

Influence of Aluminum Oxide Nanoparticles on the Physical and Mechanical Properties of Wood Composites

Anuj Kumar,^a Arun Gupta,^{a,*} Korada V. Sharma,^b and Suriati Binti Gazali,^a

Aluminum oxide nanoparticles were used as nanofillers in urea-formaldehyde (UF) resin and prepared for medium density fiberboards (MDF). The nanofillers composed weight percentage of the UF resin. The thermal and viscoelastic properties were studied using differential scanning calorimetry and dynamic mechanical analysis. The ΔH value of the UF resin showed an increase with increasing nanoparticle concentration. The core temperature during hot pressing increased with the addition of nanofillers. The formaldehyde emissions from MDF decreased with an increase in the concentration of nanofillers. The internal bonding strength and the modulus of rupture of boards were improved significantly after nanoparticle loading.

Keywords: Aluminum oxide nanoparticles; Urea formaldehyde resin; Crosslink density; Formaldehyde emission; Medium density fiberboard; Mechanical properties

Contact information: a: Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300, Kuantan, Pahang, Malaysia; b: Department of Mechanical Engineering, JNTUH College of Engineering Manthani, Centenary Colony, Pannur Village, Kamanour Mandal, Karimnagar-505212, Andhra Pradesh, India;

* Corresponding author: arun@ump.edu.my

INTRODUCTION

The global wood-based panel market was valued at more than US\$80 billion in 2011 (New Markets Research Reports 2012). Wood-based panels are typically made with a heat-curing adhesive (*i.e.*, a thermoset resin) that holds the wood fibers together. The panels have certain advantages over wood, as they are affordable and have the potential for versatile designs. The panels possess good mechanical properties and have a long service life. Two main classes of thermoset resins, phenol-based (phenol formaldehyde resin) and amino-based (urea formaldehyde (UF), melamine formaldehyde, or melamine-urea formaldehyde resins), are commonly used in panel manufacturing (Park *et al.* 2009).

UF resin has desirable properties such as curing at a low temperature (~120 °C) and providing relatively high mechanical strength to panels at an economical price (Park *et al.* 2009). The main disadvantage with the use of UF resin is the emission from the panel of formaldehyde, which is carcinogenic. To reduce formaldehyde emissions, the molar ratio (F/U) in the synthesized product also can be reduced (Myers 1984). However, the mechanical properties deteriorate, leading to an increase in moisture absorption in the panels; hence, various methods are being investigated to reduce formaldehyde emission without compromising the performance of the UF resin. Additives such as melamine and formaldehyde catchers (Dunkey 1998) are used to reduce formaldehyde emissions. Montmorillonite nanoclay (NaMMT) (Lei *et al.* 2008) and modified nano-crystalline

cellulose (Zhang *et al.* 2011) have been used as alternatives to melamine in the manufacture of wood-based panels.

Reinforcement with aluminum oxide nanoparticles (NPs) in various thermoset resins has been investigated for the development of value added products (Yu *et al.* 2011; Wetzel *et al.* 2003; Shukla and Parameswaran 2007). The addition of aluminum oxide NPs in UF resin to reduce formaldehyde emission has been undertaken by Dudkin *et al.* (2006). The present study is aimed at determining the effect of nanofiller addition on the ΔH value and on the viscoelasticity of UF resin and studying the influence of nanofillers on the mechanical properties and formaldehyde emission of medium density fiberboard (MDF). The core temperature profile during hot pressing of MDF was also investigated.

EXPERIMENTAL

Materials

UF resin of mole ratio F:U = 1:1, solid content 64.3%, density 1.282 g/cm³, pH value 8.27, and absolute viscosity 170 cps at 30 °C was provided by Dynea Malaysia Sdn Bhd. Al₂O₃ NPs of average diameter ~47 nm and surface area ~35 m²/g were procured from Sigma Aldrich. Fresh rubber wood (*Hevea brasiliensis*) fibers were supplied by Robin Resources Sdn Bhd.

Preparation of UF/Nanofillers Resins

Mixtures of UF resin and aluminium oxide were prepared by measuring out 200 g of resin and the appropriate mass of 2, 5, and 10 g of nanofillers were added to the resins and the mixture stirred using a high-shear mechanical stirrer (Heidolph model RZR 2041) using a rotation speed of 2000 rpm for 30 min combined with ultrasonic treatment. The actual weight percentage of the aluminum oxide nanoparticles in the resin was 1.0, 2.5, and 5.0 wt % of total weight of UF resin. The samples were named AL0, AL1, AL2, and AL3 according to the concentration of nanofillers.

Preparation of MDF Panels

MDF mixed with resin and NPs at various concentrations was manufactured in the laboratory. In the preparation of the pre-press mat, resin weighing 10% of the weight of the wood fibers was mixed with tropical hardwood fibers with the aid of a spray gun. The platens subjected the mat to hot pressing at 180 °C at a pressure of 25 MPa for 210 s and 270 s, referred to as the short and the long pressing times. Panels measuring 280 × 280 × 9 mm³ manufactured in this manner had an average density of 775 kg/m³.

The panels were then conditioned to a relative humidity of 65±5% and a temperature of 20 °C to attain uniform moisture content in the panels. The panels were trimmed to determine the modulus of rupture (MOR) and the internal bond strength (IB) and to estimate the formaldehyde emissions.

Measurement of the Core Temperature Profile

The wood fiber mat was pre-pressed to half the thickness of the loose mat. The core temperature was measured using three K-type thermocouples. These thermocouples were attached to the data logger for data storage every 2 s. The thermocouple wires were kept 50 mm apart. Minor deviations in the thermocouple data were due to slight

differences in elevation of the thermocouples during hot pressing. The average of three values was used for the analysis.

Characterization

Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were conducted using Q-1000 and Q-100 (TA Instruments, USA) devices, respectively. Both measurements were carried out between 30 °C and 200 °C with a heating rate of 10 °C/min in N₂ atmosphere. DMA was undertaken using the dual cantilever mode with 0.1% deformation, 15 N force, and a frequency of 1 Hz. Prior to the analysis, samples of ~15 g were sandwiched between uniform rubber wood (*Hevea brasiliensis*) veneers. The dimensions of the test samples were 12 × 3 × 60 mm³; three replicates of each sample were tested, and the average was taken. The morphology of the cured resins was examined in a FESEM (field emission scanning electron microscopy) system (JEOL JSM 840A-Oxford ISIS 300 microscope) with testing conditions of voltage in the range of 3 to 8 kV, probe current 45 nA, and a counting time 60 s. Wide angle XRD patterns of all the dried UF/nanofiller resins were obtained using Cu K α radiation in a Miniflex II, RIGAKU, X-ray diffractometer (XRD) equipped with graphite monochromatic positioned in the diffracted beam at a measuring scale XG- Cu/30 kV/15 mA, duration time 1 deg/min, sampling step 0.02 deg, and scan range 3 to 80 deg. The mechanical properties of MDF panels were evaluated according to ASTM D-1037 (1999). The internal bonding strength (IB) and the modulus of rupture (MOR) of MDF panels were estimated with a universal testing machine (AG-20kN, Shimadzu Precision universal tester, Shimadzu, Japan). The formaldehyde emission testing of the MDF panels was performed using EN-120 (1992) standards.

A one way ANOVA (analysis of variance) was used to analyze the testing results. The Tukey Test was used to conduct the means comparison between the samples with Origin 9 statistical software.

RESULTS AND DISCUSSION

DSC analysis

Figure 1 shows the DSC exothermic curves of pure UF and nanofiller-reinforced UF resins. The onset and peak curing temperature of UF resin decreased with the addition of aluminum oxide NPs. The enthalpy of the cure reaction (ΔH) (the area under the exothermic DSC curve) increased with nanofiller concentration, as shown in Table 1.

The decrease in peak curing temperature of UF resin mainly was attributed to a presumed catalytic effect of the aluminum nanoparticles (Ament *et al.* 2011). When the nanoparticles wt% was increased, the peak curing temperature was shifted towards lower temperature, indicating that the nanoparticles catalysed the curing of the UF resin. The aluminum oxide nanoparticles exhibited an effect similar to that of other thermoset resins, as reported earlier (Ament *et al.* 2011; Sheng *et al.* 2010). As noted in the cited work, aluminum nanoparticle surface provide Lewis acidity. Due to the presence of hydroxyl groups on Al₂O₃ nanoparticles, the surface acts as a catalyst and polymerized the UF resin faster. The peak at 90 °C in AL1 may be formed because at a lower percentage the nanoparticles tried to achieve bonding at an interface in UF matrix at lower temperature.

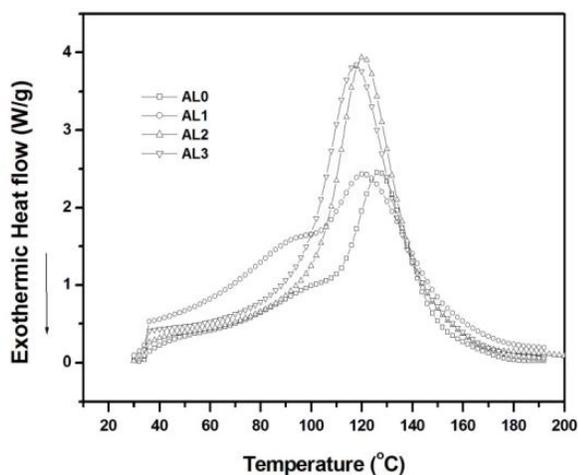


Fig. 1. DSC curves of pure UF and nanofiller-reinforced UF resins at a heating rate of 10 °C/min

Table 1. Cure Enthalpy of Resins and Peak Curing Temperature of Resins

Sample	Onset Temperature (°C)	Peak Curing Temperature (°C)	ΔH (J/g)
AL0	104.40	126	405.1
AL1	100.35	120	429.3
AL2	93.65	119	461.5
AL3	85.33	118	545

DMA Analysis

Dynamic mechanical analysis (DMA) testing has been widely used for investigating the structural and thermo-mechanical properties of thermosetting adhesives. The storage modulus (E'), a measure of the elastic nature of the material, is shown in Fig. 2a for different concentrations. It can be observed that the value of E' for all reinforced resins decreased with increasing temperature from 50 °C to 115 °C, which can be attributed to a decrease in the viscosity in the early stages of curing. Further, as the temperature increased from 115 °C to 160 °C, the E' value increased as a result of cross-linking induced by the curing reaction of the resin. The E' value reached a maximum at the vitrification point (Cai *et al.* 2010) when the curing reaction was complete.

The formaldehyde present in the free form in UF resin have a carbonyl group, which is highly nucleophilic in nature and hardly participates in addition reactions (Ogorodnikov 1984). The aluminol group of aluminum nanoparticles, which is moderately a strong acid, absorbs the free formaldehyde which is on the surface of NPs by acid-base interaction at the surface of OH group with free formaldehyde oligomers, and forms a pseudo-liquid interface bond. The interface between liquid (UF) and solid (nanoparticles) possibly forms an organic film, which decreases the interfacial energy, enhancing the absorption of formaldehyde oligomers on nanoparticles surfaces. Consequently an intermix polymer network of organic and inorganic interfaces with covalent bonds (Pomogailo *et al.* 2000) is formed.

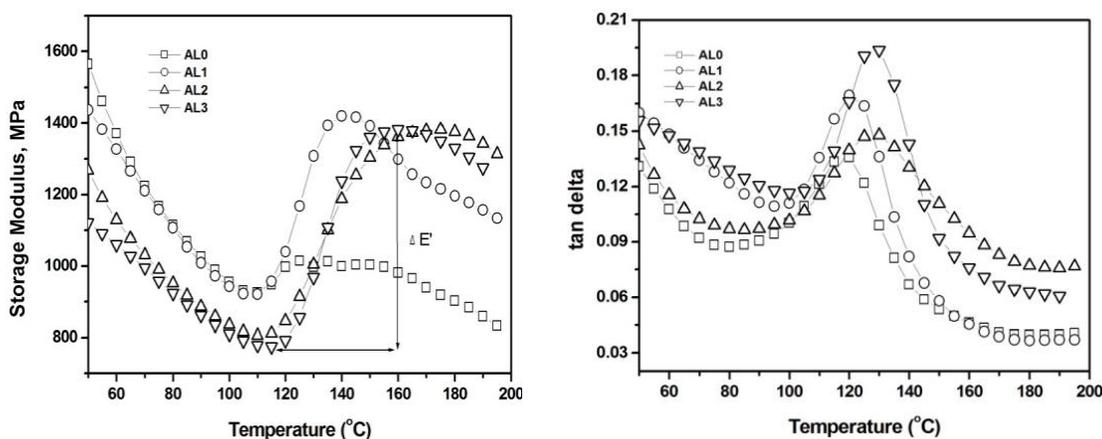


Fig. 2. Storage modulus (E') (a) and $\tan \delta$ (b) of pure UF resin and nanofiller-reinforced UF resin at a heating rate of 10 °C/min

The reinforced resins exhibited greater values of E' in comparison with pure resin, with a higher stiffness. This is because of the formation of an interpenetrating polymer network of organic and inorganic interfaces with covalent bonds. The difference ($\Delta E'$) in the values of maximum and minimum storage modulus E' is used to evaluate the rigidity of the cured resin. The experimental results indicate increasing values of rigidity with nanofiller concentration.

The gelation point for thermoset resin occurred at the initiating point for the formation of infinite molecular weight, when the viscosity of resins began to increase dramatically. This led to increases in both E' and $\tan \delta$. The point where $\tan \delta$ started increasing, as seen in Fig. 2b, was about 84 °C for AL0, while it was 85 °C, 98 °C, and 105 °C for AL1, AL2, and AL3, respectively, which could be the gel points of the UF and the corresponding UF/nanofiller resins during the curing process. Afterwards, $\tan \delta$ increased up to the peak $\tan \delta$, which has been used as the vitrification point, *i.e.*, the rubber-to-glass transition (Kim *et al.* 2006).

After vitrification, the mobility of the material decreased, but the reaction continued, resulting in a further increase in E' . The reduced mobility in the material after vitrification retards chemical conversion, but sufficient reactions can still take place, resulting in a further increase of the storage modulus until the formation of the complete crosslink plateau. Further, $\tan \delta$ will decrease after it reaches the maximum, and this peak $\tan \delta$ transition temperature can be considered the rate of curing. It describes the transition temperature of the mechanical properties of the crosslink network during the curing process of the UF resins. The storage modulus of all the UF/nanofiller resins was clearly enhanced compared with the UF resin alone, across the whole temperature range tested.

Morphology of Cured UF/Nanofillers Resins

Figure 4a shows the FESEM image of the cured UF resin. The cross-linked morphology of the UF resin was not uniform; there were gaps in the cross-linked profile that appear clearly in the FESEM image.

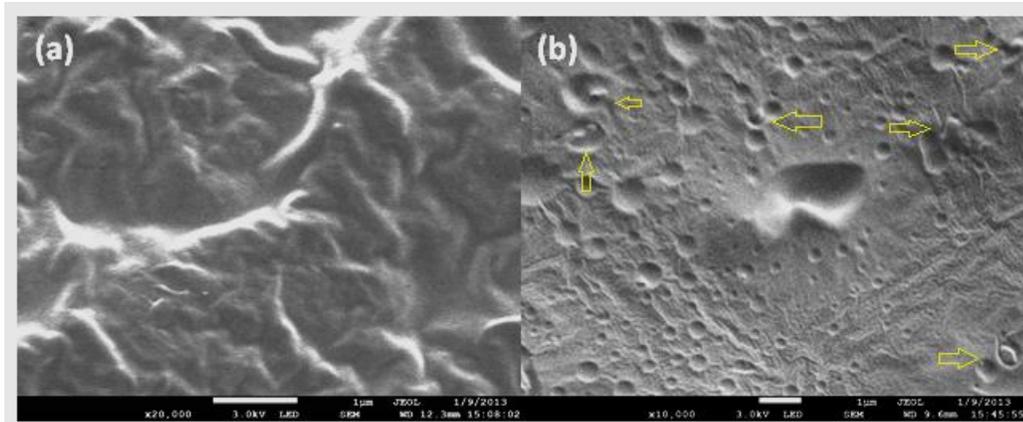


Fig. 4. FESEM images of cured resin (a) UF resin and (b) UF/nanofillers resin

X-ray Diffraction Analysis

Figure 5 shows the X-ray diffraction patterns of cured resins. The AL0 sample shows a single 2θ peak at 22.35° with d-spacing of 3.925 nm, which is the crystal structure of pure UF resin. AL1 shows a peak at 22.20° with d-spacing of 4.001 nm, AL2 shows a peak at 21.69° with d-spacing of 4.094 nm, and AL3 shows two peaks at 21.94° and 66.71° with d-spacings of 4.047 nm and 1.401 nm, respectively. These results are consistent with other reported results (Pratt *et al.* 1985; Dunky 2002).

The characteristic peak of the UF resin was confirmed in all types of UF resins without altering the crystalline nature of the UF resin. As the percentage of NPs was increased, the intensity of the 2θ peak ranging from 21° to 22.5° decreased to a lower intensity. The AL3 sample showed a second 2θ peak at 66.7° with a d-spacing of 1.401 nm, which is the crystalline peak of Al_2O_3 NPs with phase (2 0 4). This peak was formed at higher level loading of nanoparticles. This means that excess nanoparticles did not take part in the UF curing process, an effect that was apparent from the XRD results.

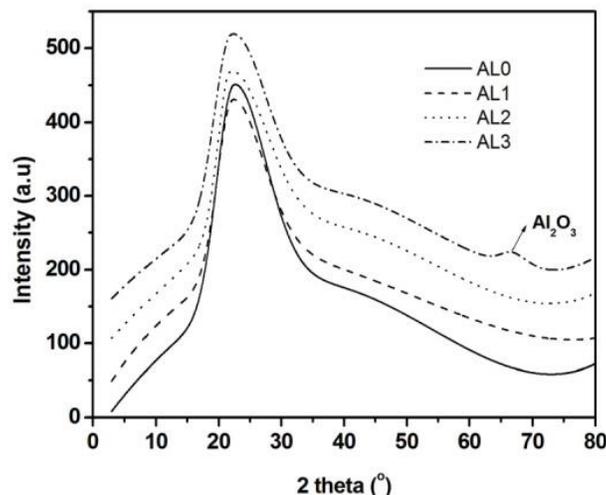


Fig. 5. X-ray diffraction patterns of cured UF resins with and without nanofiller reinforcement

Core Temperature Profile

Figure 6a shows the effect of nanofiller loading on the heat transfer properties of MDF during the hot pressing process in the form of the core temperature profile. At the

beginning of the press cycle, there was a rapid rise in the core temperature, which was due to a steep vapor pressure gradient (Bolton *et al.* 1989) that developed during the period of 15 to 70 s. From 70 to 130 s, a constant temperature in the central plane was observed, which was due to a phase change occurring in the board. The vapor formed was observed to exit from the edges of the board due to the higher vapor pressure formed at the core. Afterward, the heat transfer in the core increased gradually due to the heat conduction of fibers and the heat release during the poly-condensation curing reaction of the UF resin in the form of heat of enthalpy (ΔH). As shown in Table 1, the ΔH of UF resin increased with the addition of nanofillers. The core temperature of the board increased with the addition of nanofillers and better heat transfer during the hot pressing process of the MDF.

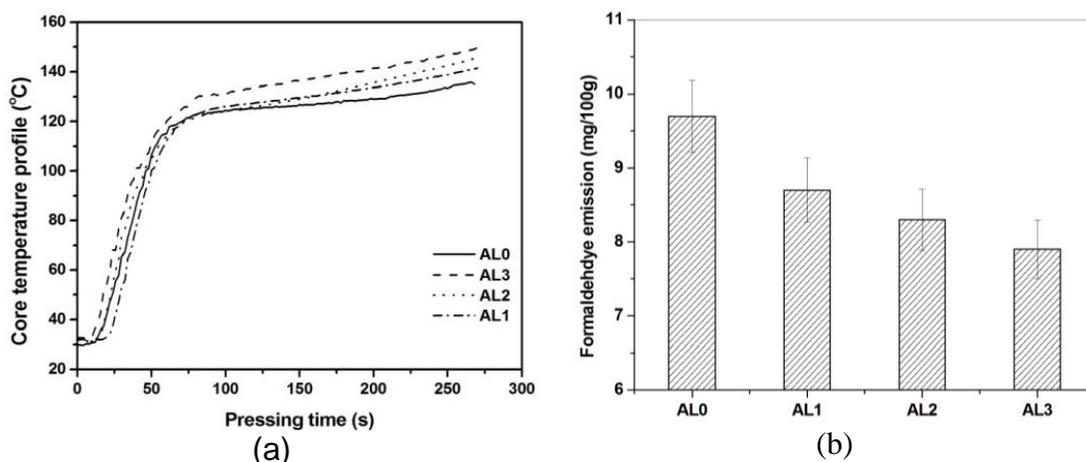


Fig. 6. Core temperature profile of the MDF during hot pressing with and without nanofiller reinforcement (a), and formaldehyde emission from the MDF panels (b)

Formaldehyde Emission from MDF Panels

Figure 6b shows the formaldehyde emission results from the testing of the MDF panels. The free formaldehyde molecules are adsorbed onto the surface of the aluminum oxide NPs (Dudkin *et al.* 2006); when the nanoparticle percentage increased, the formaldehyde emission from the MDF panels decreased. The reductions in the formaldehyde emissions of panels AL1, AL2, and AL3 were 11.7%, 14.45%, and 21.8%, respectively, lower than that of AL0 for samples

Physical and Mechanical Properties of MDF Panels

The internal bonding (IB) strength represents the strength of the resin bonding with the crosslink network in the wood fibers after hot pressing into the form of panels. Figure 7a shows the internal bonding of the MDF panels manufactured using UF and UF/nanofiller resins. The mean IB values of AL0 were 0.60 MPa and 0.69 MPa for the short and long pressing times, respectively. The IB of the MDF panels was improved significantly with increasing nanofiller concentration. The AL1 sample had the highest values, 0.85 MPa for the short pressing time, and 0.94 MPa for the long pressing time. The means of the values of the samples with the nanofillers were significantly different at the $P > 0.05$ level, as determined by the ANOVA results. With the Tukey test, the means were determined to be significantly different. The possible reason for the enhanced IB of the MDF panels was because reinforcement with aluminum oxide NPs improved the crosslink density of the UF resin; the nanoparticles increased the rate of heat transfer

during the hot pressing of the panels (Kumar *et al.* 2013; Gupta *et al.* 2013), which helped the UF resin to be cured throughout the panel.

The modulus of rupture is determined by the bending strength of the MDF panels. Figure 7b shows the mean value comparison between the control and nanofiller-reinforced samples at two pressing times. For the short pressing time, AL0 had a mean value of 40.67 MPa; AL1, AL2, and AL3 had values of 48.93, 49.63, and 50.81, respectively. These values were statistically different from each other, and the ANOVA results show that the probability is $P > 0.01734$.

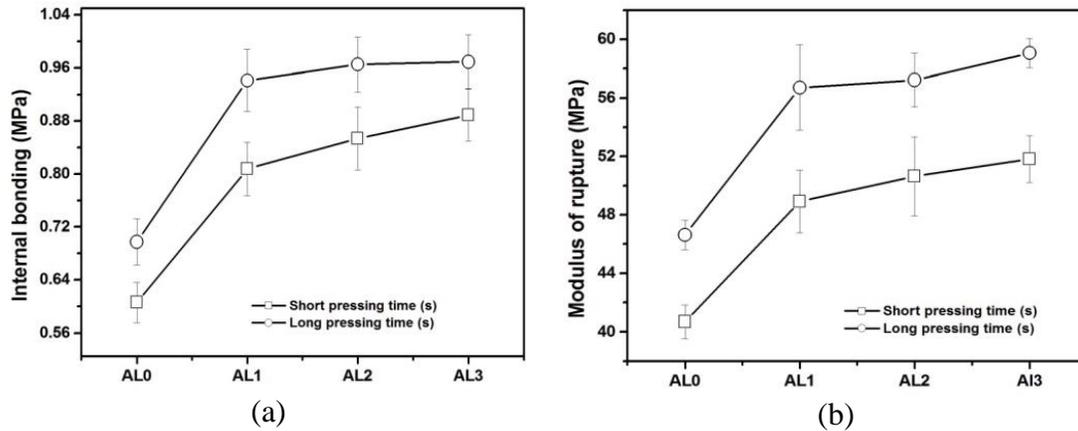


Fig. 7. Mean values of the IB (a) and the MOR (b) of the MDF samples reinforced with nanofillers

With longer pressing times, the MOR values showed the same trend as that with the short pressing times but at higher values, and the means of the control samples and nanofiller-reinforced samples were significantly different, with $P > 0.0019$. The enhanced MOR of the panels after reinforcement with nanofillers may be due to better curing of the resin during the pressing and to the crosslink density of the UF resin. However, we can conclude that nanofiller-reinforced samples resulted in better mechanical properties at the short pressing time in comparison with the control sample values at the higher pressing time.

Figure 8a shows the mean values of the control and the nanofiller-reinforced samples for both short and long pressing times.

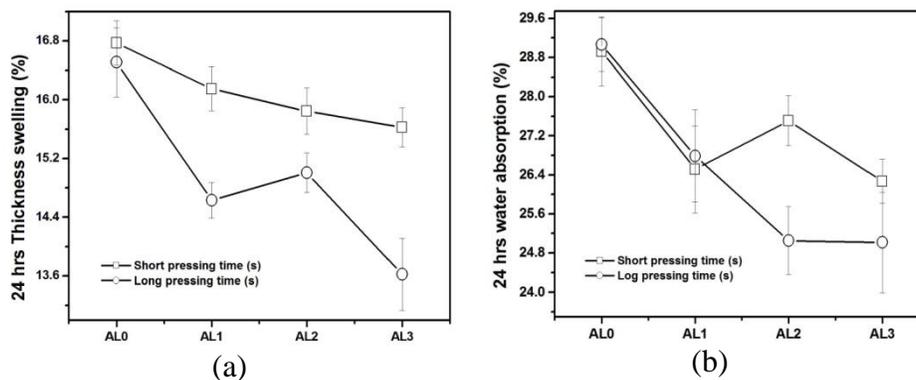


Fig. 8. Mean values of TS (a) and WA (b) of MDF samples reinforced with nanofillers

The mean values of the thickness swelling (TS) for the control sample are 16.7% and 16.5% for the short and long pressing times, respectively. The TS of the MDF panels decreased with increasing nanofiller concentration.

For the short pressing time, the TS was slightly improved after the nanofiller addition, but the means of the samples were not significantly different from each other. For the long pressing time, the mean values were significantly different from each other at the $P < 0.05$ level. The decrease in TS may be due to nanofillers blocking the pores of the wood fibers and the better curing of the UF resin throughout the panels.

Figure 8b shows the water absorption (WA) of the MDF panels with nanofiller loading. The WA decreased with increasing nanofiller concentration, and the mean values of the samples were significantly different from each other. However, the means for the short pressing time ($P < 0.0012$) and for the long pressing time ($P < 0.0044$) were far better than the $P < 0.05$ level for TS. The WA of the MDF panels improved due to the better curing of the panels during hot pressing.

CONCLUSIONS

1. The ΔH value of UF/nanofiller resin was increased by up to 35% in comparison with the UF resin, and the peak curing temperature of UF was decreased with increasing weight percent of nanoparticles.
2. The storage modulus of UF resin improved after the addition of nanofillers.
3. XRD results revealed that the presence of nanoparticles did not affect the crystalline structure of the UF resin at lower wt% of nanoparticles but at higher wt% (*i.e.* 5.0%) the crystalline structure was changed.
4. The heat transfer of boards during hot pressing also improved with the addition of nanofillers.
5. The free formaldehyde present in UF resin adsorbed on the surface of the nanoparticles, and the formaldehyde emissions of MDF were decreased by up to 24%.
6. The internal bonding strength and the modulus of rupture of MDF panels were enhanced.
7. The MDF panels showed improved properties at the short pressing time after the addition of nanofillers.

ACKNOWLEDGMENTS

The financial support from the Universiti Malaysia Pahang (Project Grant 110308) is gratefully acknowledged. The authors thank Dynea Std Bhd and M/S Robin Resources Std Bhd for the supply of resin and wood fibers used in the preparation of the MDF panels.

REFERENCES CITED

- Ament, K. A., Kessler, M. R., and Mufit, A. (2011). "Cyanate ester-alumina nanoparticle suspensions: effect of alumina concentration on viscosity and cure behavior," *Polym. Eng. Sci.* 51(7), 1404-1408.
- ASTM D1037 (1999). *Standard Test Methods for Evaluating Properties of Wood-base Fiber and Particle Panel Materials*, American Society for Testing and Materials.
- Bolton, A. J., Humphrey, P. E., and Kavvouras, P. K. (1989). "The hot pressing of dry-formed wood-based composites. Part III. Predicted vapor pressure and temperature variation with time, compared with experimental data for laboratory boards," *Holzforschung* 43(4), 265-274.
- Cai, X., Riedl, B., Wan, H., Zhang, S. Y., and Wang, X. M. (2010). "A study on the curing and viscoelastic characteristics of melamine-urea-formaldehyde adhesive in the presence of aluminum silicate nanoclays," *Compost. Part A* 41, 604-611.
- Dudkin, B. N., Krivoschapkin, V. P., and Krivoschapkina, E. F. (2006). "Effect of aluminum oxide nanoparticles on the properties of urea-formaldehyde resin," *Russian J. Appl. Chem.* 79(9), 1522-1525.
- Dunky, M. (1998). "Urea-formaldehyde (UF) adhesive adhesives for wood," *Int. J. Adhes. Adhes.* 18(2), 95-107.
- Dunky, M. (2002). "Wood adhesion and glued products," in: M. Dunky, A. Pizzi, and M. Van Leemput (eds.), *State of the Art—Report, COST-Action E13, Part I (Working Group 1, Adhesives)*, European Commission, Brussels, Belgium.
- EN 120 (1993). *Wood-based Panels-determination of Formaldehyde Content-extraction Method Called Perforator Method*, European Committee for Standardization, Brussels, Belgium.
- Gupta, A., Sharma, K. V., Yunus, R. M., and Kumar, A. (2013). "Method for increasing the rate of heat transfer of wood fibres," US Patent Application 20130048190.
- Kim, S., Kim, H. J., Kim, H. E., Lee, Y. K., and Yang, H. S. (2006). "Thermal analysis study of viscoelastic properties and activation energy of melamine-modified urea-formaldehyde resins," *J. Adhes. Sci. Technol.* 20(8), 803-816.
- Kumar, A., Gupta, A., Sharma, K. V., and Nasir, M. (2013). "Use of aluminum oxide nanoparticles in wood composites to enhance the heat transfer during hot-pressing," *Eur. J. Wood Prod.* 71(2), 193-198.
- Lei, H., Du, G., Pizzi, A., and Celzard, A. (2008). "Influence of nanoclay on urea-formaldehyde resins for wood adhesives and its model," *J. Appl. Polym. Sci.* 109(4), 2442-2451.
- Myers, G. E. (1984). "How mole ratio of UF adhesive affects formaldehyde emission and other properties: A literature critique," *For. Prod. J.* 34(5), 35-41.
- New Markets Research Reports (2012). *Global Wood-based Panels—Market Opportunity and Environment, Analyses and Forecast to 2016*, Market Publishers, London, UK, <http://www.prweb.com/releases/2012/10/prweb9990404.htm>
- Ogorodnikov, S. K. (1984). *Formaldehyde*, Khimiya, Leningrad.
- Park, B. D., Lee, S. M., and Roh, J. K. (2009). "Effects of formaldehyde/urea mole ratio and melamine content on the hydrolytic stability of cured urea-melamine-formaldehyde resin," *Eur. J. Wood. Prod.* 67, 121-130.
- Pratt, T. J., Johns, W. E., Rammon, R. M., and Plagemann, W. I. (1985). "A novel concept on the structure of cured urea-formaldehyde resin," *J. Adhes.* 17, 275-295.

- Pomogailo, A. D., Rozenberg, A. S., and Uflyand, I. E. (2000). *Metal Nanoparticles in Polymers*, Khimiya, Moscow.
- Sheng, X., Akinc, M., and Kessler, M. R. (2010). "Rheology and dynamic mechanical analysis of bisphenol E cyanate ester/alumina nanocomposites," *Polym. Eng. Sci.* 50(2), 302-311.
- Shukla, D. K., and Parameswaran, V. (2007). "Epoxy composites with 200 nm thick alumina platelets as reinforcements," *J. Mater. Sci.* 42(15), 5964-5972.
- Wetzel, B., Hauptert, F., and Zhang, M. Q. (2003). "Epoxy nanocomposites with high mechanical and tribological performance," *Compos. Sci. Technol.* 63, 2055-2057.
- Yu, J., Huang, X., Wang, L., Peng, P., Wu, C., Wu, X., and Jiang, P. (2011). "Preparation of hyperbranched aromatic polyamide grafted nanoparticles for thermal properties reinforcement of epoxy composites," *RSC Polym. Chem.* 2, 1380-1388.
- Zhang, H., Zhang, J., Song, S., Wu, G., and Pu, J. (2011). "Modified nanocrystalline cellulose from two kinds of modifiers used for improving formaldehyde emission and bonding strength of urea-formaldehyde adhesive," *BioResources* 6(4), 4430-4438.

Article submitted: May 31, 2013; Peer review completed: July 9, 2013; Revised version received: September 3, 2103; Accepted: September 14, 2013; Published: October 16, 2013.