International Journal of Adhesion & Adhesives 62 (2015) 124–129

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Physical and morphological properties of nanoclay in low molecular weight phenol formaldehyde resin by ultrasonication

F.L. Nabil [a], A. Zaidon [a,*], M. Jawaid [a], U.M.K. Anwar [a,b], E.S. Bakar [a], M.T. Paridah [a], S.M.A. Ridzuan [a], G.M. Aizat [a]

[a] *Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 42500 Serdang, Selangor, Malaysia*
[b] *Forest Products Division, Forest Research Institute Malaysia, 52109 Kepong, Selangor, Malaysia*

ARTICLE INFO

Article history:
Accepted 25 July 2015
Available online 1 August 2015

Keywords:
A. Phenolic
A. Nanofillers
B. Morphology
C. Microscopy
C. Structure property relation

ABSTRACT

The aim of the present study was to examine the characteristics and physical properties of a low molecular weight phenol formaldehyde resin (LmwPF, mw approximately 600) and modified nanoclay admixture. LmwPF resins (45% w/v) were combined separately with 0.5%, 1.0% and 1.5% w/w montmorillonite nanoclay nanomer (based on solid PF). Each of the solutions was ultrasonicated in a sonifier. The dispersion of nanoclay in LmwPF was examined using X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM). It was found that ultrasonication in a sonifier at 50 kHz for 60 min was able to disperse modified nanoclay up to 1.5% into the resin. XRD and TEM analyses showed that the nanoclay dispersion in the resin were either intercalated or exfoliated. The results also showed that the presence of nanoclay in the admixture significantly increased non-volatile content and reduced gelation time and pH values.

1. Introduction

Formaldehyde based resins such as urea formaldehyde (UF) and phenol formaldehyde (PF) are commonly used in composites regardless of the fibre source and type [1]. Bulking treatment of wood with phenol formaldehyde (PF) resin has shown satisfactory results in enhancing the quality of low density timbers [2]. PF resin impregnation at considerably high hot pressing pressures is one of the cost effective ways of improving strength properties, dimensional stability and durability of wood against decay [3, 4]. The success of this treatment is determined by the ability of resin to penetrate the cell wall of wood. PF resin with a molecular weight (Mw) of 290–480 was able to penetrate into the cell wall and increase its stability [5]. However, PF resin with Mw 820 remains in the cell lumen without resulting in any significant stability [6]. It has also been reported that PF resin with Mw 600 successfully improved the dimensional stability and properties of low density tropical hardwood, oil palm stem plywood and bamboo [4, 7, 8].

One of the drawbacks of using LmwPF is the high amount of formaldehyde emission which can occur during soaking and hot pressing. Since LmwPF resin contains a substantial amount of methylol groups in the oligomeric chains, some of these methylol groups are released as free formaldehyde upon being exposed to high temperature and humidity [9]. Previous research reveals that this problem can be overcome by incorporating a formaldehyde scavenger (urea) in treating resin [10], although the performance of the treated product is not as good as those treated without a formaldehyde scavenger.

Incorporating nano particles into the phenolic matrix could possibly reduce the use of high concentrations of LmwPF in the treatment system. The presence of nanoclay in the resin system is expected to reduce formaldehyde emission due to the silica content in the clay which has the ability to absorb free formaldehyde. In addition, the properties of the treated wood could be better enhanced. It has been reported that oriented strand board bonded with urea formaldehyde and nanoclay admixture had low formaldehyde emission compared to board bonded with neat urea formaldehyde resin [11, 12].

The development of nanoparticles such as nanoclays, nanosilica, or nanofibers has led to widespread research in this area. For such nanoparticles, nanoclay has been used by many researchers. A recent study by Rahman et al. [13] revealed that a phenolic resin and nanoclay admixture exhibited property improvements when impregnated in low density wood. Cai et al. [14] also found that the addition of nanoclay into a phenolic matrix significantly increased the surface hardness, modulus of elasticity (MOE), dimensional stability, water repellency and abrasion resistance of modified aspen wood.

---

* Corresponding author. Tel.: +603 89467167; fax: +603 89432514.
E-mail address: zaidon@upm.edu.my (A. Zaidon).

http://dx.doi.org/10.1016/j.ijadhadh.2015.07.012
0143-7496/

The ability to disperse nanoclay in phenol formaldehyde resins is challenging. The structure of nanoclays in resins of various types can be characterised as phase separated, intercalated, or exfoliated (Fig. 1). The admixture is regarded as well dispersed if the nanoclay platelets intercalate or exfoliate within the PF resin. It has been reported that it is quite difficult to disperse clay particles in a resole type phenolic resin than in a novolac type resin [15]. However, Usuki et al. [16] reported that clay particles can be successfully intercalated in a resole type resin using modified montmorillonite nanoclay during the synthesis of the PF resin. One of the potential methods to disperse the clay particles in the PF resin is through an ultrasonication technique.

Kaboorani et al. [17] used this technique to disperse nanoclay within a thermosetting polymer. Lopez et al. [18] and Sonawane et al. [19] used a sonication method to mix phenol and resole type phenolic resin with nanoclay. High-speed impinging liquid jets and strong hydrodynamic shear-forces in ultrasonication technique were able to deagglomerate the nanosize-clay. Dean et al. [20] found that better clay dispersion was observed in the sonication method than in a high shear mixing method.

The aim of this study was to investigate the physical and morphological properties of a low molecular weight phenol formaldehyde resin/nanoclay admixture synthesised using an ultrasonication technique. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to analyse the dispersion of nanoclay in the resin.

2. Materials and methods

2.1. Materials

Montmorillonite nanoclay nanomer® I 31PS grade, which had been modified with 15–35 wt(%) octadecylamine and 0.5–5 wt(%) aminopropyltriethoxy silane, was used in this study. The nanoclay filler was supplied by a local supplier and was ready to use. Resole type low molecular weight phenol formaldehyde (LMwPF) resin (mw, 600), with 45% solid content was used as the matrix. The resin was supplied by Malaysian Adhesive Chemical Sdn. Bhd., Shah Alam, Malaysia.

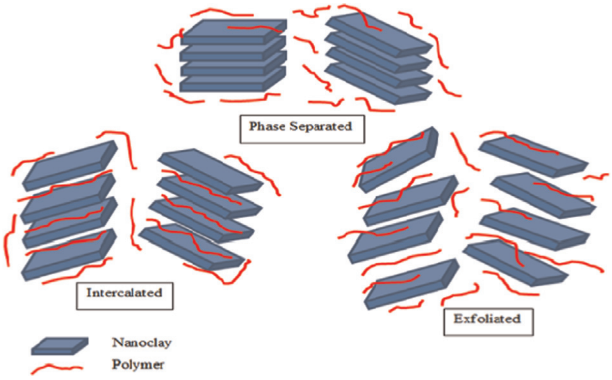

Fig. 1. Dispersion mechanism of nanoclay in resin.

2.2. Optimising the ultrasonication parameters

A preliminary study was conducted to determine the optimum ultrasonication parameters to fully disperse the nanoclay in the polymer matrix. First, LmwPF with 0.5% nanoclay (w/w based on solid PF) admixture was sonicated at 50 kHz amplitude for 20 min. For every 60 s of sonication, the process was pulsed for 5 s to avoid heat generation in the mixture. The obtained solution is shown in Fig. 2a, where the presence of a few nanoclay lumps is clearly visible, indicating that the nanoclay was not well dispersed. Then, the sonication time was increased to 40 min and the result in Fig. 2b shows that nanoclay lumps were still present but in a smaller amount compared to the former. After several trials, it was concluded that a sonication time of at least 60 min is required to disperse the nanoclay in the polymer matrix (Fig. 2c). For further experiments, the admixture was synthesised at 50 kHz for 60 min.

2.3. Synthesization of LmwPF/nanoclay admixture

Three admixtures were prepared for this purpose. Sample 1 consisted of 45% LmwPF and 0.5% nanoclay (w/w based on solid PF), sample 2 had 45% LmwPF and 1.0% nanoclay and sample 3 contained 45% LmwPF and 1.5% nanoclay. Before the admixtures were prepared, the nanoclay was first dried in an oven at 65 ± 2 °C for 24 h. They were synthesised following the developed protocol.

2.4. Physical properties

2.4.1. Non-volatile content

Non-volatile content was determined by weighing 1 g of each LmwPF/nanoclay admixture in an aluminium foil and dried in an oven at 103 ± 2 °C for 3 h. The dried mixture was cooled in a desiccator, and the oven-dry weight was determined. The percentage of the non-volatile content was calculated using Eq. (1), as follows.

$$\text{Non–volatile content}(\%) = 100\left[(W_1 - W_o)/W_1\right] \tag{1}$$

where, W_1 is the weight of the initial mixture (g) and W_O is the weight of dried mixture (g).

2.4.2. Gelation time

Five grams of each mixture was placed in a beaker and then heated in a water bath at 100 ± 2 °C. While heating, the mixture was continuously stirred with a glass rod until the mixture gelled.

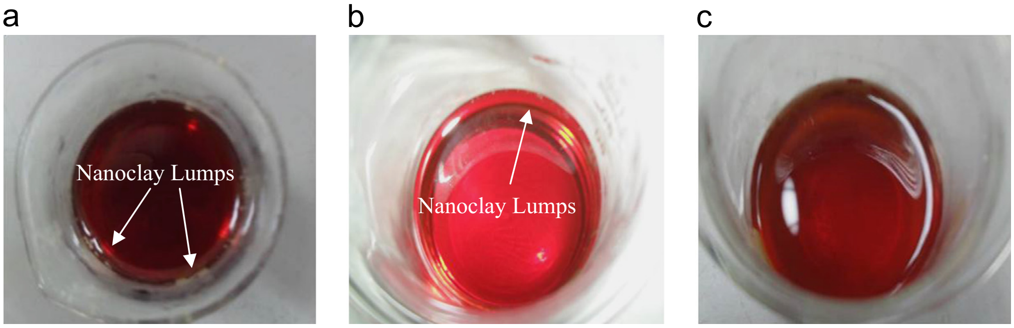

Fig. 2. Appearance of 20 min sonication time of LmwPF/nanoclay. (b) Appearance of 40 min sonication time of LmwPF/nanoclay. (c) Appearance of 60 min sonication time of LmwPF/nanoclay.

Table 1
Summary of the analysis of variance (ANOVA) of LmwPF/nanoclay.

Variables	df	Non-volatile content (Solid content)	Gelation time	pH value
Treatments	8	0.09^{ns}	0.00**	0.03*

Note: ns: not significant.
** Significantly different at $p \leq 0.01$.
* Significantly different at $p \leq 0.05$.

The time from the beginning of heating until gelation was recorded.

2.5. *pH value*

The pH metre was first calibrated with buffer solutions having pH 4.0, followed by pH 10.0 prior to pH measurement of samples. Each sample was determined by weighing 50 g of the solutions into a 100 ml beaker. The pH of the resin was determined by immersing the electrode into the resin using a digital pH metre (Mettler Toledo DELTA320). The reading was recorded after 3–5 min at 30 °C [21].

2.6. *Morphological properties of the LmwPF/nanoclay mixture*

2.6.1. *X-ray diffraction (XRD)*

The characteristics of the nano particles in the polymer matrix were analysed using X-ray diffraction (XRD). The admixtures were first cured by heating in a forced circulation oven at 103 ± 2 °C for 3 h. The cured admixture was then ground into a powder and the analysis was performed using an X-ray diffractometer (Bruker AXS 8 Advance model). The nanoclay powder and the admixture were examined separately using Cu Ka radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. The X-ray patterns were plotted within the range of 3–10°(2θ) at a rate of 0.02°/0.1 s. According to Bragg's law, any increase in interlayer spacing can be identified by a shift of the diffraction peak to lower angles, leading eventually to featureless patterns (exfoliated structures). The peak was calculated according to Bragg's law (Eq. (2)), as follows.

$$\text{Sin}\,\theta = \theta/2d_{001} \qquad (2)$$

where θ is the observed peak, λ is 0.15406 nm, and d_{001} is platelet gallery height.

2.6.2. *Transmission electron microscopy (TEM)*

The dispersion of the nanoclay in the polymer matrix was further confirmed by analysing the cured admixture using a transmission electron microscope (TEM, model HITACHI H7100). Each admixture solution was first poured into a cylindrical mould and dried at 103 ± 2 °C in a forced circulation oven for 3 h. An ultra-thin film (100 nm) polymer was cut from the polymer using an ultra microtome (Leica EMFCS Ultracut microtome) and subsequently analysed under the TEM at 100 kV.

2.7. *Statistical analysis*

An analysis of variance (ANOVA) was employed to determine any significant differences in the physical property values among the admixtures. The means were separated using Duncan's Multiple Range Test. Statistical processor social science (SPSS V22) was used to analyse the data.

3. Results and discussion

3.1. *Physical properties of LmwPF/nanoclay admixture*

Table 1 summarises the analysis of variance (ANOVA) for the physical properties of the polymer admixtures. The results showed that incorporating nanoclay into the PF resin did not significantly affect the non-volatile content. However some significance in relation to gelation time and pH was observed. As anticipated, the percentage of non-volatile content in the admixture (63.07–64.30%) was relatively higher than for the phenolic resin without nanoclay, i.e., 56.8% (Table 2). The results also suggested that the non-volatile content increased as the amount of nanoclay added increased. However the difference was not significant. The appearances of the polymer matrix, with or without the presence of nanoclay, are shown in Fig. 3, Fig. 4, Fig. 5 and Fig. 6. A clear and transparent polymer matrix was observed (Fig. 3a and b) in the neat polymer. However, for those with nanoclay, the appearance of the matrix was opaque and no sign of phase separation could be seen on the cross section of the polymer matrix (Fig. 4a and b). The same was true for the polymer matrix which had a higher amount of nanoclay (Fig. 5 and Fig. 6), with a difference observed on the degree of opacity. The higher degree of opacity reflected that a higher amount of nanoclay was well dispersed in the polymer matrix. In another study, Natali et al. [22] reported the same findings on the phase separation on commercial grade phenolic resin admixed with nanoclay.

Gelation time of the admixture was found to be affected by nanoclay content. The gelation time of the phenolic resin was 19 min. This value was shown to reduce following nanoclay addition. Within the range of the nanoclay contents investigated, the shortest gelation time was 11 min for the admixture with 1.5% nanoclay. The results found here are in good agreement with studies conducted by Fink [23] and Xiong et al. [24], where incorporation of nanoclay successfully reduced the gelation time of commercial grade phenolic resin. Shorter curing time of phenolic resin gives an advantage to the process of fabrication of *impreg* or *compreg* products, whereby the cost of processing may be reduced.

The presence of nanoclay was also found to reduce the pH value of the LmwPF resin. The value decreased from 9.03 for the resin without nanoclay to 8.64 for the resin with 1.5% nanoclay. This shows that the range of nanoclay content used in this study reduced the pH values of the admixtures whilst maintaining an alkaline state, thereby shortening the curing time of the resin.

3.2. *X-ray diffraction*

X-ray diffraction tools are frequently used to characterise the morphology of nanoparticles in a polymer matrix. XRD has been widely used to probe the dispersability and the changes in silicate-gallery spacing (d_{001}) from XRD patterns. It has been reported that

Table 2
Effect of LmwPF with and without nanoclay on non-volatile content (solid content), gelation time and pH value.

Nanoclay content	Solid content (%)	Gelation time (Min)	pH value
0	56.58^{a}(0.16)	19^{c}(0.2)	9.03^{b} (1.2)
0.5%	63.07^{b} (1.5)	17^{c} (0.06)	8.99^{b} (2.0)
1.0%	63.57^{b} (1.7)	12^{b} (0.06)	8.76^{a} (1.7)
1.5%	64.3^{b} (3.8)	11^{a} (0.03)	8.64^{a} (2.6)

Note: Means followed with the same letters
^{a,b,c} in the same column are not significantly different (at $p \leq 0.05$) according to least significant different (Duncan) method.
Values in parentheses are standard deviations.

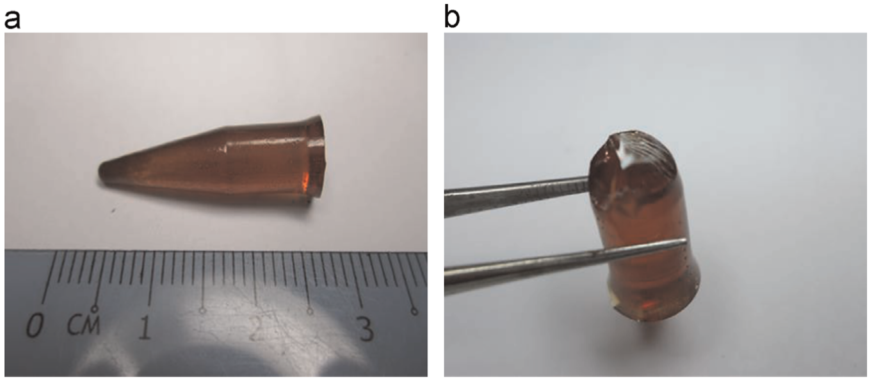

Fig. 3. Appearance of LmwPF without nanoclay. (b) Surface area of LmwPF without nanoclay.

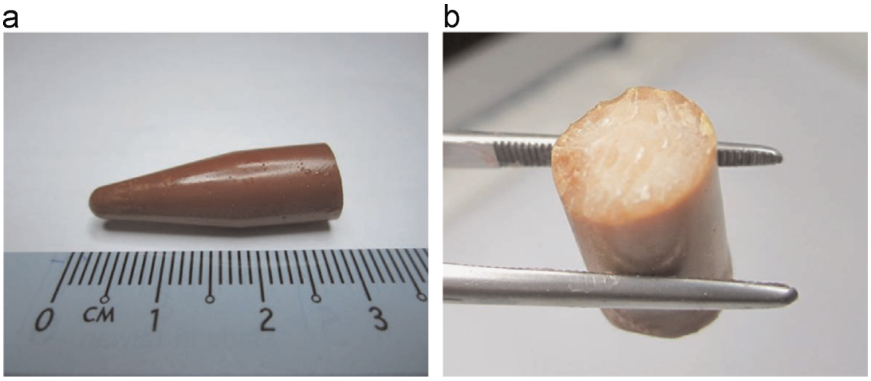

Fig. 4. Appearance of LmwPF/nanoclay with 0.5% (w/w based on solid PF) nanoclay content. (b) No phase separation between nanoclay and LmwPF could be observed on the surface area.

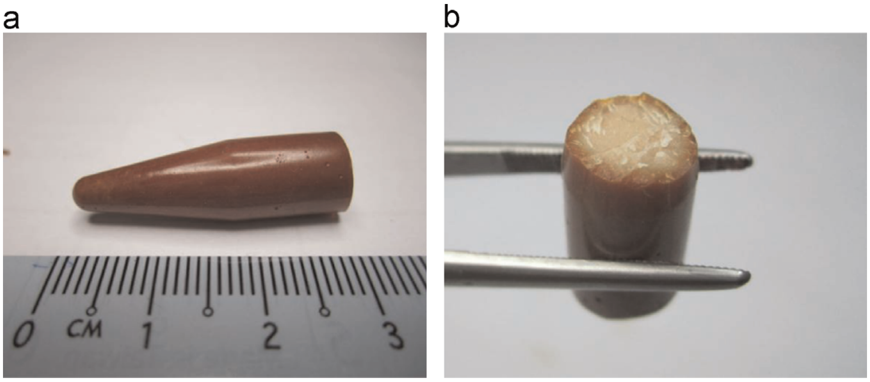

Fig. 5. Appearance of LmwPF/nanoclay with 1.0% (w/w based on solid PF) nanoclay content. (b) No phase separation between nanoclay and LmwPF could be observed on the surface area.

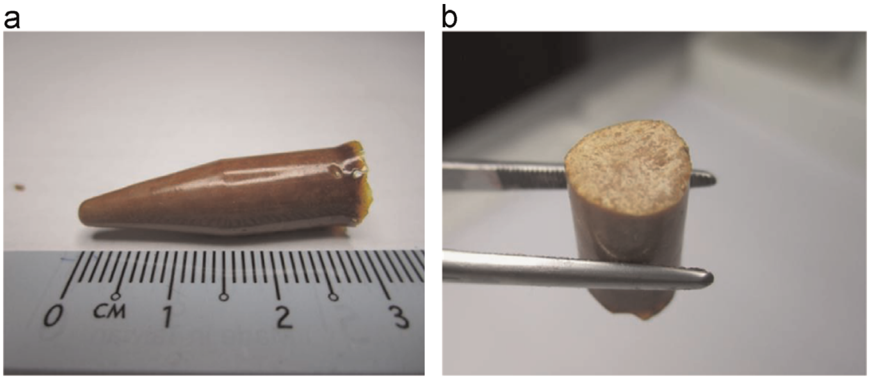

Fig. 6. Appearance of LmwPF/nanoclay with 1.5% (w/w based on solid PF) nanoclay content. (b) No phase separation between nanoclay and LmwPF could be observed on the surface area.

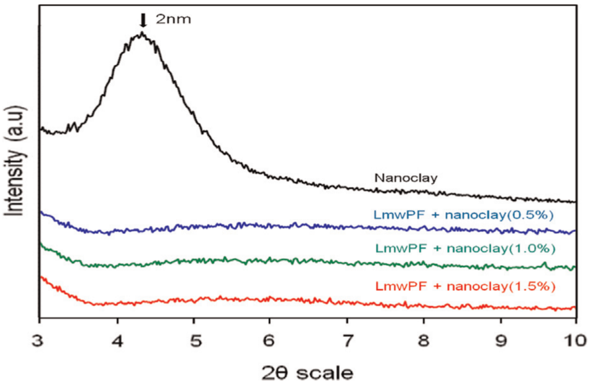

Fig. 7. X-ray diffraction pattern of LmwPF/nanoclay.

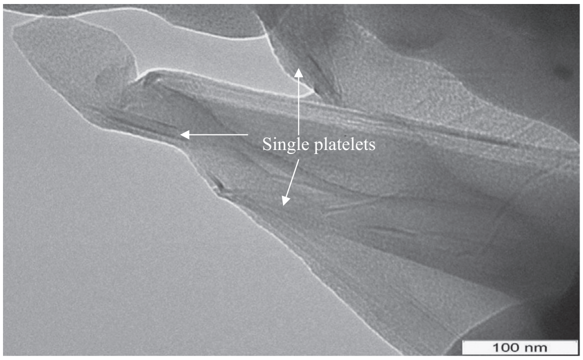

Fig. 8. TEM picture of 0.5% (w/w based on solid PF) nanoclay content in low molecular weight phenol formaldehyde resin.

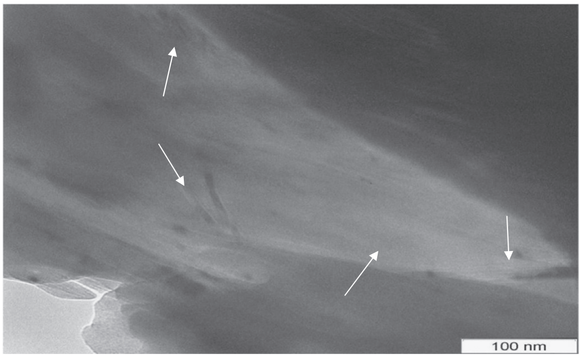

Fig. 9. TEM picture of 1.0% (w/w based on solid PF) nanoclay content in low molecular weight phenol formaldehyde resin. Grey clouds represent polymer and dark lines represent nanoclay.

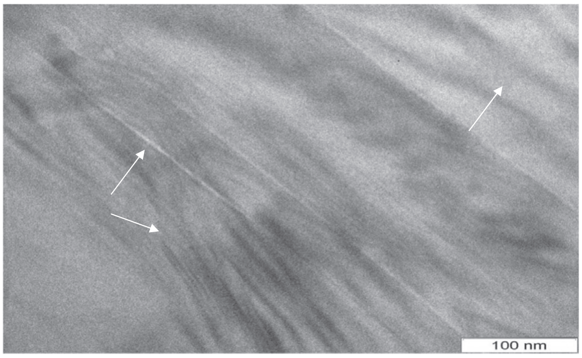

Fig. 10. TEM picture of 1.5% (w/w based on solid PF) nanoclay content in low molecular weight phenol formaldehyde resin. Grey clouds represent polymer and dark lines represent nanoclay.

XRD can measure the degree of silicate layer dispersion and delamination [25]. This method has also been found to successfully determine the intercalation of nanoparticles in phenolic resin by measuring the gallery distance before and after intercalation [22, 26, 27]. Fig. 7 shows the XRD pattern for polymer admixtures at different nanoclay contents. The peak of neat nanoclay (Nanomer® I31PS) in powder form was used as a reference. The XRD patterns based on Braggs laws Eq. ($2d\sin\theta=\lambda$) showed that the basal spacing of the neat nanoclay was 2.00 nm ($2\theta=4.340°$).

It was found that all the polymer admixtures exhibited no diffraction peaks when compared to neat nanoclay which reflected the incorporation of LmwPF molecules into the interplatelet gallery. This suggests that the amount of nanoclay used in this study was well dispersed in the PF resin. It has been reported that when the characteristic peak reduces in intensity, or changes to a low angle after curing, the nanostructure is considered to be intercalated [27]. However, when no peak is observed in the profiles, and the spacing between platelets is large, this indicates that the platelets are singular and may be exfoliated [18, 28]. This phenomenon indicates that low molecular weight phenol formaldehyde resin can enter the nanoclay layers (intragallery) and separate them. Based on the XRD patterns, nanoclay of 1.5% (based on solid PF) could be the most appropriate amount to be well dispersed in 45% LmwPF resin.

3.3. *Transmission electron microscopy (TEM) analyses*

Transmission electron microscopy analysis was carried out to examine the degree of dispersion in the admixture. This tool has been used by previous researchers to examine the dispersion of nanoclay in phenolic resin [29, 30]. TEM pictures related to the three specimens produced are shown in Figs. 8, 9 and 10. Based on the results, the behaviour of the intercalated state of nanoclay in the resin was well dispersed regardless of the nanoclay content. In particular, specimens with 0.5% nanoclay (Fig. 8) clearly showed a few single platelets, which indicated that there was dispersion in the polymer matrix. This finding is in good agreement with the results of an earlier study using a low amount of nanoclay in phenolic resin [30].

Figs. 9 and 10 show the dispersion of the polymer matrix with higher nanoclay contents of 1.0% and 1.5%, respectively. The pictures show grey clouds and dark lines which represent phenolic resin and nanoclay, respectively. Jiang et al. [27] revealed that the band of this phenomenon reflects that the dispersion is in an exfoliated state. This TEM analysis confirmed the results of the XRD (Fig. 7), where no peak was observed in the polymer admixture.

4. Conclusions

An ultrasonication technique using a sonication bath at a frequency of 50 kHz for 60 min can successfully disperse modified nanoclay up to a loading of 1.5% (based on solid PF) into 45% low molecular weight phenol formaldehyde resin. XRD and TEM analyses confirmed that the nanoclay platelets were either intercalated or exfoliated. Incorporation of this modified nanoclay at concentrations ranging from 0.5% to 1.5% into the resin significantly affected non-volatile content, gelation time and pH values of the polymer matrix. The non-volatile content of the admixture increased, but both gelation time and pH values decreased as the nanoclay content increased. The pH values of the admixtures remained in the alkaline state at all nanoclay concentrations.

Acknowledgement

The researchers would like to thank the Ministry of Science Technology and Environment, Malaysia, for providing the research grant (03-01-04-SF1396).

References

[1] Nasir M, Gupta A, Beg MDH, Chua GK, Kumar A. Fabrication of medium density fibreboard from enzyme treated rubber wood (Hevea brasiliensis) fibre and modified organosolv lignin. Int J Adhes Adhes 2013;44:99–104.

[2] Hill CAS. Wood modification; chemical, thermal and other processes. Chichester: John Wiley and Sons; 2006.

[3] Ryu JY, Takahashi M, Immamura Y, Sato T. Biological resistance of phenol-resin treated wood. Mokuzai Gakkaishi 1991;37(9):852–8.

[4] ZaidonA, BakarES, ParidahMT. Compreg laminates made from low density tropical hardwood. In: Proceedings of the International Convention of Society of Wood Science and Technology and United Nation Economic Commission for Europe, Geneva, October 11–14; 2010.

[5] Rowel RM. Chemical modification of wood. In: Rowell RM, editor. Boco Raton: CRC Press; 2005. p. 381–420.

[6] Furuno T, Imamura Y, Kajita H. The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. Wood Sci Technol 2004;37:349–61.

[7] Paridah MT, Loh YF. Enhancing the performance of oil palm stem plywood via treatment with low molecular weight phenol formaldehyde. In: Sapuan SM, editor. Selangor: Universiti Putra Malaysia Press; 2009. p. 281–99.

[8] Anwar UMK, Hiziroglu S, Hamdan H, Abd Latif M. Effect of outdoor exposure on some properties of resin-treated plybamboo. Indus Crops Prod 2011;33:140–5.

[9] Hoong YB, Paridah MT, Loh YF, Koh MP, Luqman CA, Zaidon A. Acacia mangium tannin as formaldehyde scavenger for low molecular weight phenol formaldehyde resin in bonding tropical plywood. J Adhes Sci Technol 2010;24:1563–664.

[10] Rabia'tol Adawiyah MA, Zaidon A, Nur Izreen FA, Bakar ES, Mohd Hamami S, Paridah MT. Addition of urea as formaldehyde scavenger for low molecular weight phenol formaldehyde-treated compreg wood. J Trop Forest Sci 2012;24 (3):348–57.

[11] Salari A, Tabarsa T, Khazaeian A, Ahmadreza S. Effect of nanoclay on some applied properties of oriented strand board (OSB) made from underutilized low quality paulownia (Paulownia fortunei) wood. J Wood Sci 2012;58:513–24.

[12] Salari A, Tabarsa T, Khazaeian A, Ahmadreza S. Improving some of applied properties of oriented strand board (OSB) made from underutilized low quality paulownia (Paulownia fortunie) wood employing nano-SiO2. Indus Crops Prod 2013;42:1–9.

[13] Rahman MR, Hamdan S, Islam MS, Saleh AA. Influence of nanoclay/phenol formaldehyde resin on wood polymer nanocomposites. J Appl Sci 2012;12:1481–7.

[14] Cai X, Riedl B, Zhang SY, Wan H. The impact of the nature of nanofillers on the performance of wood polymer nanocomposites. Composites Part A 2008;39:727–38.

[15] Lee J, Giannelis EP. Synthesis and characterization of unsaturated polyester and phenolic resin nanocomposites. synthesis and characterization of unsaturated polyester and phenolic resin nanocomposites. Polym Preprint 1997;38 (2):688–9.

[16] UsukiA, MizutaniT, FukushimaY, FujimotoM, FukumoriK, KojimaY, et al. Composite Materials Containing a Layered Silicate, United States Patent 4889885;1989.

[17] Kaboorani A, Riedl B, Blanchet P. Ultrasonication technique: a method for dispersing nano-clay in wood adhesives. J Nanomater 2013;3:1–9.

[18] Lopez M, Blanco M, Martin M, Mondragon I. Influence of cure conditions on properties of resol/layered silicate nanocomposites. Polym Eng Sci 2012;52:1161–72.

[19] Sonawane S, Chaudhari P, Ghodke S, Ambade S, Gulig S, Mirikar,, et al. A combined effect of ultrasound and nanoclay on adsorption of phenol. Ultrason Sonochem 2008;15:1033–7.

[20] Dean K, Krstina J, Tian W, Varley RJ. Effect of ultrasonic dispersion methods on thermal and mechanical properties of organoclay epoxy nanocomposites. Macromol Mater Eng 2007;292:415–27.

[21] Anonymous. Resin Adhesive Characterization Procedures. Adhesive Laboratory, Mississippi Forest Products Laboratory, Mississippi State University, Mississippi, 1989.

[22] Natali M, Kenny J, Torre L. Phenolic matrix nanocomposites based on commercial grade resols: synthesis and characterization. Compos Sci Technol 2010;70(4):571–7.

[23] Fink JK. Reactive polymers fundamentals and applications: a concise guide to industrial polymer. Norwich: William Andrew; 2003.

[24] Xiong J, Li Y, Wang W, Xia C. Preparation of montmorillonite modified phenolic resin for shell process. Foundry J Agency Res Dev 2009;6(2):119–23.

[25] Aboubakr SH, Kandil UF, Taha MR. Creep of epoxy–clay nanocomposite adhesive at the FRP interface: A multi-scale investigation. Int J Adhes Adhes 2014;54:1–12.

[26] Jiang-ying Y, Lian-qi W, Xian-kun C. Preparation and properties of phenolic resin/ montmorillonite intercalation nanocomposites. J Wuhan Univ Technol-Mater Sci Ed 2003;18:64–7.

[27] Jiang W, Chen SH, Chen Y. Nanocomposites from phenolic resin and various organo-modified montmorillonites: preparation and thermal stability. J Appl Polym Sci 2006;102:5336–43.

[28] Snyder R. Characterization of nanoclay nanocomposites, composites and polycon. USA: American Composites Manufacturers Association; 2007. p. 17–9 October.

[29] Djebbar M, Djafri F, Bouchekara M, Djafri A. Adsorption of phenol on natural clay. Appl Water Sci 2012;2:77–86.

[30] Roh SC, Kwan HJ, Kim CK. nanocomposites of novolac type phenolic resins and organoclays: the effects of the resin molecular weight and the amine salt structure on the morphology and the mechanical properties of the composites. Macromol Res 2012;20(5):496–502.