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

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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.

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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.

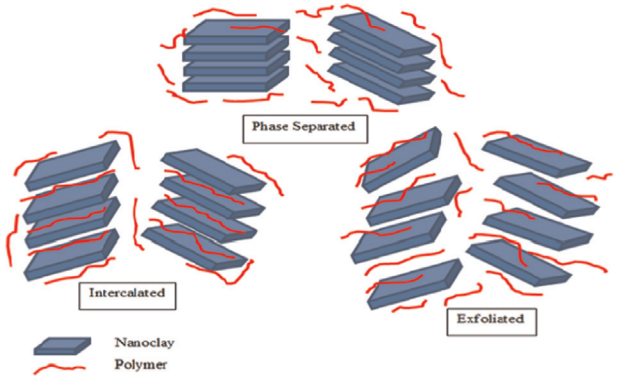

Fig. 1. Dispersion mechanism of nanoclay in resin.

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.

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

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.

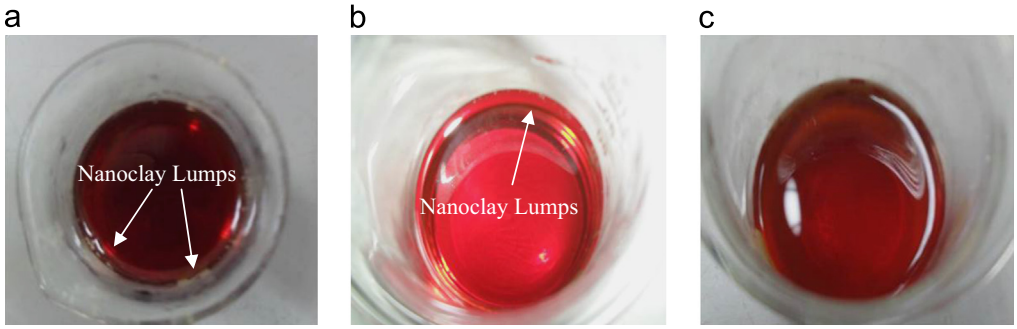

Fig. 2. Appearance of 20 min sonication time of LmwPF/nanoclay. (b) Appearance of 40 min sonication time of LmwPF/nanoclay. (c) Appearance of 60 min sonication time of LmwPF/nanoclay.