

EFFECTS OF ADDITION OF NANOCLAY IN PHENOL-FORMALDEHYDE RESINS ON THE PROPERTIES OF LANTANA CAMARA FIBRE COMPOSITES

Gillela S¹, Yadav SM^{1, *}, Sihag K¹, Kelkar BU^{1, 2}, Dangtungee R^{3, 4} & Bhuyar P^{3, 4}

¹Department of Forest Products and Utilization, Forest College and Research Institute, Hyderabad 502279, Telangana, India

²Institute of Wood Science and Technology, Malleswaram, Bangalore 560 003, India

³Organic Agriculture Management, International College, Maejo University, Nong Han, San Sai, Chiang Mai 50290, Thailand

⁴International Industry and Agriculture Innovation Research Center, International College, Maejo University, Nong Han, San Sai, Chiang Mai 50290, Thailand

*sumitmyadav13@gmail.com

Submitted January 2023; accepted May 2023

This work investigated the effect of the modification of phenol-formaldehyde resins using different concentrations of nanoclay on specific physical and mechanical properties of *Lantana camara* composites. Different concentrations, i.e. 1, 2.5, 4 and 5 wt% nanoclay were added to phenol-formaldehyde adhesive. To ensure uniform distribution, the mixture was stirred mechanically followed by ultrasonication. Following the nanoclay concentrations, the mixtures were labelled accordingly as PF/NC-1, PF/NC-2.5, PF/NC-4 and PF/NC-5. Composites were made from *L. camara* particles mixed with 12% (w/w) nanoclay-fortified phenol-formaldehyde resins. *Lantana camara* composites were fabricated in a hydraulic hot press at a pressure of 21 kg cm⁻² and curing temperature 150 °C for 15 min. The physical and mechanical properties of *L. camara* composites were evaluated following Indian Standards specification IS 3087 (2005). The results revealed that the physical and mechanical properties of *L. camara* composites improved compared with the composites prepared using unmodified phenol-formaldehyde. Composite prepared using phenol-formaldehyde modified with 4% nanoclay showed better performance than the rest of the concentrations. A slight decline in mechanical properties was observed in *L. camara* composites when 5% nanoclay was used due to accumulation of nanoparticles.

Keywords: Modified phenol-formaldehyde, physical properties, mechanical properties

INTRODUCTION

The increased environmental consciousness motivated researchers worldwide to investigate natural fibre polymer composites as a more affordable alternative to synthetic fibre polymer composites. Initially, natural fibre composites gained interest in the academic world, but later they acquired attention in several industrial applications, with the automobile and construction industries serving as primary drivers (Yadav & Yusoh 2015, Sarasini & Fiore 2018). Natural fibres are readily available at a relatively low cost, and the ease of production has enticed researchers to investigate the feasibility of locally available, inexpensive fibres for reinforcement purposes and the extent to which they satisfy the required specifications

of goods for different applications (Bledzki & Gassan 1999). Natural fibres are good renewable resources that are biodegradable and lightweight but have lower strength than synthetic fibres. The energy-intensive manufacturing processes of synthetic fibres and polymers have raised serious questions about the sustainability of conventional composites (Sanjay et al. 2018, Sarasini & Fiore 2018). Natural fibres, such as flax, sisal, bamboo, cotton, banana, ramie, jute, hemp, kenaf, *Lantana*, coir and baggase, have been utilised in the production of composites, sporting goods, parcel racks, musical instruments, vehicle parts and also in the construction field.

India has many potential natural resources

in abundance. Most of them come from forests or agriculture. The potential of the forest weed *Lantana camara* as fibre reinforcement in polymer composites has not been thoroughly investigated. *Lantana camara* is a massively branched shrub that can grow as compact clusters and dense thickets in various environments. The wood is strong and durable, and the stems are thin and square in cross-section with recurved prickles (Reddy 2013). Most of the leaves are about 6 cm long with fine hairs, and the height of the plant is about 2–4 m. It is distributed widely throughout India. Different parts of this plant are used in pharmaceuticals. The root has antimicrobial properties, and stems are utilised as biofuel, low-cost furniture, handicrafts, household items and composites manufacturing (Kannan et al. 2008, Ganjewala et al. 2009, Deo 2010).

Different types of resins, such as phenol-formaldehyde, urea-formaldehyde, epoxy, polypropylene, ethylene vinyl acetate and polyester have been used in the fabrication of natural fibre composites. However, till now, only epoxy, polypropylene and ethylene vinyl acetate resins have been widely used in the fabrication of *L. camara* composites. In this study, phenol-formaldehyde resins were used in the fabrication of *L. camara* composites. Phenol-formaldehyde resin is produced by the interaction of phenol with formaldehyde. Several unique properties of phenolic resins, such as fire retardant, excellent strength properties, thermal stability, dimensional stability, and high-water resistance, have improved their utilisation in the construction, automobile and aerospace industries (Nair 2004, Pilato 2013, Eslami et al. 2015, Tao et al. 2019). Phenolic resins have excellent cost characteristics that outshine current polymers and, thus, are used extensively as binders for wood, paper, glass and other substrates (Nair 2004, Pilato 2013). However, phenol-formaldehyde resins are brittle at room temperature; therefore, many studies have been carried out to enhance their properties through various reinforcements such as fibres, nanofillers and thermoplastic adhesives.

Layered silicate clay minerals are often used as nanofillers due to their availability and adaptability (Ray & Okamoto 2003). Nanofillers may be added in solid form to polymer matrix and lignocellulosic fibres (Yadav & Yusoh 2016,

2019). Nanoparticles have higher surface area, even at low addition levels, which can effectively be used to enhance strength properties, curing behaviour, and fire retardancy of thermosetting polymers (Njuguna et al. 2008, Lubis et al. 2021). Various researchers are currently studying several nano-based materials, such as carbon nanotubes, nanosilica, nanocellulose, and graphene, to better understand their suitability as filler materials in different polymers (Zaghloul et al. 2021). Nanoclay is a natural filler obtained from natural rocks composed of minute crystallites of aluminosilicates in varying quantities along with alkali and alkaline earth metals (Pavlidou & Papaspyrides 2008, Eslami et al. 2015). Montmorillonite and organoclays are extensively used in nanoclay-reinforced polymer composites due to their abundance, high aspect ratio and high reactivity (Yadav & Yusoh 2016, 2019).

There are different types of dispersion methods of nanoclay in a polymer matrix, such as sonication, mechanical stirring, ball milling, high shear mixing, slurry process, and high-pressure mixing. Among these, mechanical stirring followed by the sonication method are simple, cost-effective, and less time-consuming than other methods (Ho et al. 2006).

This study investigated the effect of modified phenol-formaldehyde resins using different concentrations of nanoclay on important resins properties. The primary objective of this research was to develop *L. camara* composites bonded using different concentrations of nanoclay dispersed in phenol-formaldehyde resins. The objective was to understand the effects of using nanoclay fortified phenol-formaldehyde resin for preparation of particleboards. The impact of the addition of nanoclay in phenol-formaldehyde on specific physical and mechanical characteristics of *L. camara* composites was investigated.

MATERIALS AND METHODS

Materials

Lantana camara stems were collected from the Givotia plantation at Forest Research Centre, Mulugu, Telangana, India. All chemicals (phenol (99%), formalin (37%), sodium hydroxide (99%) and nanoclay) used were

commercially purchased and used without further purification.

Synthesis of phenol-formaldehyde resin

Phenol-formaldehyde resins were prepared by taking the molar ratio of phenol to formalin at 1:1.5. Phenol (500 mL), formalin (750 mL) and distilled water (700 mL) were poured into a round bottom flask. Sodium hydroxide pellets (5% w/v of phenol) were added to 50 mL distilled water and mixed into the chemical solution to maintain pH at 9.0–9.5. The mixture was transferred to a resin kettle and was then boiled at 85 °C for 40 min. After that, the temperature was gradually raised, and the composite resins was refluxed for 30 min. The solution was then poured out from the resin kettle into a beaker and kept aside for 24 hours before preparing the composites.

Modification of phenol-formaldehyde resins

Phenol-formaldehyde resins were modified using nanoclay as filler material. The actual weight of the nanoclay for the modification process is summarised in Table 1. In this work, the amount of nanoclay added was calculated based on the solids content of the phenol-formaldehyde resins. The following formula was used to calculate the actual weight of nanoclay needed for the modification of the phenol-formaldehyde resins.

$$\text{Amount of nanoclay added} = \frac{\text{amount of resin (mL)} \times \text{solids content of the resin (\%)}}{100}$$

Each of the nanoclay concentration (1, 2.5, 4 and 5 wt%) was dispersed into the phenol-formaldehyde resins using mechanical stirring

followed by ultrasonication. The mechanical stirring was carried out using an automated stirring machine and a magnetic stirrer bar was placed inside the beaker containing the resins mixture and covered with aluminium foil. The resins mixture beaker was kept on a hotplate at about 900 rpm for 1 hour (Figure 1). In the next stage, the same resins mixture was placed in an ultrasonicator at a frequency of 40 kHz for 1 hour (Solyman et al. 2017). Lastly, the beaker was placed in a cold water bath to avoid effect of heat on the solution, and the temperature was kept constant at 25 °C (Nabil et al. 2015).

Characterisation of modified phenol-formaldehyde resins

Non-volatile solids content

The solids content of phenol-formaldehyde resins was determined by calculating the weight of non-volatile content after drying, i.e. after evaporation of water from known quantity of adhesive. Liquid adhesive was poured into a dry and clean glass Petri dish and actual weight was measured using a digital balance. The Petri dish was kept in an oven at 100 ± 2 °C for 24 hours and the weight of the remaining adhesive was recorded and the percentage of non-volatile content of the adhesive was calculated with respect to initial weight.

pH

An amount of 50 mL resin was poured into a 100 mL beaker, and the pH value was recorded using a digital pH meter.

Flow time

A B-4 ford cup viscometer was used to measure the flow time of phenol-formaldehyde resins. The nanoclay-modified resins were poured into

Table 1 Designed formulations for the modification process

Phenol-formaldehyde (mL)	Amount of nanoclay (w/v %)	Actual weight of nanoclay (g)
1000	1.0	3.8
1000	2.5	9.5
1000	4.0	15.2
1000	5.0	19.0

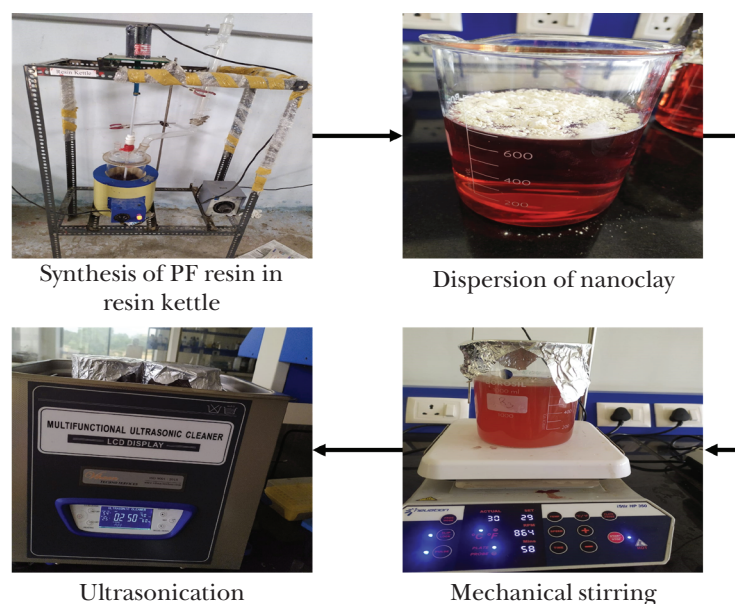


Figure 1 Synthesis and modification of phenol-formaldehyde (PF) resin with nanoclay

the ford cup, and the time the resins took to pass through the ford cup was recorded. The flow time was expressed in seconds.

Preparation of particles

The freshly collected *L. camara* stems were dried in the oven at 105 °C for 2 days. The dried stems were cut into pieces and then converted into particles using a mechanical crusher. These particles were passed through a 60-mesh sieve to obtain uniform particle size of 3–5 mm and then dried to achieve up to 6–8% moisture content before adding phenol-formaldehyde.

Fabrication of *Lantana camara* composites

The required amount of phenol-formaldehyde, *L. camara* particles and nanoclay, were weighed using a digital balance with an accuracy of 0.01 g (Table 2). Dried *L. camara* particles (1000 g) and 12% phenol-formaldehyde resins and the different concentrations of nanoclay were mixed manually in a container. The blended resins particles were air dried at a temperature of 25 ± 2 °C for 6–8 hours to attain a moisture content of 8–10%. The dried particles were then used for mat formation process. In this process, two caul plates were placed on the floor and applied with wax which acted as a release agent. A wooden frame of size 25.4 cm × 25.4 cm

was used for mat formation and pre-pressing (Figure 2).

The resin-blended particles were uniformly laid to form a mat in the wooden frame, and another caul plate was placed over the mat after pre-pressing. The mat between two caul plates was hot pressed at constant pressure and temperature, i.e. 21 kg cm⁻², 150 °C, for 15 min. The composites were removed immediately from the hot press and were conditioned for 2–3 weeks at room temperature and $75 \pm 2\%$ relative humidity. For every combination, five panels were prepared and tested for various physical properties, namely, density, moisture content, water absorption, thickness swelling and mechanical properties namely, MOR, MOE, internal bonding and screw withdrawal strength as specified in the Indian Standards for particle boards of wood and other lignocellulosic materials (IS 3087 2005).

Statistical analysis

SPSS software (IBM, version 20) was used to analyse any changes in the physicommechanical properties of *L. camara* composites at different nanoclay loading levels among the treatment combinations. One-way analysis of variance (ANOVA) was used at the critical difference of 5% significance level. Post-hoc-Tukey test was conducted to analyse the effect of addition of

Table 2 Combination of *L. camara* particles, phenol-formaldehyde and nanoclay

Sample	<i>Lantana camara</i> particles (wt%)	Resin content (%)	Nanoclay (wt%)
LCC	1000	12	0
LCC-1	1000	12	1
LCC-2.5	1000	12	2.5
LCC-4	1000	12	4
LCC-5	1000	12	5

LCC = *Lantana camara* composite; LCC, LCC-1, LCC-2.5, LCC- 4 and LCC-5 correspond to 0, 1, 2.5, 4 and 5 wt% nanoclay in *L. camara* composite

**Figure 2** Fabrication of *L. camara* composites

different concentrations of nanoclay in phenol-formaldehyde adhesive on various properties of the composite.

RESULTS AND DISCUSSION

Characterisation of modified phenol-formaldehyde resins

The physical properties of control and modified phenol-formaldehyde resins, including non-volatile solids content, pH and flow time, are given in Table 3. Four different weight percentages of nanoclay loading studied in this experiment were coded accordingly as PF/NC-1, PF/NC-2.5, PF/NC-4 and PF/NC-5. Results revealed that the addition of 1, 2.5, 4 and 5 wt% of nanoclay showed a decline in the flow time

compared with unmodified PF resins. This is attributed to proper dispersion of nanoclay in phenol-formaldehyde resins. However, compared with neat phenol-formaldehyde resins, modified phenol-formaldehyde resins had higher percentages of solids content. Similar results have been reported by Nabil et al. (2015) and Yadav et al. (2021).

The pH of modified phenol-formaldehyde resins was not affected by the presence of nanoclay. The pH values were lower in nanoclay modified phenol-formaldehyde resins, i.e. decreasing from 9.70 in neat phenol-formaldehyde resins to 9.55 in PF/NC-5 (Table 3). However, the variations in pH values were not significant. The pH reported in the current study is well within the accepted limits of 8–10. Curing time of resins is reduced in alkaline condition (Nabil et al. 2015).

Physical properties of *Lantana camara* composites

Density

The densities of control and nanoclay-loaded composites are tabulated in Table 4. The density of the control board was 807 kg m^{-3} . The addition of nanoclay in phenol-formaldehyde adhesive showed a gradual increment in the density of the composite. Composites with 1, 2.5, 4, and 5 wt% nanoclay had densities of 843, 860, 874, and 888 kg m^{-3} respectively. The increase in density can be attributed to the role of nanoclay particles in pore filling and proper distribution of nanoclay into the polymer matrix (Yadav & Yusoh 2019). These results followed the trend that has been observed in nanoclay modified wood-plastic composites, in which their densities were reported to improve as the concentration of nanoclay increased in polypropylene matrix (Yadav & Yusoh 2019). On the other hand, there are studies that reported a reduction in the density of the composites, especially when higher nanoclay loading percentages were used due to the accumulation of nanoclay particles

(Hakamy et al. 2014). However, in the current study, no such observations were recorded. It is interesting to note that all prepared composites fulfilled the minimum requirement of density following IS 3087 (2005). The results of the statistical analysis carried out for various physical properties are given in Table 5. The analysis confirmed that density increment of the *L. camara* composites after nanoclay addition was significantly different at 95% confidence interval.

Moisture content

The addition of nanoclay into the phenol-formaldehyde resins significantly influenced the moisture content of *L. camara* composites ($p < 0.01$) (Table 4). The moisture contents of LCC, LCC-1, LCC-2.5, LCC- 4 and LCC-5 were 7.80, 6.94, 6.42, 6.12 and 5.90% respectively. Compared with the control, the highest reduction in moisture content (~24%) was observed in LCC-5. These results revealed that incorporating nanoclay into the composite decreased the moisture content values of *L. camara* composites. The decrease in moisture

Table 3 Properties of phenol-formaldehyde resins (PF) without and with nanoclay (NC) loading

Resin sample	Non-volatile solids content (%) [*]	pH [*]	Flow time (s)
PF	37.1 ± 0.3	9.70 ± 0.5	$16.8 \pm 0.1a$
PF/NC-1	38.2 ± 0.5	9.61 ± 0.4	$16.2 \pm 0.3ab$
PF/NC-2.5	38.4 ± 0.2	9.59 ± 0.7	$15.5 \pm 0.8b$
PF/NC-4	38.8 ± 0.6	9.58 ± 0.2	$15.3 \pm 0.2b$
PF/NC-5	38.0 ± 0.2	9.55 ± 0.5	$15.1 \pm 0.6b$

NC-1, NC-2.5, NC-4 and NC-5 correspond to 0, 1, 2.5, 4 and 5 wt% nanoclay added to PF; ^{*}not significant, values followed by the same letter are not statistically different at $p \leq 0.01$ according to the one-way ANOVA test

Table 4 Physical properties of *L. camara* composites with different contents of nanoclay loading

Sample	Density (kg m^{-3})	Moisture content (%)	Water absorption (%)	Thickness swelling (%)
LCC	$807 \pm 1.291a$	$7.80 \pm 0.068a$	$22.74 \pm 0.100a$	9.80 ± 0.041
LCC-1	$843 \pm 1.190b$	$6.94 \pm 0.017b$	$20.95 \pm 0.193b$	8.77 ± 0.206
LCC-2.5	$860 \pm 2.102c$	$6.42 \pm 0.009c$	$20.00 \pm 0.206bc$	9.27 ± 0.193
LCC- 4	$874 \pm 3.326d$	$6.12 \pm 0.009d$	$19.66 \pm 0.144c$	8.15 ± 0.144
LCC-5	$888 \pm 5.391e$	$5.90 \pm 0.079e$	$19.02 \pm 0.287e$	7.77 ± 0.287

LCC = *Lantana camara* composite; LCC, LCC-1, LCC-2.5, LCC- 4 and LCC-5 correspond to 0, 1, 2.5, 4 and 5 wt% nanoclay in *L. camara* composite; values followed by the same letter are not statistically different at $p \leq 0.05$ according to the one-way ANOVA test

Table 5 ANOVA of physical properties of *L. camara* composite panel prepared using different nanoclay content

Independent variable	Dependent variable	Mean square	F-value	p-value
Nanoclay (%)	Density	3942.175	103.469	< 0.01
	Moisture content	2.309	255.544	< 0.01
	Water absorption	8.355	36.220	< 0.01
	Surface absorption	2.694	18.267	< 0.01

content can be attributed to the proper filling of gaps and the voids of the particles with nanoclay that prevented water permeability into the composites (Madhoushi et al. 2014, Jawaidd et al. 2011).

On the other hand, the number of voids also impacts moisture absorption; the higher number of void content, the higher moisture content (Kim et al. 2005). The higher moisture in the composite prepared with unmodified phenol-formaldehyde can be attributed to higher free hydroxyl molecules (Ashori & Sheshmani 2010). This result concurs with that of a study by Kim et al. (2005) where three types of clay (quaternary alkylamine-modified montmorillonite (KH-MT), quaternary ammonium-modified montmorillonite (Cloisite 20A) and octadecylamine-modified montmorillonite (I30P)) were incorporated into an epoxy matrix. The authors reported that lower moisture absorption was seen in 5 wt% Cloisite 20A and I30P due to lower diffusion and better dispersion of clay particles than KH-MT. The majority of *L. camara* composites fulfilled the specification given for moisture content as per IS 3087 (2005).

Water absorption

A water absorption test was conducted for 2 hours for *L. camara* composites (Table 4). Water absorption behaviour will indicate the resistance of *L. camara* composites with and without nanoclay towards natural conditions. A decreasing pattern in water absorption was observed with increasing nanoclay content, similar to the moisture content of *L. camara* composites. The water uptake values for LCC, LCC-1, LCC-2.5, LCC-4 and LCC-5 were 22.74, 20.95, 20.00, 19.66 and 19.02% respectively. The hydrophilic nature of natural fibres creates voids, holes, cracks and microgaps between the matrix and filler and this can result in higher moisture content (Yadav & Yusoh 2019) and

incorporating nanoclay reduced the water uptake in composites.

The nanoclay used may have filled the voids and fibre lumens, which inhibited water from penetrating deeper into the composites by capillary action (Tabari et al. 2011, Madhoushi et al. 2014). The main reason for water absorption is the presence of hydroxyl groups in significant components of natural fibres. Additionally, the presence of porous structures in *L. camara* particles helps to speed up water absorption by capillary forces (Sadik et al. 2021). The *L. camara* composites met the specified water absorption value as per IS 3087 (2005). As a result, the presence of nanoclay dramatically decreased the water absorption in *L. camara* composites boards filled with nanoclay (Table 4). The post-doc results confirmed that the nanoclay addition resulted in significant reduction of water absorption. Chee et al. (2020) reported that organically modified montmorillonite in bamboo/kenaf/epoxy hybrid nanocomposites showed a decrease of 4.19% in moisture absorption compared with bamboo/kenaf/epoxy hybrid halloysite nanotube and bamboo/kenaf/epoxy hybrid montmorillonite at 1% nanofiller loading rate.

Surface absorption and thickness swelling

Thickness swelling values of the nanoclay-reinforced and unreinforced *L. camara* composites after soaking in water for 2 hours are shown in Table 4. The thickness swelling values of LCC, LCC-1, LCC-2.5, LCC-4 and LCC-5 were observed to be 9.80, 9.27, 8.77, 8.15 and 7.77% respectively. Thickness swelling of the nanoclay-reinforced *L. camara* composites decreased compared with total composites after soaking. The highest reduction in thickness swelling was observed in LCC-5, about 20%, compared with unmodified *L. camara* composite. This can be attributed to the better adhesion between

filler and polymeric matrix and pore filling by nanoclay particles, reducing the probability of water entering the composites (Tabari et al. 2011, Zahedsheijani et al. 2012). Nanoclay particles had a positive and significant impact on the thickness swelling of *L. camara* composites, especially at higher loading levels ($p < 0.01$) as shown in Table 5. Lower nanoclay loading did not significantly affect water absorption and thickness swelling of composites (Sadik et al. 2021). Swelling due to surface absorption of the composites decreased with higher nanoclay loading. The trend is similar to that of moisture content and water absorption. This trend was also observed in wood–plastic composites made of linear low-density polyethylene and rice husk reinforced with nanomaterials such as nanoclay and nanosilica (Sadik et al. 2021).

Mechanical properties

Modulus of rupture

The bending strength of the sample under a vertical load is described as the modulus of rupture (MOR). The results conclude that the addition of nanoclay in the phenol-formaldehyde resins in *L. camara* composites improved the flexural characteristics of composites compared with control samples. As shown in Table 6, MOR values for LCC was 11.82 MPa, 12.63 MPa for LCC-1, 14.027 MPa for LCC-2.5, 15.72 MPa for LCC-4 and 14.22 MPa for LCC-5 (Table 6). Incorporating nanoclay into polymer matrix improves strength properties of the polymer (Lei et al. 2010). The composite made using 4 wt% nanoclay exhibited the highest improvement compared with the composite prepared using unmodified phenol-formaldehyde. The higher increment in LCC-4 can be attributed to better nanoclay dispersion, the higher availability of physical cross-linking points and solid interfacial interactions, which can result in high bending resistance by transferring effective stress from matrix to fibres. Quantity, size, apparent coefficient, shape, crystal structure, and method of dispersion of nanoclay into the polymer matrix affect the strength properties of composites (Kord & Kiakojouri 2011). However, the incorporation of 5 wt% nanoclay showed a reduction of 9% in the bending strength of *L. camara* composite compared with LCC-4

due to the accumulation of nanoclay particles. Optimum addition of nanoclay can be beneficial in enhancing the MOR of *L. camara* composites (Lei et al. 2010). Similarly, in the current study, the addition of nanoclay had a significant effect on mechanical properties of LCC, as supported by statistical results represented in Table 7 ($p < 0.01$).

In another study, Candan and Akbulut (2015) evaluated the MOR property of urea formaldehyde/nanofiller-reinforced particleboard composites with different nanomaterials, namely, nano-SiO₂, nano-Al₂O₃, and nano-ZnO. The amounts of nanomaterials used were 1 and 3 wt% and results showed that both nano-SiO₂ and nano-Al₂O₃ improved MOR values but not nano-ZnO.

Modulus of elasticity

Modulus of elasticity (MOE), i.e. bending stiffness values of different *L. camara* composites, are tabulated in Table 6. MOE values of LCC, LCC-1, LCC-2.5, LCC-4 and LCC-5 were 1985.2, 2065.5, 2095.0, 2115.7 and 2104.2 MPa respectively. MOE first increased up to 4 wt% and then decreased at 5 wt%. The reduction of MOE in LCC-5 was observed to be significant ($p < 0.01$) (Table 6). The incorporation of 4 wt% nanoclay in the LCC-4 sample showed improved MOE, which was 6% compared with LCC (without nanoclay) due to uniform dispersion of nanoclay resulting in enhanced interfacial interactions. The addition of a higher amount of nanoclay may create difficulty in obtaining a uniform mixture between a higher amount of nanoclay and phenol-formaldehyde resins (Lei et al. 2010, Candan & Akbulut 2015).

Internal bonding strength

The internal bonding strength values of *L. camara* composites are given in Table 6. The bonding strength was 0.620 MPa for LCC, 0.765 MPa for LCC-1, 0.820 MPa for LCC-2.5, and 0.838 MPa for LCC-4. The results showed that further incorporation of nanoclay into the composite decreased the bonding strength in LCC-5 (0.820 MPa). but the drop was non-significant ($p < 0.01$). This observation is similar to MOR and MOE results of *L. camara*

Table 6 Mechanical properties of *L. camara* composites with different contents of nanoclay

Sample	MOR (MPa)	MOE (MPa)	Internal bonding strength	Screw withdrawal strength (N)
LCC	11.82 ± 0.008a	1985.2 ± 1.250a	0.620 ± 0.011a	2015.00 ± 1.291a
LCC-1	12.63 ± 0.009b	2065.5 ± 1.555b	0.765 ± 0.012b	2115.00 ± 1.291b
LCC-2.5	14.03 ± 0.009c	2095.0 ± 1.472c	0.820 ± 0.009bc	2165.25 ± 1.493c
LCC-4	15.72 ± 0.011d	2115.7 ± 1.250d	0.838 ± 0.017c	2174.25 ± 0.854d
LCC-5	14.22 ± 0.011e	2104.2 ± 1.493e	0.820 ± 0.010c	2171.50 ± 0.645d

LCC = *Lantana camara* composite; LCC, LCC-1, LCC-2.5, LCC-4 and LCC-5 correspond to 0, 1, 2.5, 4 and 5 wt% nanoclay; MOR = modulus of rupture, MOE = modulus of elasticity; values followed by the same letter are not statistically different at p-value ≤ 0.01 according to one-way ANOVA test

Table 7 ANOVA of mechanical properties of *L. camara* composite panel prepared using different nanoclay contents

Independent variable	Dependent variable	Mean square	F-value	p-value
Nanoclay (%)	MOR	9.121	24002.487	< 0.01
	MOE	11044.325	1389.223	< 0.01
	Internal bonding strength	0.032	60.181	< 0.01

MOR = modulus of rupture, MOE = modulus of elasticity

composites. Similar results were reported by Xu et al. (2011) and Fang et al. (2014). Interaction between wood and adhesive and the removal of gaps from the wood surface by the nanoparticles improves bonding strength of plywood panels (Xu et al. 2011). Fang et al. (2014) also reported similar results in *Pinus kesiya* plywood bonded with phenol-formaldehyde modified using various contents of montmorillonite (1–5 wt%).

Screw withdrawal strength

Screw withdrawal values for *L. camara* composites were 2015 N for LCC, 2115 N for LCC-1, 2165.25 N for LCC-2.5, 2174.25 for LCC-4 and 2171.5 for LCC-5 (Table 6). There was a slight gradual increase in screw withdrawal strength as nanoclay loading increased, although the value for LCC-5 decreased slightly but the readings were not significant ($p < 0.01$). This study showed that nanoclay addition did not result in significant improvement in screw withdrawal properties, which was similar to findings by Salari et al. (2013), Madhoushi et al. (2014) and Candan and Akbulut (2015). Due to the low interfacial adhesion between the polymer matrices and the lignocellulosic biomass, adding nanoclay to *L. camara* composites results in weak interfacial bonding and decreased screw pullout strength.

CONCLUSION

This research investigated the modification of phenol-formaldehyde resins using nanoclay and its effects on the physical and mechanical properties of *L. camara* composites. Results show that as the nanoclay levels (i.e. 1, 2.5, 4, and 5 wt%) increased, the solids content of modified phenol-formaldehyde resins also increased compared with neat phenol-formaldehyde resin. However, flow time and pH decreased slightly. The modification of phenol-formaldehyde resins by nanoclay improved interaction and adhesion between *L. camara* particles and the resins. Incorporating nanoclay into phenol-formaldehyde has significantly affected the physical and mechanical properties of *L. camara* composites. The results revealed that integrating high content of nanoclay (5 wt%) enhanced density by 10% and reduced moisture content by 24%, water absorption by 17% and swelling due to surface absorption by 20% compared with control. However, the mechanical properties of composites decreased at 5 wt% of nanoclay in LCC-5. The improvement in physical and mechanical properties of LCC-4 highlighted the effectiveness of nanoclay as reinforcement in composites, and the high impact of nanoclay was achieved at 4 wt%.

It showed that nanoclay loading at 4 wt% exhibited an increment in MOR by 32%, MOE by 6%, internal bonding strength by 35% and screw withdrawal strength by 7.8%. From these results it was concluded that the addition of 4% of nanoclay in phenol-formaldehyde resin resulted in optimum improvements in various physical and mechanical properties of *L. camara* composite. Addition of more than nanoclay 4% did not result in any significant improvements in physico-mechanical properties. Thus, it was concluded that proper dispersion of nanoclay and proportion of nanoclay content influenced adhesion and overall improvement in the properties of phenol-formaldehyde resins, thus affecting the physical and mechanical properties of *L. camara* composites and can be utilised for various value-added applications such as panelling, furniture and decorative crafts.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Forest College and Research Institute, Hyderabad, India.

REFERENCES

- ASHORI A & SHESHMANI S. 2010. Hybrid composites made from recycled materials: moisture absorption and thickness swelling behavior. *Bioresource Technology* 101: 4717–4720. <https://doi.org/10.1016/j.biortech.2010.01.060>
- BLEDZKI AK & GASSAN J. 1999. Composites reinforced with cellulose based fibres. *Progress in Polymer Science* 24: 221–274. [https://doi.org/10.1016/S0079-6700\(98\)00018-5](https://doi.org/10.1016/S0079-6700(98)00018-5)
- CANDAN Z & AKBULUT T. 2015. Physical and mechanical properties of nanoreinforced particleboard composites. *Maderas. Ciencia y Tecnología* 17: 319–334. <http://dx.doi.org/10.4067/S0718-221X2015005000030>
- CHEE SS, JAWAID M, SULTAN MTH, ALOTHMAN OY & ABDULLAH LC. 2020. Effects of nanoclay on physical and dimensional stability of bamboo/kenaf/nanoclay reinforced epoxy hybrid nanocomposites. *Journal of Materials Research and Technology* 9: 5871–5880. <https://doi.org/10.1016/j.jmrt.2020.03.114>
- DEO CR. 2010. Polymer matrix composite using natural fiber *Lantana-camara*. PhD thesis, National Institute of Technology, Rourkela.
- ESLAMI Z, YAZDANI F & MIRZAPOUR MA. 2015. Thermal and mechanical properties of phenolic-based composites reinforced by carbon fibres and multiwall carbon nanotubes. *Composites Part A: Applied Science and Manufacturing* 72: 22–31. <https://doi.org/10.1016/j.compositesa.2015.01.015>
- FANG Q, CUI HW & DU GB. 2014. Montmorillonite reinforced phenol formaldehyde resin: preparation, characterization, and application in wood bonding. *International Journal of Adhesion and Adhesives* 49: 33–37. <http://dx.doi.org/10.1016/j.ijadhadh.2013.12.011>
- GANJEWALA D, SAM S & KHAN KH. 2009. Biochemical compositions and antibacterial activities of *Lantana camara* plants with yellow, lavender, red and white flowers. *Eurasian Journal of BioSciences* 3: 69–77. doi:10.5053/ejobios.2009.3.0.10
- HAKAMY A, SHAIKH FUA & LOW IM. 2014. Thermal and mechanical properties of hemp fabric-reinforced nanoclay-cement nanocomposites. *Journal of Materials Science* 49: 1684–1694. <https://doi.org/10.1007/s10853-013-7853-0>
- HO MW, LAM CK, LAU KT, NG DHL & HUI D. 2006. Mechanical properties of epoxy-based composites using nanoclays. *Composite Structures* 75: 415–421. <https://doi.org/10.1016/j.compstruct.2006.04.051>
- IS (INDIAN STANDARDS) 3087. 2005. *Particle Boards of Wood and Other Lignocellulosic Materials for General Purposes Specification*. Bureau of Indian Standards, New Delhi.
- JAWAID MHPS, ABDUL KHALIL HPS, NOORUNNISA K & ABU BAKAR A. 2011. Hybrid composites made from oil palm empty fruit bunches/jute fibres: water absorption, thickness swelling and density behaviours. *Journal of Polymers and the Environment* 19: 106–109. <https://doi.org/10.1007/s10924-010-0203-2>
- KANNAN R, ARAVIND NA, JOSEPH G, GANESHAIAH KN & SHAANKER RU. 2008. *Lantana* craft: a weed for a need. *Biotech News* 3: 9–11.
- KIM JK, HU C, WOO RS & SHAM ML. 2005. Moisture barrier characteristics of organoclay-epoxy nanocomposites. *Composites Science and Technology* 65: 805–813. <https://doi.org/10.1016/j.compscitech.2004.10.014>
- KORD B & KIAKOJOURI SMH. 2011. Effect of nanoclay dispersion on physical and mechanical properties of wood flour/polypropylene/glass fiber hybrid composites. *BioResources* 6: 1741–1751.
- LEI H, DU G, PIZZI A, CELZARD A & FANG Q. 2010. Influence of nanoclay on phenol-formaldehyde and phenol-urea-formaldehyde resins for wood adhesives. *Journal of Adhesion Science and Technology* 24: 1567–1576. <https://doi.org/10.1163/016942410X500945>
- LUBIS MAR, YADAV SM & PARK BD. 2021. Modification of oxidized starch polymer with nanoclay for enhanced adhesion and free formaldehyde emission of plywood. *Journal of Polymers and the Environment* 29: 2993–3003. <https://link.springer.com/article/10.1007/s10924-021-02101-w>
- MADHOUSHI M, CHAVOOSHI A, ASHORI A, ANSELL MP & SHAKERI A. 2014. Properties of wood plastic composite panels made from waste sanding dusts and nanoclay. *Journal of Composite Materials* 48: 1661–1669. <https://doi.org/10.1177/0021998313489899>
- NABIL FL, ZAIDON A, JAWAID M ET AL. 2015. Physical and

- morphological properties of nanoclay in low molecular weight phenol formaldehyde resin by ultrasonication. *International Journal of Adhesion and Adhesives* 62: 124–129. <https://doi.org/10.1016/j.ijadhadh.2015.07.012>
- NAIR CPR. 2004. Advances in addition-cure phenolic resins. *Progress in Polymer Science* 29: 401–498. <http://dx.doi.org/10.1016/j.progpolymsci.2004.01.004>
- NJUGUNA JAK, PIELICHOWSKI K & DESAI S. 2008. Nanofiller-reinforced polymer nanocomposites. *Polymers for Advanced Technologies* 19: 947–959. <http://dx.doi.org/10.1002/pat.1074>
- PAVLIDOU S & PAPASPYRIDES CD. 2008. A review on polymer-layered silicate nanocomposites. *Progress in Polymer Science* 33: 1119–1198. <https://doi.org/10.1016/j.progpolymsci.2008.07.008>
- PILATO L. 2013. Phenolic resins: 100 years and still going strong. *Reactive and Functional Polymers* 73: 270–277. <http://dx.doi.org/10.1016/j.reactfunctpolym.2012.07.008>
- RAY SS & OKAMOTO M. 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science* 28: 1539–1641. <https://doi.org/10.1016/j.progpolymsci.2003.08.002>
- REDDY NM. 2013. *Lantana camara* Linn. chemical constituents and medicinal properties: a review. *Scholars Academic Journal of Pharmacy* 2: 445–448.
- SADIK WAA, EL DEMERDASH AGM, ABBAS R & BEDIR A. 2021. Effect of nanosilica and nanoclay on the mechanical, physical, and morphological properties of recycled linear low-density polyethylene/rice husk composites. *Journal of Polymers and the Environment* 29: 1600–1615. <https://doi.org/10.1007/s10924-020-01983-6>
- SALARI A, TABARSA T, KHAZAEIAN A & SARAEIAN A. 2013. Improving some of applied properties of oriented strand board (OSB) made from underutilized low-quality paulownia (*Paulownia fortunei*) wood employing nano-SiO₂. *Industrial Crops and Products* 42: 1–9. <https://doi.org/10.1016/j.indcrop.2012.05.010>
- SANJAY MR, MADHU P, JAWAID M, SENTHAMARAIKANNAN P, SENTHIL S & PRADEEP S. 2018. Characterization and properties of natural fiber polymer composites: a comprehensive review. *Journal of Cleaner Production* 172: 566–581. <https://doi.org/10.1016/j.jclepro.2017.10.101>
- SARASINI F & FIORE V. 2018. A systematic literature review on less common natural fibres and their biocomposites. *Journal of Cleaner Production* 195: 240–267. <https://doi.org/10.1016/j.jclepro.2018.05.197>
- SOLYMAN WSE, NAGIUB HM, ALIAN NA, SHAKER NO & KANDIL UF. 2017. Synthesis and characterization of phenol/formaldehyde nanocomposites: studying the effect of incorporating reactive rubber nanoparticles or cloisite-30B nanoclay on the mechanical properties, morphology and thermal stability. *Journal of Radiation Research and Applied Sciences* 10: 72–79. <https://doi.org/10.1016/j.jrras.2016.12.003>
- TABARI HZ, NOURBAKSH A, ASHORI A ET AL. 2011. Effects of nanoclay and coupling agent on the physico-mechanical, morphological, and thermal properties of wood flour/polypropylene composites. *Polymer Engineering and Science* 51: 272–277. <http://dx.doi.org/10.1002/pen.21823>
- TAO Y, LI P, CAI L & SHI SQ. 2019. Flammability and mechanical properties of composites fabricated with CaCO₃-filled pine flakes and phenol formaldehyde resin. *Composites Part B: Engineering* 167: 1–6. <http://dx.doi.org/10.1016/j.compositesb.2018.12.005>
- XU HN, MA S, LV W & WANG Z. 2011. Soy protein adhesives improved by SiO₂ nanoparticles for plywoods. *Pigment & Resin Technology* 40: 91–195. <http://dx.doi.org/10.1108/03699421111130469>
- YADAV SM & YUSOH KB. 2015. Mechanical and physical properties of wood-plastic composites made of polypropylene, wood flour and nanoclay. *International Journal of Agriculture, Forestry and Plantation* 1: 52–58.
- YADAV SM & YUSOH KB. 2016. Preparation and characterization of wood plastic composite reinforced by organoclay. *Journal of the Indian Academy of Wood Science* 13: 118–131. <http://dx.doi.org/10.1007/s13196-016-0175-5>
- YADAV SM & YUSOH KB. 2019. Sub-surface mechanical properties and sub-surface creep behavior of wood-plastic composites reinforced by organoclay. *Science and Engineering of Composite Materials* 26: 114–121. <http://dx.doi.org/10.1515/secm-2016-0291>
- YADAV SM, LUBIS MAR, WIBOWO ES & PARK BD. 2021. Effects of nanoclay modification with transition metal ion on the performance of urea-formaldehyde resin adhesives. *Polymer Bulletin* 78: 2375–2388.
- ZAGHLOUL MYM, ZAGHLOUL MOUSTAFA MY & ZAGHLOUL MAI MY. 2021. Developments in polyester composite materials—an in-depth review on natural fibres and nano fillers. *Composite Structures* 278: 114698. <https://doi.org/10.1016/j.compstruct.2021.114698>
- ZAHEDSHEIJANI R, FAEZIPOUR M, TARMIAN A, LAYEGHI M & YOUSEFI H. 2012. The effect of Na⁺ montmorillonite (NaMMT) nanoclay on thermal properties of medium density fiberboard (MDF). *European Journal of Wood and Wood Products* 70: 565–571. <http://dx.doi.org/10.1007/s00107-011-0583-6>