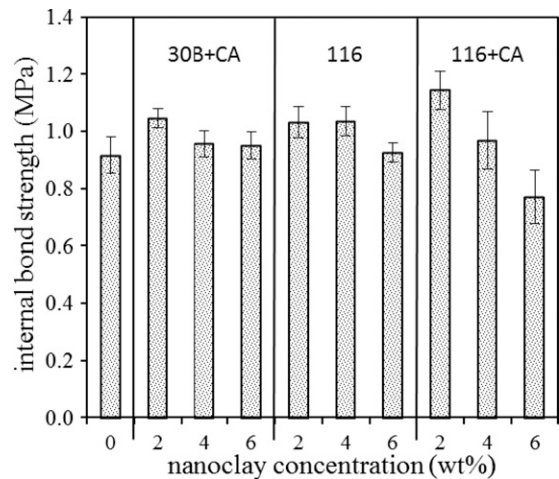


Figure 4. Mean internal bond values for particleboards made with melamine formaldehyde mixed with different concentrations of nanoclays with and without coupling agents; $n = 42$ for each mean.

116 + coupling agent significantly improved IB compared with pure MF and, perhaps more importantly, there was no significant deterioration in IB if a higher loading (6%) of 30B was used (Fig 4). This is consistent with the lap-shear bond strength tests in that 2% 30B and 2% 116 + coupling agent increased average

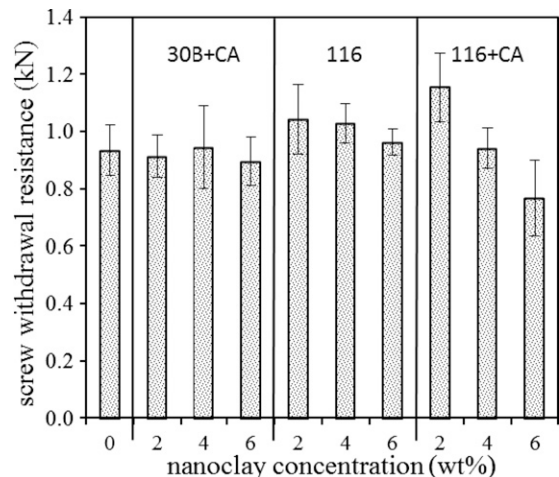


Figure 5. Mean screw withdrawal resistance values for particleboards made with melamine formaldehyde mixed with different concentrations of nanoclays with and without coupling agents; $n = 12$ for each mean.

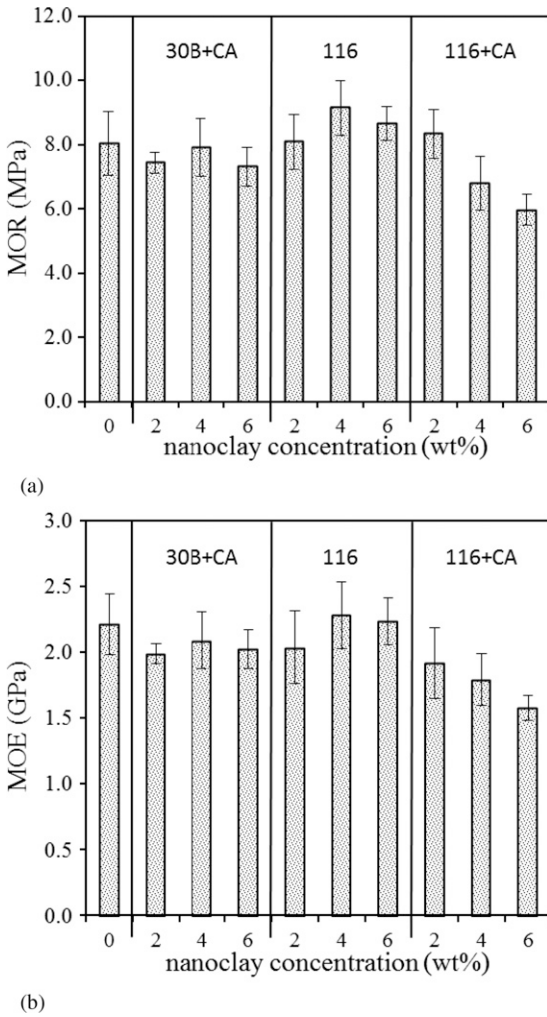


Figure 6. (a) mean modulus of rupture (MOR) in bending and (b) modulus of elasticity (MOE) in bending for particleboards made with melamine formaldehyde mixed with different concentrations of nanoclays with and without coupling agents; n = 6 for each mean.

bond strength. The use of a coupling agent with 116 had a deleterious effect on IB, which decreased sharply with increasing loading of the clay + coupling agent.

Edge Screw Withdrawal. Edge SWR, which applies both shearing and tensile forces on the bonded particles in the core of the composite, is strongly linked to IB strength (Semple and Smith 2005) and, therefore, the trends observed

were very similar to IB strength. SWR (Fig 5) was largely unaffected by resin-clay mixes, except for the 116 + coupling agent. The 2% 116 + coupling agent resulted in a significantly higher average SWR than the control. However, the main result was that SWR of PB bonded with MF containing 6% weight substitution of nanoclay (either 30B or 116) was the same as PB bonded with pure MF resin.

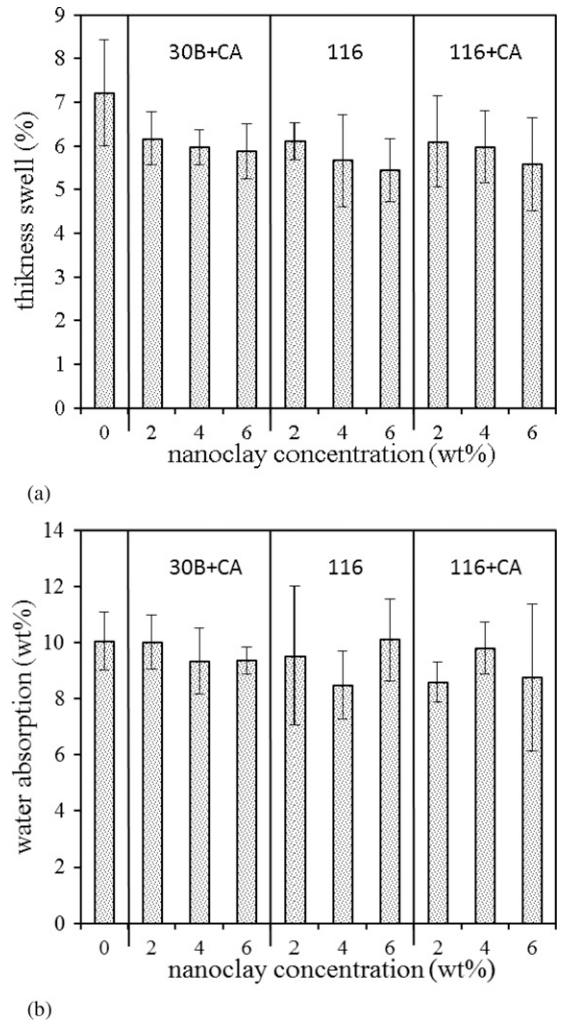


Figure 7. Mean 24-h (a) thickness swell and (b) water absorption values for particleboards made with melamine formaldehyde mixed with different concentrations of nanoclays with and without coupling agents; n = 6 for each mean.

Flexure in Bending (modulus of rupture/modulus of elasticity). From Figs 6a and b, sample *n* was smaller (six per treatment), and variance within treatment groups was large such that observed differences among treatments were not statistically significant. Addition of 30B + coupling agent or 116 alone did not alter MOR and MOE greatly. Only the 116 + coupling agent at high loading decreased MOR and MOE to less than control boards bonded with pure MF. In summary, the effect of nanoclay on PB flexural properties was minor, suggesting it may be possible to substitute MF resin with up to 6% nanoclay filler and no coupling agent.

Thickness Swell/Water Absorption. There were no statistically significant effects of using MF + nanoclay mixes to bond PB on its water absorption or TS, even at 6% clay loading (Fig 7). Some resin–nanoclay treatments decreased TS, such as 6% 116 + coupling agent, consistent with findings from previous studies using nanoclays to manufacture MDF (Ashori and Nourbakhsh 2009) or adding them to solid wood (Cai et al 2010). However, there was not the marked decrease in water uptake reported for MDF by Ashori and Nourbakhsh (2009). It is impossible to tell if the decreases in TS observed here were coincidental or caused by the particles being bonded more strongly, as suggested by the ABES lap-shear and PB IB strength results or by nanoclay particles blocking access into the wood particles by water, as suggested by Ashori and Nourbakhsh (2009).

CONCLUSIONS

The main findings are as follows:

1. The organic modified Cloisite 30B nanoclay was shown through XRD analysis to exfoliate into UF and MF resin, whereas natural, unmodified nanofill 116 appeared to be intercalated only, undergoing a small increase in platelet interlayer spacing but with no full separation and dispersal of platelets into the resin.
2. DSC tests suggested that adding both nanoclays at increasing loadings up to 6% had minimal effects on the curing dynamics of the resins. However, adding coupling agent decreased the heat of reaction (ΔH).
3. Despite the DSC results, adding 2% w/w of nanofill 116 with or without coupling agent enhanced wood bond strength of MF resin despite decreasing the amount of active bonding ingredient in the mix. For UF resin, addition of 2% nanoclays and coupling agent decreased wood bonding strength.
4. Some PB properties were improved with the addition of 2% nanoclay to MF resin, eg 2% 116 + coupling agent significantly increased both IB and SWR in PB and 2% 30B + coupling agent significantly improved SWR, a strong determinant of core strength and integrity. Adding increasing amounts of nanoclay up to 6% decreased TS of PB, in some cases significantly, as in the case of 6% 116 + coupling agent.
5. Generally, MF resin containing up to 6% nanoclay had no significant detrimental effects on PB properties. The only exception to this was when 4 or 6% 116 was added with a coupling agent, which resulted in strength properties dropping markedly. The results present considerable opportunities for offsetting resin costs (particularly MF) by partial substitution with cheaper natural nanoclay fillers without the need for a coupling agent. Further tests would need to be done to determine if an even greater proportion of the resin, possibly up to 10%, can be substituted with nanoclay filler.

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REFERENCES

- Alexandre M, Dubois P (2000) Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater Sci Eng Rep* 28(1-2):1-63.

- Ashori A, Nourbakhsh A (2009) Effects of nanoclay as a reinforcement filler on the physical and mechanical properties of wood-based composite. *J Composite Mater* 43(18):1869-1875.
- ASTM (2006) D1037-6 Standard test methods for evaluating properties of wood-base fiber and particle panel materials. American Society for Testing and Materials, West Conshohocken, PA.
- Becker O, Cheng YB, Varley RJ, Simon GP (2003) Layered silicate nanocomposites based on various high-functionality epoxy resins: The influence of cure temperature on morphology, mechanical properties, and free volume. *Macromolecules* 36(5):1616-1625.
- Bragg WH, Bragg WL (1913) The reflection of X-rays by crystals. *P Roy Soc Lond A Mat* 88(605):428-438.
- Cai X, Riedl B, Wan H, Zhang SY, Wang XM (2010) A study on the curing viscoelastic characteristics of melamine-urea-formaldehyde resin in the presence of aluminium silicate nanoclays. *Compos Part A-Appl S* 41(5):604-611.
- Clark D (2011) Forestry product annual market review 2010-2011. Geneva Timber and Forest Study Paper No. 27, UNECE/FAO, Geneva, Switzerland, 150 pp.
- Deka BK, Maji TK (2010) Effect of coupling agent and nanoclay on properties of HDPE, LDPE, PP, PVC blend and phragmites karka nanocomposite. *Compos Sci Technol* 70(12):1755-1761.
- Doyle M, Hagstrand PO, Manson JA (2003) Influence of chemical composition on the rheological behavior of condensation reaction resins. *Polym Eng Sci* 43(2):297-305.
- Faruk O, Matuana L (2008) Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Compos Sci Technol* 68(9):2073-2077.
- Fu J, Naguib HE (2006) Effect of nanoclay on the mechanical properties of PMMA/clay nanocomposite foams. *J Cell Plast* 42(4):325-342.
- Giannelis EP, Krishnamoorti R, Manias E (1999) Polymer-silicate nanocomposites: Model systems for confined polymers and polymer brushes. *Adv Polym Sci* 138:106-147.
- Han MS, Kim YH, Han SJ, Choi SJ, Kim SB, Kim WN (2008) Effects of a silane coupling agent on the exfoliation of organoclay layers in polyurethane/organoclay nanocomposite foams. *J Appl Polym Sci* 110:376-386.
- Hetzer M, De Kee D (2008) Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: A review. *Chem Eng Res Des* 86(10):1083-1093.
- Kim J, Lee D, Oh T, Lee D (2003) Characteristics of nitrile-butadiene rubber layered silicate nanocomposites with silane coupling agent. *J Appl Polym Sci* 89: 2633-2640.
- Kim S, Kim HJ (2006) Comparison of standard methods and gas chromatography method in determination of formaldehyde emission from MDF bonded with formaldehyde-based resins. *Biores Technol* 96(13):1457-1464.
- Labidi S, Azema N, Perrin D, Lopez-Cuesta JM (2010) Organo-modified montmorillonite/poly(ϵ -caprolactone) nanocomposites prepared by melt intercalation in a twin-screw extruder. *Pol Deg Stab* 95(3):382-388.
- Lei H, Du G, Pizzi A, Celzard A (2008) Influence of nanoclay on urea-formaldehyde resins for wood adhesives and its model. *J Appl Polym Sci* 109:2442-2451.
- Lin QJ, Liu JH, Rao JP, Yang G (2005) Study on the property of nano-SiO₂/urea formaldehyde resin. *Sci Sinica* 41(2):129-135.
- Meyers GE (1984) How mole ratio of UF resin affects formaldehyde emission and other properties: A literature critique. *Forest Prod J* 34(5):35-41.
- Meyers GE (1989) Advances in methods to reduce formaldehyde emission. Pages 58-64 in MP Hamel, ed. *Proc Composite board products for furniture and cabinets—Innovation in manufacture and utilization*, November 11-13, 1986, Greensboro, NC. Forest Products Research Soc, Madison, WI.
- Park B, Kim J (2008) Dynamic mechanical analysis of urea-formaldehyde resin adhesives with different formaldehyde-to-urea molar ratios. *J Appl Polym Sci* 108:2045-2051.
- Pavlidou S, Papaspyrides CD (2008) A review on polymer-layered silicate nanocomposites. *Prog Polym Sci* 33 (12):1119-1198.
- Pepke E (2010) Forestry products annual market review 2009-2010, Geneva Timber and Forest Study Paper No. 25, UNECE/FAO, Geneva, Switzerland, 166 pp.
- Pizzi A (1994) *Advances in wood adhesives technology*. Marcel Dekker, New York, NY.
- RISI (2011) Particleboard and MDF commentary—Production. www.risiinfo.com/Marketing/Commentaries/MDF.pdf (15 March 2012).
- Sackey EK, Semple KE, Smith GD (2008) Improving core bond strength of particleboard through particle size redistribution. *Wood Sci Technol* 40(2):214-224.
- Semple KE, Smith GD (2005) Prediction of internal bond strength in particleboard from screw withdrawal resistance models. *Wood Sci Technol* 38(2):256-267.
- Sinha Ray S, Okamoto M (2003) Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog Polym Sci* 28(11):1539-1641.
- Ton-That MT, Ngo TD, Ding P, Fang G, Cole KC, Hoa SV (2004) Epoxy nanocomposites: Analysis and kinetics of cure. *Polym Eng Sci* 44(6):1132-1141.
- Wang S, Qiu H, Zhou J, Wellwood R (2008) Phyllosilicate modified resins for lignocellulosic fiber based composite panels. US Patent 2008/0234423 A1.
- Zerda AS, Lesser AJ (2001) Intercalated clay nanocomposites: Morphology, mechanics, and fracture behavior. *J Polym Sci B Pol Phys* 39:1137-1146.
- Zhao Y, Wang K, Zhu F, Xue P, Jia M (2006) Properties of poly(vinyl chloride)/wood flour/montmorillonite composites: Effects of coupling agents and layered silicate. *Polym Degrad Stabil* 91(12):2874-2883.