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Reduction in formaldehyde emission liberation from urea formaldehyde due to Closite Na^+ addition

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Abstract
The study investigates the role of nanoclay (Closite Na^+) in lowering the formaldehyde liberation from the particle boards. Closite Na^+ was added in various concentrations (0%, 1%, 3%, and 5%) to urea formaldehyde (UF) resin. Particle boards were prepared with the resin and placed in desiccator for formaldehyde measurement. Formaldehyde emission was measured for boards with and without nanoclay loading levels as per Japanese standard 1460 (2001). It was observed that with addition of Closite Na^+ there was noticeable reduction in formaldehyde emission from boards. Lowest emission was observed in the test samples with 1% nano-clay loading.

Keywords: closite Na^+, urea formaldehyde, particle boards, formaldehyde emission

Introduction

Urea formaldehyde is the most widely used adhesives of wood industry. They are known fortheir high reactivity and ease of application. However, their big disadvantage is of formaldehyde emission due to hydrolytic instability of the cured UF resins. Reduction in F/U molar ratio has also been adopted as a strategy in the last decade to decrease formaldehyde emission (Myer 1984). Additives in the form of scavengers, melamine and nano-fillers are also being put to use for reducing formaldehyde emission. Use of nano-fillers to decrease the emissions is quite new. These nano-scale particles with large surface area when added to adhesive have shown significant reduction in emissions. Montmorillonite (NaMMT) nanoclay and other nano particles have been used as alternative to Melamine and Formaldehyde Scavenger (Lei *et al*. 2008) [8]. In the initial studies, decrease in formaldehyde emission form urea formaldehyde adhesives modified with nano-aluminium oxide (Dudkin *et al*. 2006) [3], nano-silica (Lin *et al*. 2006) [6] and nano-crystalline cellulose (Zhenga *et al*. 2003) [13] have been reported. Kumar *et al*. (2013) [6] observed that the free formaldehyde present in UF resin is absorbed on the surface of nano-particles and emission was reduced by 24%. The result also revealed that nano-particles do not affect the crystalline nature of the UF resin at lower levels but at higher levels the crystalline structure was changed. Roumeli *et al*. (2012) [12] reported that due to addition of nano SiO_2 the free formaldehyde emissions were just lowered compared with neat UF in all hybrids. Candan and Akbulut (2013) [2] concluded that the formaldehyde emission values of the plywood panels using 1% Nano-Zinc Oxide, 1% Nano-Aluminium Oxide, and 3% Nano-Silicon Oxide decreased by around 50%, 30%, and 20%, respectively. Against this background a study was taken up to observe the effect of different levels of nanoclay (Cloisite Na^+) on formaldehyde emission from particle boards.

Materials and Method

Bamboo culms were chipped by sickle and were soaked in water for 24 hours. The soaked chips were processed through a Condux mill to obtain particles. Particles were air dried to moisture content of 6%. Urea-Formaldehyde (UF) resin having flow time of 18.30 seconds with a solid content of 50% was prepared in the laboratory. The Cloisite Na^+ (Nano filler) used in this study was procured from Connell Bros. Company (India) Pvt. Ltd. Mumbai. Specifications for nanoclay are listed in Table 1. Three loading levels of nanoclay (1% N_1, 3% N_3 and 5% N_5) based on resin dry weight were used in the manufacture of particle boards. Nanoclay was mixed with the UF resin using a mechanical blender at a speed of 4500 rpm for 10 minutes.

Manufacturing Particle board

UF resin (10% dry wt of particles) was uniformly sprayed on the particles inside a rotary blender at pressure 100 lbs/inch^2. The caul plates were heated up in the hot press and paraffin wax was applied on them. A wooden frame of size 21" x 21" was kept on the plate. The resin-blended particles were uniformly laid to form a mat in wooden frame. This was then manually pre-pressed for 5 minutes to consolidate the thickness of the board. The mats were pressed in a hot press at specific pressure of 21.0 kg/cm^2 and temperature 110°C for 15 minutes. Particle boards were conditioned to moisture content 10 to 12%, for 2-3 days at room temperature before converting to samples. For control and each loading levels of nanoclay three replicate boards were made. For the experimental set-up of each nanoclay loading level 20 samples were placed in the desiccator. Each sample was of size 15 x 5 x 0.7 cm^2 The total surface area for 20 samples (3560 cm^2) was used for estimating formaldehyde emission.Samples preparation was done according to Japanese Building Standards (JIS A 1460: 2001).

Methodology for formaldehyde emission estimation

The desiccator and the glass crystallizing dishes (usually, three pieces) were rinsed thoroughly with water and dried before carrying out test. 300 ml of water was placed in each glass crystallizing dish, which was centrally located at the bottom of the desiccator. The stainless steel wire net was placed on the glass crystallizing dish inside desiccator, and the specimen supports with metal clamp were be placed on it. A desiccator with no test pieces attached was control. The temperature inside the desiccator shall be measured continuously at an interval not exceeding 15 min, and the temperature during the test period was recorded. Background formaldehyde was measured using a desiccator containing no test piece.

Concentration of formaldehyde in the standard stock solution calculated using the procedure and formula mentioned in JIS 1460 (2001) is 30 mg/l. This standard solution is used to prepare calibration curve by UV spectrophotometer. Correlation between the quantity of formaldehyde (0mg to 3mg) and the absorbance was plotted and slope of calibration curve (F) on the standard solution of formaldehyde was obtained by graphical method. The absorbance of formaldehyde in the solution of blank test sample and the solution with test samples N_0, N_1, N_3, and N_5 were measured in UV spectrophotometer at 412 nm wavelength. Concentration of formaldehyde emitted from test samples (G) was calculated according to the formula mentioned in JIS 1460 (2001).

$$G = F^* (Ad - Ab)^* 3560/S$$

Where,

G = Concentration of Formaldehyde from the test pieces (mg/L)

Ad = Absorbance of solution inside desiccator containing test pieces.

Ab = Absorbance of Background Formaldehyde.

F = Slope of calibration curve on the standard solution of Formaldehyde. (Mg/l)

S = Surface area of test Piece.

Results and Discussion

This work indicated the possibility of using nano sized particles of Closite Na$^+$ for controlling emission of formaldehyde from the particle boards. Absorbance of different aliquot levels of formaldehyde standard solution was measured by UV- spectrophotometer (Table 2). Correlation between the quantity of formaldehyde and the absorbance was plotted and slope (F) was obtained (Figure 1). The plotted values give a linear equation y = 0.313 x + 0.081 and linear regression (R_2) of 0.991. Slope (F) of curve is 0.313 mg/l. It can be inferred from the calibrations curve that it follows a linear path. The concentration of formaldehyde emitted from the test pieces into the solution inside desiccator is calculated by Equation 1. The measured absorbance values at 421 nm using spectrophotometer are given in Table 3 along with the mean surface area of each set of samples. The concentration of formaldehyde in solutions (G) for N_0 (as a control) N_1, N_3 and N_5 was calculated to be 2.14 mg/l, 0.626 mg/l, 0.845 mg/l and 0.788 mg/l respectively (Table 3). It can be seen that huge reduction has resulted due to the nanoclay addition in the range of 60% to 70% as a result of different loading levels. Salari *et al.* 2012 [10] has also inferred that depending on the addition of the nanoclay in the panels, the formaldehyde emissions values ranged upto 43% lower than the panels made with untreated UF adhesive. Candan and Akbulut in 2015 [1] also reported that the level of nanoclay significantly affects the formaldehyde emission values of the particleboard and plywood. The particleboards containing urea-glyoxalated lignin-formaldehyde (GLUF) resin and addition of nanoclay (sodium-montmorillonite (NaMMT) up to 1.5%) yielded lower formaldehyde emission as well as water absorption content than those made from the neat GLUF resins (Hamed *et al.* 2017) [4]. Lei *et al* 2008 have inferred that Nano-clays and nano SiO_2 can reduce formaldehyde emissions as they have string absorbability as well as high barrier property.

It can be observed in Table 3 that formaldehyde liberation was higher with higher loading levels. It is well known that nano-materials have high surface area. Increase in the loading levels of the nano-particle may have caused aggregation in the resin, negatively affecting the formaldehyde emission (Candan and Akbulut 2013) [2]. Salem and Bohm 2013, observed in his work on particle boards that with the incorporation of nano-particles into the MUF resin, low formaldehyde emission particle boards could be made. Dudkin *et al* (2006) [3] reported that sorption of formaldehyde on the alumina oxide nano particle surface is accompanied by hydrophobic-hydrophilic effects caused by interactions between the surface and formaldehyde oligomers.

Conclusion

The results of the present work indicate that the release of formaldehyde from bamboo particle boards bonded with urea-formaldehyde resin systems can be reduced noticeably by adding Closite Na$^+$ as filler. It can be concluded that addition of 1% of nanoclay to UF rein has significantly lowered the formaldehyde emission. Samples without nanoclay addition emitted about 3.4 times more formaldehyde compared to boards with 1% nanoclay loadings. Higher concentrations of nanoclay 3% also resulted in much lower emission as compared to control boards. Even though the amount of nanoclay that could be supplemented into the resin is restricted to a low content, nanoclay fillers were able to replace the formaldehyde emission. Also simple mechanical mixing can effectively disperse the nanoclay in the resin matrix.

Table 1: Specifications of Nano clay

Composition	Moisture (%)	Dry particle size µm (d50)	Packed bulk density (g/l)	Density (g/cm^3)	x-ray results nm (d001)	Colour
Cloisite Na^+	4-9	<25	568	2.86	1.17	Off white

Table 2: Absorbance for Formaldehyde Standard solution

Aliquot levels (ml)	0	5	10	20	50	100
Absorbance	0.082	0.211	0.442	0.544	0.648	0.874

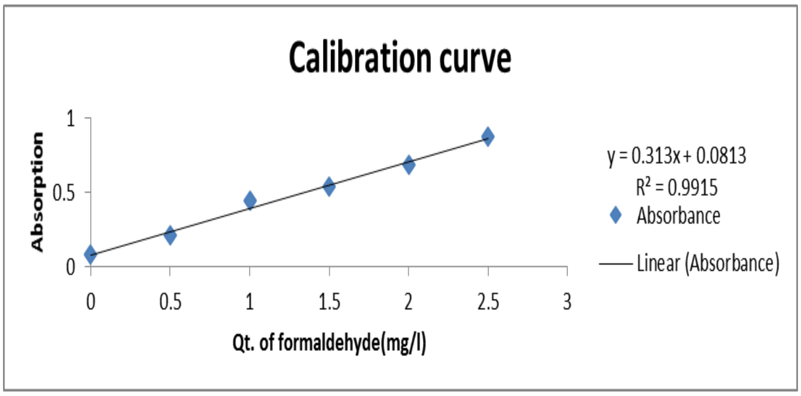

Fig 1: Correlation between the quantity of formaldehyde and the absorbance

Table 3: Results obtained UV- Spectroscopy with water as a solution

Test samples	Absorbance (A)	Measured Concentration (%)	Surface area of each set of samples (cm^2)	Calculated Concentration of formaldehyde (mg/l)
Blank Formaldehyde	1.62 (A_b)	165.2	3560	Nil
N_0	1.96 (A_d)	214.9	3560	2.14
N_1	1.72 (A_d)	211.2	3560	0.626
N_3	1.75 (A_d)	188.8	3560	0.845
N_5	1.74 (A_d)	187.9	3560	0.788

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