Effects of Nanoclay Modification with Aminopropyltriethoxysilane (APTES) on the Performance of Urea–formaldehyde Resin Adhesives

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Urea-formaldehyde (UF) resins, as the most common adhesives for wood-based composites, emit formaldehyde, which is forcing producers to find a solution to this problem. Using scavengers is a practical way of reducing formaldehyde emissions, but sometimes these materials change the properties of the adhesive. This study investigated the effect of adding nanoclay and nanoclay modified with aminopropyltriethoxysilane (APTES), as scavengers, on the formaldehyde emission and the properties of the urea-formaldehyde resin. Modification of nanoclay with APTES was confirmed by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis. After the addition of nanoclay and modified nanoclay to the urea-formaldehyde resin, the emission of formaldehyde decreased by 22% and 61%, and the physical and mechanical properties were improved. The FTIR, XRD, and differential scanning calorimetry results showed that the addition of nanoclay and modified nanoclay improved the characteristics of the adhesive, reduced the crystalline areas, and delayed the curing of the adhesive. Additionally, according to thermogravimetric analysis results, addition of nanoclay and modified nanoclay increased the thermal stability and reduced the weight loss of urea formaldehyde resin.

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INTRODUCTION

The oldest thermoset resins are those based on formaldehyde and are urea-formaldehyde (UF) resins (Wibowo *et al.* 2020). For high reactivity, fast curing time, low cost, clear color, and strong bonding ability, UF resins are often used as adhesives in producing wood-based composites such as particleboard, medium-density fiberboard, and plywood (Dunky 1998; Park *et al.* 2006). However, they have a significant problem: formaldehyde emissions (He *et al.* 2012). The UF resin-bonded wood-based composites typically release free formaldehyde or formaldehyde produced during hydrolysis. Formaldehyde emissions cause indoor air pollution and health problems, which have become a significant concern in recent decades (Kaiser 1989). As a result, numerous researchers have tried to lower these emissions from wood-based composites (Lee *et al.* 2020; Wibowo *et al.* 2020).

The addition of proper additives, often known as formaldehyde scavengers, is one way that helps reduce formaldehyde emissions from wood-based composites. Formaldehyde scavengers, which may be used post-treatment and as a modifier added to the resin during homogenization, are generally defined as compounds with the potential to bind free formaldehyde. These include chemicals, mineral particles, phenolic substances, protein-rich particles, nanoparticles, *etc.* (Tohmura *et al.* 2001; Park and Jeong 2011b; Zaidon *et al.* 2015; Antov *et al.* 2020; Kristak *et al.* 2022). It is still an aim for UF resins to develop such additives that lessen harmful emissions without degrading the mechanical and physical properties of wood-based composites (Kawalerczyk *et al.* 2022).

The most functional reactive group for formaldehyde adsorption is the amine (NH$_2$) group. Both the resin's free formaldehyde and the panel's hydrolyzed formaldehyde can react with amine groups (Park and Jeong 2011a). Although this reaction reduces the formaldehyde emission, it also reduces cross-links, because formaldehyde is necessary to complete these links. For this reason, using basic amine additives sometimes decreases the mechanical properties of panels. Therefore, it is necessary to use a reinforcing material such as nanoclay in addition to basic amine additives.

Nanoclay can be utilized to improve the crosslinking of UF resin. The performance of UF resin can be enhanced by using nanoclays, such as montmorillonite (MMT), either by intercalation or exfoliation. Intercalation of the monomers into the clay layers triggers the gallery distance expansion, followed by the polymer chain growing and perhaps forming a cross-linked network during curing (Lei *et al.* 2008; Lei *et al.* 2010; Wu *et al.* 2019; Wibowo *et al.* 2020). One of the technical issues with using nanoclay is the nanoparticles' clumping and aggregate formation that causes blocking the adhesive nozzles and creates a point for stress concentration (Shokri and Yegani 2017). The chemical modification of nanoclay is the best solution for this issue.

According to several studies, the nanoclay surface can be modified by 3-aminopropyltriethoxysilane (APTES). The APTES may react with nanoclay on one end and polymer on the other (Bertuoli *et al.* 2014; Feiz *et al.* 2018; Khanjanzadeh *et al.* 2018). Modifying nanoclay with APTES, as a basic amine additive, can reduce formaldehyde emissions (Khanjanzadeh *et al.* 2018; Khorramabadi *et al.* 2023). It is also expected to prevent clumping and aggregation of nanoclay particles and improve their distribution in the material matrix (Bertuoli *et al.* 2014; Shokri and Yegani 2017; Khorramabadi *et al.* 2023). In addition, using modified nanoclay improves the physical and mechanical properties of MDF panels because nanoclay can cross-link with UF resin. On the other hand, nanoclay as a filler distributes stress in the material matrix, thus improving physical and mechanical resistance (Lei *et al.* 2008; Roumeli *et al.* 2012; Shokri and Yegani 2017; Khorramabadi *et al.* 2023). Therefore, in addition to investigating the effect of modified nanoclay on formaldehyde release and the physical and mechanical properties of MDF panels, it is necessary to study its impact on the properties of the UF resin. It can help to comprehensively investigate the effect of multifunctional additives on the properties of UF resin and MDF panels.

This study considered the effect of nanoclay (NC) and modified nanoclay with APTES (NCA) on formaldehyde emissions and UF adhesive. To confirm the amino groups in the nanoclay structure, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) were used. The FTIR was used to consider functional groups of UF resin before and after adding nanoclay and modified nanoclay. In addition, XRD was also utilized to compare the crystallinity of resin. Furthermore, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were also used to investigate the influence of nanoclay

and modified nanoclay on the thermal curing behavior of UF resins. Finally, the formaldehyde emissions and physical and mechanical properties of MDF containing 2.5% nanoclay and modified nanoclay were examined.

EXPERIMENTAL

Materials

Natural montmorillonite (MMT) as nanoclay was bought from Sigma-Aldrich Burlington, Massachusetts, United States. The APTES was bought from Merck Chemical Co., Darmstadt, Germany. Particle size, density, specific surface area, moisture, ion exchange capacity, and space between particles (Å) of nanoclay are 0 to 5.7(nm), 0.5 to 0.7(g /cm^3), 220 to 270(m^2/gr), 1 to 2 (%), 48 (meg/100 gr) and 60(Å), respectively.

Methods

Nanoclay modification

A total of 1 g of nanoclay was dried at 60 °C for 24 h before being dispersed in 100 mL of distilled water with magnetic stirring for 1 h. Separately, 1 g of APTES was dissolved in 100 mL of distilled water and added to the nanoclay. For 30 min, the clay mineral and APTES mixture were mixed at 30 °C. Then, the modified nanoclay was separated, washed with distilled water, and dried at 60 °C for 24 h (Bertuoli *et al.* 2014).

FTIR spectroscopy

Fourier infrared (FTIR) spectroscopy (TENSOR 27; Brucker, Billerica, Massachusetts, U.S) was used to confirm amino groups in the clay minerals. Additionally, this analysis was conducted to determine the functional groups of UF resin and modified UF resins. For preparing modified UF resins, UF resin was mixed with 2.5% nanoclay and modified nanoclay (based on the solid content of UF resin) for 10 min. Samples were made by adding 3% NH$_4$Cl (30 wt%) as a hardener to the liquid UF resins. A total of 3 g of the mixture was put in aluminum weighing boats to cure for 24 h at 50 °C. Then, for analysis, all samples were ground to a powder. The powders of UF resin, modified UF resins, nanoclay, and modified nanoclay were scanned using the KBr pellet method (5 mg sample in 300 mg KBr) with a spectral resolution of 8 cm^{-1}, spanning 400 to 4000 cm^{-1}.

XRD analysis

To prove the modification of nanoclay in the range of 0 to 10° and to analyze the crystallinity of neat UF resin and modified resin in the range of 10 to 80°, an XRD (D8 ADVANCE; Bruker, Bremen, Germany) with a CuK radiation source (= 0.15406 nm) was used. Powder samples of nanoclay, modified nanoclay, UF resin, and modified UF resins were scanned using XRD at room temperature from 0 to 50° with a step of 0.02°/min. The d$_{001}$ d-spacing values of the silicate layers of nanoclay and modified nanoclay were calculated using Bragg's equation.

DSC analysis

The curing behavior of UF resin and modified UF resins was examined using DSC DSC (DSC8231; Rigaku, Tokyo, Japan. About 5 to 6 mg of the sample was mixed with 3% NH$_4$Cl (based on the amount of solids in the UF resin). The mixture was put in a high-

pressure capsule pan and sealed to keep water from evaporating during DSC scanning. Each sample was heated from 30 to 200 °C at a heating rate of 10 °C/min under a nitrogen flow. The onset temperature, peak temperature, and reaction heat were recorded. The area of the exothermic peak was added together to obtain the reaction heat, which was given as joules per gram (J/g) of solid resin.

TGA analysis

The TGA (TGD-9800; ADVANCE RIKO, Meguro-ku, Tokyo) was performed on the UF resin and modified UF resin samples to determine the weight loss as a function of temperature. Approximately 5 mg of the samples were analyzed and heated from 25 to 500 °C at a rate of 10 °C/min under nitrogen.

Preparation of fiberboards

The boards were manufactured using 12% UF resin based on the oven-dry weight of wood fibers and 3% ammonium chloride (30% wt) oven-dry weight of the resin. The Production Parameters of MDF Panels are presented in Table 1.

After pre-testing and evaluating mechanical and physical properties and formaldehyde emission of MDF boards, the optimal treatment to add nanoclay and modified nanoclay was determined 2.5%. So, nanoclay and modified nanoclay were added to the resin at 2.5% based on the oven-dry weight of the resin and, at room temperature, were mixed with UF resin for 10 min.

Table 1. The Production Parameters of MDF Panels

Production Parameters	Values
Press temperature (°C)	175
Press pressure (kg/cm^2)	35
Mat dimension (mm^2)	320 × 310
Press time (min)	5
Thickness (m)	10
Density(g/cm$^{3)}$)	0.75

Formaldehyde emission

Using the desiccator method, the formaldehyde emissions from MDF samples were evaluated according to ISO 12460-4 (2016) standard. The total area of the ends, sides, and faces was estimated as roughly 1800 cm^2. Before testing, the samples were conditioned for a week at (20 °C) and (65 %) relative humidity (RH).

The desiccator was filled with the samples. The desiccator, without any test samples, was used as the control sample. Using a UV spectrophotometer (SmartSpecTM Plus; BIORAD, Hercules, California, US) with a wavelength of 412 nm, the absorbance of formaldehyde in a solution containing a blank test sample and a solution containing test samples was assessed after 24 h. For every panel variation, there were two repetitions. A third repetition is performed only when there is a 20% or greater difference between the two measurements.

Mechanical and physical testing

The physical and mechanical properties of the boards without (UF) and with nanoclay (UF+ NC) and modified nanoclay (UF+ NCA) were investigated after placing them for three weeks at a temperature of 20 °C and humidity of 65%. Thickness swelling

(TS) for 24 h was measured according to EN 317 standards. In addition, the modulus of rupture (MOR) and modulus of elasticity (MOE) were analyzed by the EN 310 standard. Finally, internal bonding (IB) was determined by the EN 319 standard.

RESULTS AND DISCUSSION

Nanoclay Modification

Figure 1 shows the received FTIR data of nanoclay and modified nanoclay. The absorption bands at 1450 cm^{-1}, the band at 1570 cm^{-1}, and the band at 2850 cm^{-1} are related to the stretching asymmetric and symmetric CH$_2$ groups, NH$_2$'s bending vibration, and the stretching vibrations of the CH band, respectively (Piscitelli *et al.* 2010; Park and Jeong 2011a; Mishra *et al.* 2012; Shokri and Yegani 2017; Khorramabadi *et al.* 2023). Changing the -CH and -NH bands in FTIR demonstrated that APTES had effectively functionalized the nanoclay surface (Piscitelli *et al.* 2010; Mishra *et al.* 2012; Khorramabadi *et al.* 2023).
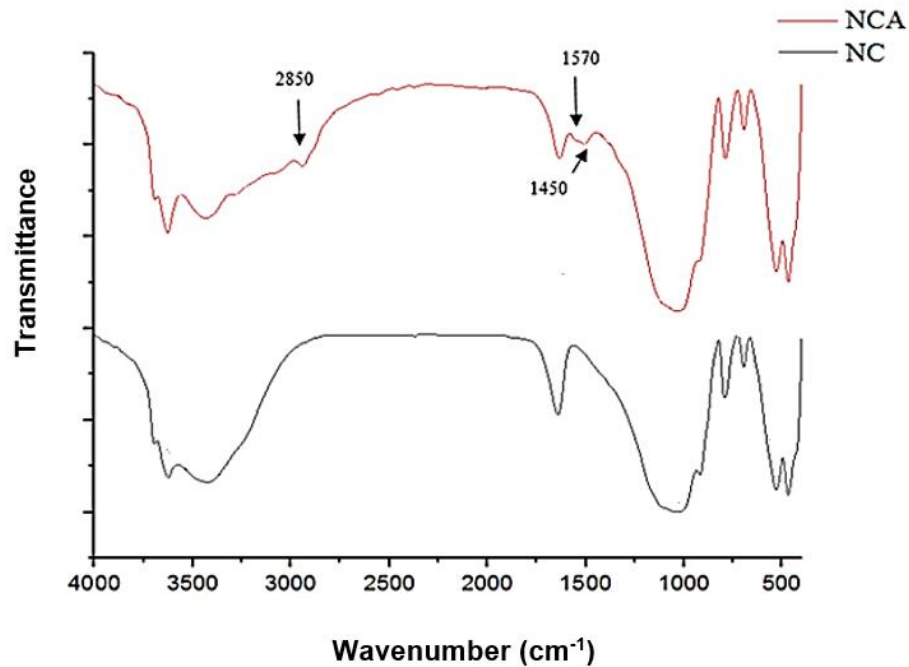

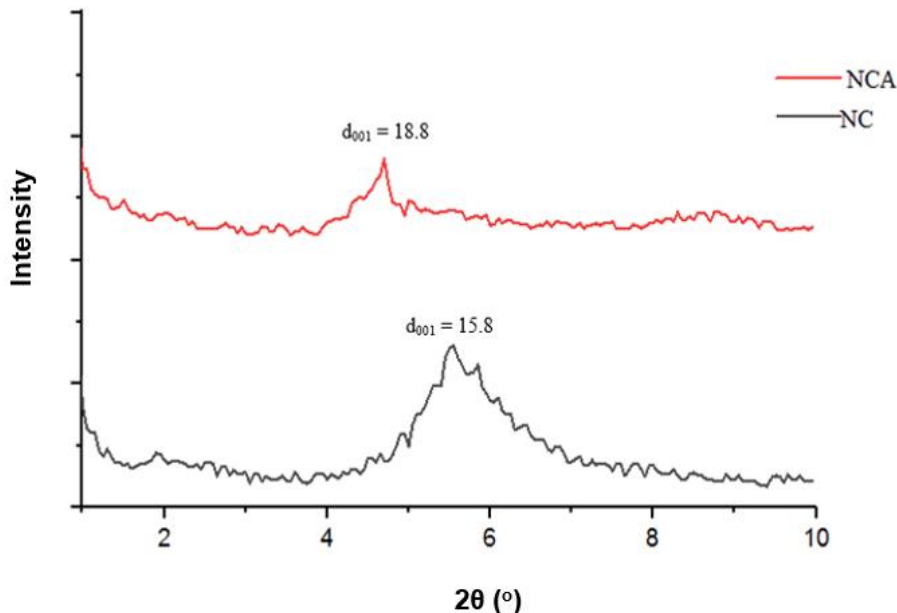**Fig .1.** FTIR of the nanoclay and modified nanoclay

Fig. 2. X-ray of the nanoclay and modified nanoclay

An increase in d-spacing indicates the intercalation of nanoclay. The nanoclay peak was at $2\theta = 5.55°$ with a basal spacing of 15.8 (Fig. 2). After modification, this peak shifted to 4.7° with a basal spacing of d001 = 18.8. An increase in d-spacing indicates APTES molecules were intercalated or grafted in the interlayer region or at the clay's edges (Shanmugharaj *et al.* 2006, Mishra *et al.* 2012; Khorramabadi *et al*. 2023).

Formaldehyde emission

Figure 3 shows how formaldehyde emissions from MDF boards were affected by the quantity of nanoclay and modified nanoclay. The addition of nanoclay and modified nanoclay to the urea-formaldehyde resin at 2.5% reduced the formaldehyde emissions by 22% and 61%, respectively. The reduction in formaldehyde emissions from the boards made with modified nanoclay was sufficient to meet the E1 standard. Therefore, by adding modified nanoclay, it is possible to make safe boards that do not endanger human health.

The interaction of nanoclay with resin and the creation of C-O-Si rings may cause decreased formaldehyde emission after adding nanoclay. This reaction increased the bond strength and reduced the amount of free formaldehyde (Pizzi 1994; Lin *et al.* 2006; Khorramabadi *et al.* 2023). After addition of modified nanoclay, amine groups react with formaldehyde released from urea formaldehyde resin. Therefore, the density of amino methylene bonds throughout the resin chain is reduced (Pizzi 1994; Ghani *et al.* 2018; Khorramabadi *et al.* 2023). For this reason, the amount of formaldehyde emissions in boards made with modified nanoclay is much lower than in boards made with pure resin and boards containing nanoclay.
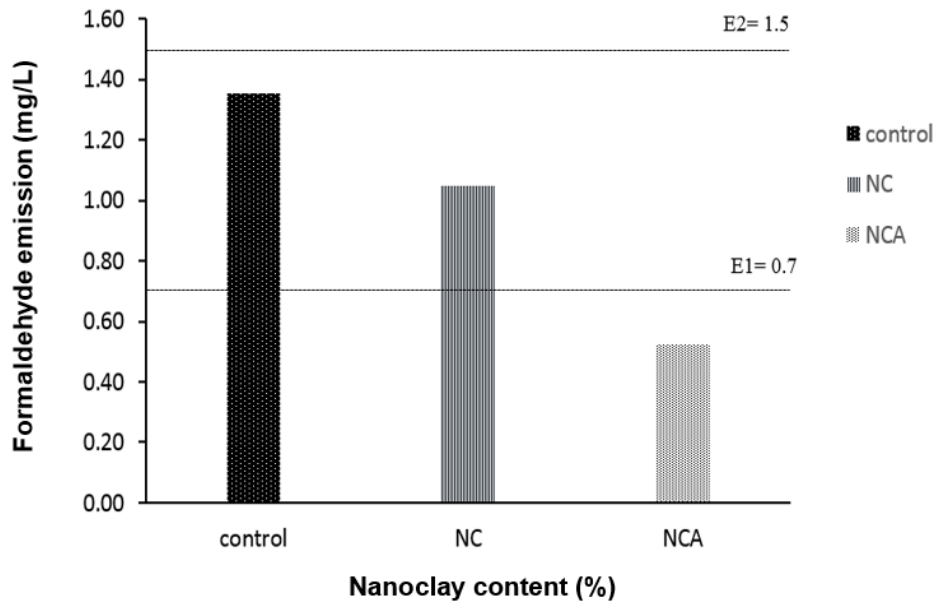
Fig. 3. The effect of nanoclay and modified nanoclay on the formaldehyde emission

Mechanical and physical properties

This study showed that the MOR, MOE, and IB values of panels containing nanoclay and modified nanoclay increased compared to the control samples (Table 2). Nanoclay, as a filler, leads to the distribution of stress throughout the matrix of the material and increases the specific surface to the volume of materials (Lei *et al.* 2008; Roumeli *et al.* 2012; Shokri and Yegani 2017; Khorramabadi *et al.* 2023). On the other hand, modified nanoclay increased the mechanical properties more than nanoclay. After the modification of the nanoclay, the APTES are placed in the interlayer space of the clay plate, preventing its clumping and aggregation. Clumps and aggregates are points for stress concentration, so their removal improves the dispersion of nanoclay particles and thus increases the mechanical strength (Bertuoli *et al.* 2014; Shokri and Yegani 2017; Khorramabadi *et al.* 2023). Finally, reducing the amount of free formaldehyde showed that formaldehyde had been utilized in forming the polymer network (Ashori and Nourbakhsh 2009; Khorramabadi *et al.* 2023). The expansion of the polymer network created a more robust and impenetrable structure against water. For this reason, the TS decreased after adding nanoclay and modified nanoclay (Ashori and Nourbakhsh 2009; Khorramabadi *et al.* 2023).

Table 2. Mechanical and Physical Properties of MDF Panels

Sample Code	MOR (MPa)	MOE (MPa)	IB (MPa)	TS (%)
UF	23	2580.7	0.61	15.7
UF+ NC	28.1	2916.09	0.68	13.5
UF+ NCA	31.1	2932.90	0.74	11.5

FTIR spectra

The UF resin is identified chemically as poly(methylene ether hydroxymethyl ureas). The silanol group, also known as the SiOH group, is present in the clay that includes SiO_2 particles (Bikiaris *et al.* 2006; Roumeli *et al.* 2012). This group may react with macromolecular end groups and a hydroxyl group. Dimethylolurea is created during the synthesis of urea and formaldehyde resins, and two of its hydroxyl groups are readily accessible to interact with the silanol groups of SiO_2 (Bikiaris *et al.* 2006; Roumeli *et al.* 2012). The FTIR spectra and peak assignments of UF resins and UF resin with 2.5% content of nanoclay and modified nanoclay are shown in Fig. 4. The figure shows the wide peak corresponding to the hydrogen-bonded OH and NH stretching of primary aliphatic amines at 3350 to 3300 cm^{-1} (Jada 1988; Roumeli *et al.* 2012). The band related to the -OCH_3 aliphatic ether at 2985 to 2920 cm^{-1}, C=O stretching of primary amide I at 1650 to 1620 cm^{-1}, amide II, the mixture of C-N stretching and NH deformation at 1570 to 1510 cm^{-1}, and C-N stretching of CH_2-N at 1380 to 1330 can be seen. Around 1160 to 1120 cm^{-1}, the peak corresponding to the C-O stretching of aliphatic ethers is evident (Samaržija-Jovanović *et al.* 2011; Ateş *et al.* 2013; Kızılcan and Mermutlu 2014; Liu *et al.* 2017). The peak at 1050 to 1020 cm^{-1} is described as the peak of the free NH_2 group (Liu *et al.* 2017).

The absorbance band at around 1630 cm^{-1} is assigned to the C=O amide vibration. There are differences between neat (0% TMI-BNT) and modified UF resins with 2.5% nanoclay and modified nanoclay (Jada 1988; Socrates 2004; Wibowo *et al.* 2020). After adding nanoclay and modified nanoclay, the UF resins' peaks changed, indicating that some hydrogen bonds between C=O and N-H in the UF polymer had been blocked. Due to this blockage of some hydrogen bonds, the C=O bond became stronger. Intercalation or exfoliation of nanoclay and modified nanoclay inside UF resins may account for blocking of hydrogen bonds (Wibowo *et al.* 2020). This can block the formation of hydrogen bonds between C=O and NH groups and prevent the creation of an ordered structure. Additionally, it can extend polymer chains. These polymer chains are located in the space between silicate layers and separate them from each other (Nuryawan *et al.* 2014; Pershina *et al.* 2017; Wibowo *et al.* 2020). The formation of new hydrogen bonds between the N-H of the UF polymer and the surface OH groups of the nanoclay is most likely to occur after the intercalation of UF resins by the silicate layers of nanoclay and modified nanoclay. The spectrum of modified UF resins with 2.5% nanoclay and modified nanoclay showed a change of the N-H peaks at about 3300 cm^{-1}, which confirmed this idea (Socrates 2004; Wibowo *et al.* 2020). Furthermore, the intensities of peaks of C-N and C-O at around 1346 and 1125 cm^{-1}, which are assigned to hydroxymethyl ($HOCH_2NH$-) and ether linkage (-NCH_2OCH_2NH-), changed (Park *et al.* 2003; Socrates 2004; Wibowo *et al.* 2020). Following a reduction in these peaks' intensity, the C-N of the methylene linkage (-$HNCH_2NH$-) at around 1025 cm^{-1} changed (Socrates 2004; Ateş *et al.* 2013). Combining nanoclay and modified nanoclay with Uf resin increased cross-linking, eventually improving UF resins' adhesion strength.
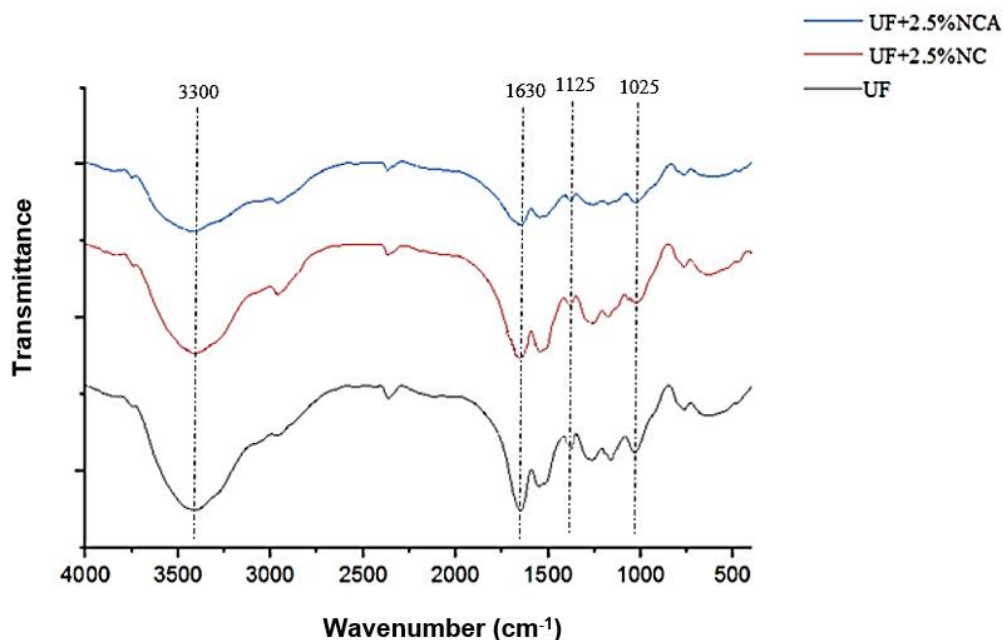
Fig. 4. FTIR of UF resins after adding nanoclay and modified nanoclay

X-ray diffraction

The XRD analysis was used to investigate the changes in the crystallinity of the UF resin and modified UF resin and the distribution of nanoclay. Figure 5 shows the XRD spectrum of nanoclay, UF resin, UF resin containing 2.5% nanoclay, and modified nanoclay in the range of 0 to 10°. The peak 2θ of montmorillonite is formed at 5.55°, with a base distance of 15.8. After adding nanoclay and modified nanoclay to UF resin, this peak was removed, indicating the nanoclay sheets became separated and well distributed in the urea-formaldehyde resin matrix (Lei *et al.* 2008; Liu *et al.* 2018).

Additionally, the XRD test was used to investigate the amount of changes in the crystalline structure of UF resin before and after adding nanoclay and modified nanoclay. These changes were investigated in the range of 10 to 80°. Figure 5 shows the XRD spectrum of UF resin and UF resin containing 2.5% nanoclay and modified nanoclay. The crystalline areas of urea formaldehyde resin showed peaks at 21:70°, 23:40°, 31:60°, and 45:30°. In the 21:70° and 23:40° regions, no changes were observed in the crystal regions. However, in the areas 31:60° and 45:30°, the height of the peaks formed for modified UF resins decreased. This reduction is indicative of the decrease in crystalline regions of UF resin.

The addition of nanoclay and modified nanoclay to UF resins blocked the hydrogen bonds between C=O and N-H groups, which prevented the formation of a well-ordered structure. Thus, it could facilitate the formation of a branched structure in UF resins, followed by a more extensive cross-linked network during curing was created that caused the amorphous structure (Wibowo *et al.* 2020; Yadav *et al.* 2021). Further, the crystalline areas were mainly composed of dimethylol urea connections (Liu *et al.* 2018). The requirement for forming these connections is a high amount of formaldehyde. Therefore, reducing the crystalline regions in the mentioned areas can indicate the discarding of free formaldehyde due to the reaction of nanoclay and modified nanoclay (Hassannejad *et al.* 2018; Liu *et al.* 2018).
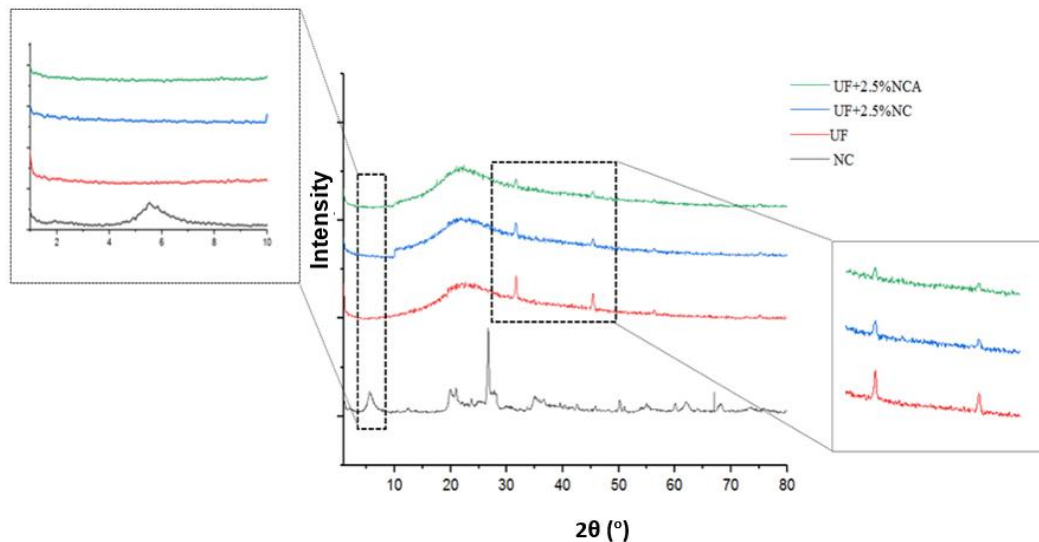
Fig. 5. XRD of UF resins after adding nanoclay and modified nanoclay

DSC analysis

The curing of UF resin is an irreversible exothermic reaction, which shows itself in DSC as an exothermic peak. The UF resin is a complex process affected by numerous factors, including pH, viscosity, and reactive group concentration. According to Fig. 6, adding nanoclay and modified nanoclay did not affect the glass transition stage of UF resin. However, their addition delayed the curing temperature of the resin.

The delay resulting from an altered interphase surrounding each particle or aggregate was due to the nanoparticles' formation of hydrogen bonds with the polymer chain (Roumeli *et al.* 2012). Consequently, the mobility of the polymer chain, which is required for the polymer to cure, is reduced in samples with a higher concentration of nanoparticles, thus requiring more energy for the cross-linking process (Roumeli *et al.* 2012). Additionally, nanoparticles operate as a physical barrier that disrupts the matrix's continuity, making it more difficult for the reactive groups of urea and formaldehyde to approach and interact (Roumeli *et al.* 2012; Xian 2012; Dukarska and Bartkowiak 2016). Further, nanoclay has a higher heat capacity than pure UF resin; hence its addition increases the heat capacity of the resin (Dukarska and Bartkowiak 2016). Several studies have examined the influence of nanoparticle type, size, dispersion degree, and concentration on the heat capacity of different nanomaterials (Keblinski *et al.* 2002; Wang *et al.* 2006). They all demonstrate that nanostructures cause an increase in the heat capacity of diverse materials (Keblinski *et al.* 2002; Wang *et al.* 2006; Dudda and Shin 2013; Lasfargues *et al.* 2015; Dukarska and Bartkowiak 2016).

In contrast, using modified nanoclay caused the homogeneity of the adhesive to continue to improve. The nanoparticles became dispersed to a high degree, and a high specific surface area was developed (Jesionowski and Krysztafkiewicz 2001; Dukarska and Bartkowiak 2016). As a result, the amount of nanoclay agglomerates was reduced, and the adhesives' heat capacity increased (Jesionowski and Krysztafkiewicz 2001; Dukarska and Bartkowiak 2016).

The presence of more free formaldehyde in UF adhesives with no formaldehyde scavenger compared to adhesives containing nanoclay and modified nanoclay powder may also be another reason for its delay (Rammon *et al.* 1986; Hassannejad *et al.* 2018). The free formaldehyde ratio is often one of the essential parameters that affects how well a resin performs, and greater values of this ratio enhance the resin's reactivity (Kyzas *et al.* 2009; Hassannejad *et al.* 2018). The higher the free formaldehyde content in UF resin, the more hydrochloric acid is released by interaction with ammonium chloride as a catalyst, resulting in a more reactive adhesive system (Hassannejad *et al.* 2018).
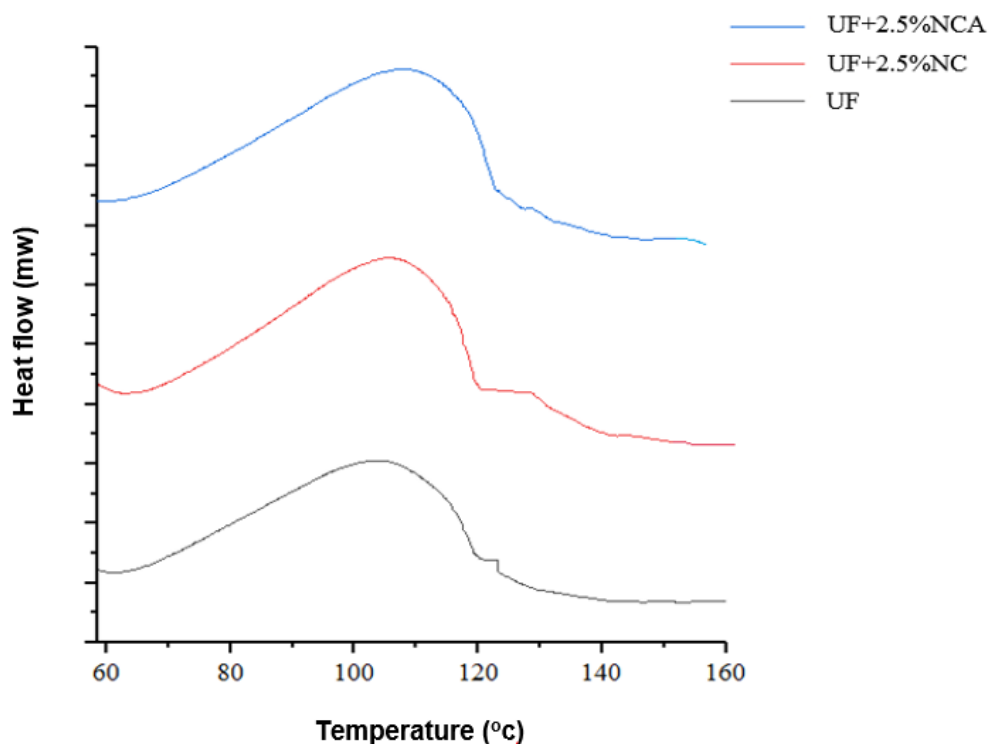

Fig. 6. DSC of UF resins after adding nanoclay and modified nanoclay

The addition of nanoclay and modified nanoclay to UF resin did not affect ΔH (Table 3). For all adhesive systems, reaction heats were nearly equal to 48 J/g. The reaction temperatures for the formation of monomethylolurea in solution and its subsequent conversion to dimethylolurea were studied. Thus, the similar exothermic heat seen in all adhesive systems can be related to the approximately equal molar proportion of monomethylol and dimethylol (Li and Bai 2005; Hassannejad *et al.* 2018).

Table 3. Onset Temperature, Peak Temperature, and Reaction Heat of UF Resin Having a Different Composition

Sample Code	Onset Temperature (°C)	Peak Temperature (°C)	Reaction Heat (J/g)
UF	79.3	115.9	48.65
UF + 2.5%NC	84.8	117.8	47.98
UF + 2.5%NCA	78.9	119.6	47.74

TGA analysis

The TGA results for urea formaldehyde resin before and after adding nanoclay and modified nanoclay are shown in Fig. 7. The first weight reduction of urea formaldehyde resin occurred in the temperature range of 50 to 100 °C. This weight loss is related to water's evaporation and free formaldehyde removal. The second weight-loss stage occurred after the temperature of 200 °C (Boran *et al.* 2011; Bertuoli *et al.* 2014; Moya *et al.* 2015; de Cademartori *et al.* 2019). The reason for this weight loss is the breaking and disintegration of the urea formaldehyde resin polymer network due to the release of formaldehyde from the methylene ether groups. The highest degradation rate occurs when stable methylene bonds are degraded (Roumeli *et al.* 2012; de Cademartori *et al.* 2019).

The addition of nanoclay and modified nanoclay considerably reduced the amount of weight loss. This is related to the thermal stability and anti-fire properties of nanoclay (Roumeli *et al.* 2012; Chen *et al.* 2017). In contrast, nanoclay was dispersed in the urea-formaldehyde resin matrix and thereby created a physical barrier for heat transfer. This caused a delay in the disintegration and destruction of the urea formaldehyde resin polymer network (Roumeli *et al.* 2012; Moya *et al.* 2015; Chen *et al.* 2017).

The weight loss of urea formaldehyde resin containing modified nanoclay was higher than urea formaldehyde resin containing nanoclay. The weight loss of UF resins containing modified nanoclay was higher than nanoclay due to the presence of organic compounds (Moya *et al.* 2015; Ghani *et al.* 2018). However, the weight loss of urea-formaldehyde resin containing modified nanoclay was lower than that of urea-formaldehyde resin.

Table 4. Thermogravimetric Data of the UF Resin Having a Different Composition

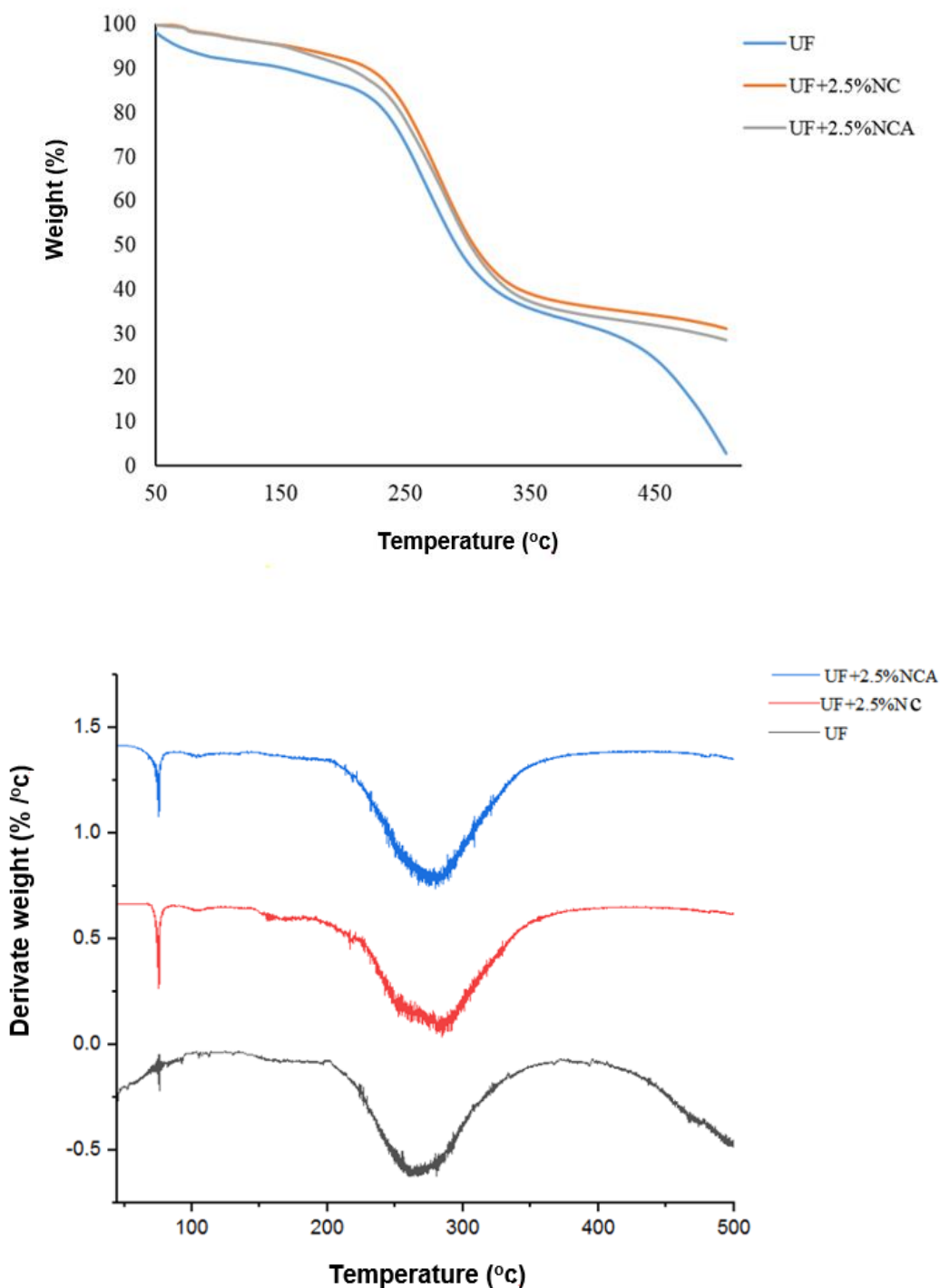| Sample Code	$T_{10\%}$	T_{max}	Weight Loss (%)
UF	151	263	97.3
UF+2.5%NC	219	300	69.5
UF+2.5%NCA	203	291	72.1

Fig. 7. TGA and DTG of UF resins after adding nanoclay and modified nanoclay

CONCLUSIONS

1. Both Fourier transform infrared (FTIR) and X-ray diffraction (XRD) results showed that modification of nanoclay with aminopropyltriethoxysilane (APTES) was successful.

2. Modified nanoclay with APTES reduced formaldehyde emissions by 62%. Meanwhile, adding nanoclay reduced the formaldehyde emission by only 22%.

3. The physical and mechanical properties of medium density fiberboard (MDF) specimens improved after adding nanoclay and modified nanoclay.

4. The formation of linear molecules and hydrogen bonds was confirmed for urea-formaldehyde (UF) resins after adding nanoclay and modified nanoclay by FTIR analysis.

5. The XRD characterization showed that nanoclay and modified nanoclay could reduce the crystallinity of UF resins and increase their amorphous nature. The decreased crystallinity indicated that nanoclay and modified nanoclay were intercalated in the UF polymer and separated some hydrogen bonds between each polymer. This was supported by the shift observed for C=O and N-H vibrations in FTIR spectra.

6. Both DSC and TGA results showed addition of nanoclay and modified nanoclay delayed the curing reaction of UF resins and reduced the amount of weight loss in the course of pyrolysis.

7. The benefits of using the modified nanoclay in UF adhesive are reducing the amount of formaldehyde emission greatly and blocking hydrogen bonds between linear molecules of UF resins, considerably preventing them from exhibiting their poor performance compared to other resins.

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