Influence of Nanoclay on Urea-Formaldehyde Resins for Wood Adhesives and Its Model

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ABSTRACT: The addition of small percentages of Na^+-montmorillonite (NaMMT) nanoclay appears to improve considerably the performance of thermosetting urea-formaldehyde (UF) resins used as adhesives for plywood and for wood particleboard. X-ray diffraction (XRD) studies indicated that NaMMT loses the periodic atomic structure when mixed in small proportions in the acid-curing environment characteristic of the curing of UF resins. This can be interpreted as becoming exfoliated under such conditions. The partly crystalline structure of the ordered zones of the UF resins is maintained but at a slightly lower level. Differential scanning calorimetry (DSC) indicated that NaMMT has an accelerating effect on the curing of the UF resin. It also appears to lead to a more controlled rate of crosslinking implying a more regular hardened network. The influence of NaMMT addition was particularly noted in plywood by the increase in water resistance of the UF-bonded panel. In the case of wood particleboard even the dry internal bond strength of the panel, a direct indication of the performance of the resin, improved with small additions of NaMMT. A hypothesis and model of the reasons why such improvement to the performance of UF resins by addition of nanoclay should occur has been presented. This is based on the application of percolation theory to the networking capability of the clay nanoplatelets. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2442–2451, 2008

Key words: resins; nanocomposites; networks; adhesives; modeling

INTRODUCTION

The wood panels industry heavily relies on the use of synthetic resins and adhesives. Adhesive bonded products of some kind or other constitute about 80% of the wood products on the market to-day. In short, without adhesives and resins this industry would not exist.[1] The adhesives used for these panels in 1998 (data from the European Panels Federation) were of 3.2 million tons resin solids, of which 2.6 millions being urea-formaldehyde (UF) resins used for interior grade applications.

The wood panels industry then relies on polycondensation resins, to-day mainly urea-formaldehyde (UF) resins. Performance standards have been established throughout the world for wood composite boards. Thus, the percentages on wood of adhesives/resins used for the manufacture of these products to satisfy the requirements of such standards varies little around typical percentage values. These are characteristic for each type of resin and process used. The resin binder constitutes the more expensive materials cost component. It is one of the parameters of which it is not possible to change markedly the percentage as this will cause a very marked decrease in performance, hence failure to satisfy the relevant standard specifications. Thus, any additive of relatively low cost which can improve the performance of the resin, implying at equal performance lower resin consumption, is of particular interest.

Impressive enhancement of properties by inclusion of submicron-size fillers in plastics and elastomers has stimulated considerable research on performance upgrading of thermoplastic resins by addition of such materials.[2] Clay nanocomposites of different types yield a marked increase in a number of properties of thermoplastic and other resins and composites.[3–9]

This article then deals with the addition of different types of montmorillonite nanoclays to thermosetting UF resins to study: (1) the improvement in performance of the resin by measuring the improved performance of wood panels/composites bonded with UF/nanoclays, and (2) study the effect of the resin on the level of exfoliation of the nanoclays.

EXPERIMENTAL

Materials

Montmorillonite nanoclays

The raw Na^+-montmorillonite (MMT) used with a cation exchange capacity (CEC) value of 100 meq/100 g

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clay, was purchased from Huate Group in ZHE JIANG, China. Organo-montmorillonite (OMMT) was purchased from same company. This material was prepared by an ion exchange reaction between Na^+-montmorillonite and $CH_3(CH_2)_{15}$—$N(CH_3)_3$ Br. Acid-modified montmorillonite(HMMT) was obtained from Na^+-montmorillonite according to a method already presented in the literature.[10]

Montmorillonite in which less than 10% of the particles in the dry clay have a diameter greater than 13 μm was used.

Urea-formaldehyde resins and preparation of UF/nanoclay composites

Three different UF resins were used. For particleboard a commercial UF resin of urea : formaldehyde molar ratio 1 : 1.1 was used. For plywood both a commercial UF resin and a laboratory manufactured resin both of urea : formaldehyde molar ratio 1 : 1.5. The laboratory UF resin was prepared according to the following commercial resin procedure: 478.5 g Formurea (a liquid concentrate composed of 57% formaldehyde, 23% urea and 20% water obtained from Dynea, Krems, Austria) were charged under continuous mechanical stirring in a glass reactor equipped with a reflux condenser, thermometer and pH electrode and the temperature raised to 50°C. Urea (114.1 g) in water (111.5 g) was then charged while the temperature was maintained at 50°C. The pH was then adjusted to 4.8–5.0 with a 22% NaOH water solution and 8.4 g melamine were charged in the reactor. The temperature was increased to 70°C and the pH adjusted to 7.2–7.6. The temperature was then raised as fast as possible to 90°C. The pH now dropped by itself to 6.3–6.6. Once 90°C had been reached the pH is adjusted to 5.4–5.6. The temperature was increased to 95°C and 85.1 g second urea added to the reacting mixture. When the viscosity, measured at 50°C, reached 220–250 centipoises the pH was adjusted in the 7.0–7.5 range with a 22% NaOH water solution. Immediately after adjusting the pH 0.6 g Borax was added, followed by 36.4 g third urea, the temperature decreased rapidly to 65–70°C and maintained at this level for 25 min. The resin is then cooled down to 25–30°C and the pH adjusted to 8.0–8.5 with a 22% NaOH solution. The characteristics of the finished resin where pH 8.0–8.5; solids content 64–66%, gel time of 50–80 s at 100°C; U : F molar ratio 1 : 1.5. The UF resin was mixed with the montmorillonite clay by mechanically stirring for 5 min at room temperature and then leaving the mixture overnight.

Testing

X-ray diffraction

Wide angle X-ray analysis (XRD) was carried out to investigate the effectiveness of the clay intercalation and if any change in crystalline structure of the UF resin occurred. XRD samples of UF resins hardened at 103°C in an oven after mixing with it 0, 4, and 9% NaMMT were powdered and mounted on a Phillips XRD powder diffractometer for analysis. A 2θ angle range from 2 to 100° in reflection mode was scanned at 2°/min. A computer controlled wide angle goniometer coupled to a sealed tube Cu source K_α radiation (λ = 1.54056 Å) was used. The Cu K_α radiation was filtered electronically with a thin Ni filter. The interlayer could be calculated when possible from the (001) lattice plane diffraction peak using Bragg's equation. Some consideration on the cristallinity level of UF resins with and without NaMMT could be obtained from the XRD investigation.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was done on UF resins to which 2% ammonium sulfate hardener was added as a 30% solution in water and to which 0 and 4% NaMMT nanoclay was added. This was done to study the influence of the nanoclay on the hardening rate of the UF resin. A Perkin–Elmer differential scanning calorimeter was used for the analysis at a heating rate of 10°C/min. The scans were done in air.

Termomechanical analysis

The resins were tested dynamically by thermomechanical analysis (TMA) on a Mettler apparatus. Triplicate samples of beech wood alone, and of two beech wood plys each 0.6-mm thick bonded with each system, for a total samples dimensions of 21 × 6 × 1.2 mm^3 were tested in nonisothermal mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection in bending $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$, where L is the span, b the width, h the thickness of the specimen, F the force exercised on it, and f the resultant deflection, allows the calculation of the Young's modulus E for each case tested.

Wood panels preparation

The performance of the UF/nanoclay composites was tested by preparing laboratory plywood an wood particleboard and evaluating respectively, their tensile and internal bond (IB) strengths.

Duplicate one layer laboratory particleboard of 350 × 310 × 16 mm dimensions were prepared by

adding 10% total resin solids content on dry wood particles. 28 kg/cm^2 was the maximum pressure used, followed by a decreasing pressure cycle. Press temperature at 195°C and a total pressing time of 5 min were used. The panels' constant thickness was fixed by placing metal stops between the pressing platens. The aimed average density for all the panels was 700 kg/m^3. The panels, after light surface sanding, were tested for dry internal bond (I.B.) strength. Formaldehyde emission was measured by the dessicator test method according to standard specification AS/NZS 1859.1 2004.[11]

Duplicate three-layer laboratory plywood panels of 450 × 450 × 6 mm were prepared using two urea-formaldehyde (UF) adhesives of U : F molar ratio = 1 : 1.5 and beech (*Fagus sylvatica*) veneers. To all these glue mixes were added (a) 2% ammonium sulfate hardener, solids on UF resin solids, the ammonium sulfate being predissolved to a 30% solution in water, and (b) either wheat flour or sodium montmorillonite (NaMMT) by weight on the UF resin solids content used, as indicated in the tables and the figures. The glue-spread used was of 300–320 g/m^2 of liquid glue-mix double glue line (dgl). Pressing time was 5 min at 120°C and 11 kg/cm^2 pressure. The plywood panels were cut according to EN 314. After being tested for dry tensile strength other specimens were placed in boiling water for 15 and 25 min and several of them tested for residual tensile strength. Moisture resistance was evaluated by immersing in boiling water 10 tensile strength specimens for 15 or 25 min followed by drying them overnight at room temperature.

DISCUSSION

The XRD pattern of the NaMMT nanoclay, and of the UF resin with and without different amounts of nanoclay is shown in Figure 1(a,b). Figure 1(a) reports the 2θ angle spectrum 2–100° and Figure 1(b) the 2–15° the 2θ angle range. The peaks appearing at 7.03° corresponds to NaMMT. The strong peaks at about 22.5, 25.8, 33.3, and 40.4° are from the lattice planes of the hardened urea-formaldehyde resin.[12] Figure 1(b) shows the measured intensity data over the characteristic 2θ range for NaMMT. In the case of the pure NaMMT the strong 2θ peak at 7.03° corresponds to a *d*-spacing of 1.26 nm according to the Bragg equation.[4] For the UF/NaMMT system the (001) peak disappeared both at 4 and at 8% NaMMT. This indicates that the periodic atomic structure of ordered zones of the nanoclay does not exist anymore. This has already been interpreted by other authors[3] in other polymer systems by deducing that NaMMT is completely exfoliated. Accordingly, here too it would appear that NaMMT is exfoliated when mixed with a UF resin.
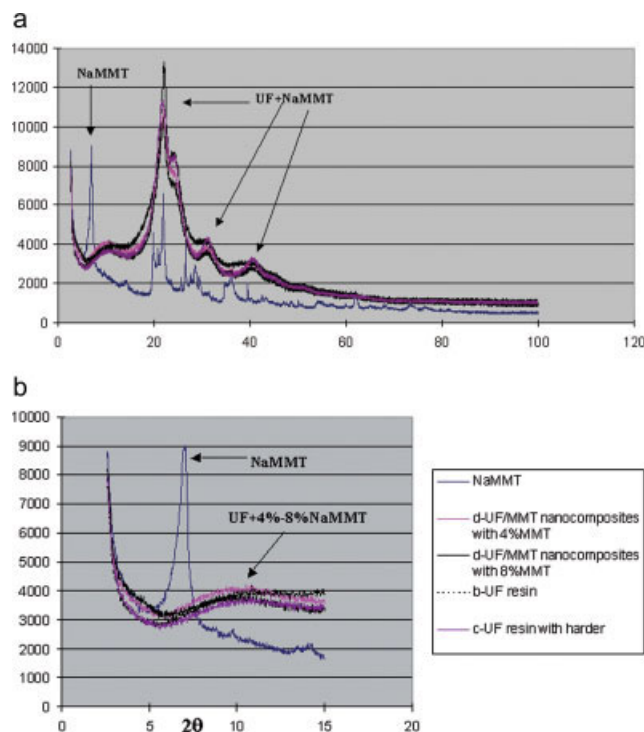
Figure 1 X-ray diffraction (XRD) spectra for NaMMT, UF resin, and UF + 4%NaMMT and UF + 8%NaMMT. (a) in the 2θ angle range 2–100°. (b) in the 2θ angle range 2–15°. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The XRD pattern of the UF resin in the 2θ range 20–40° was not affected by the addition of NaMMT as the peaks position remained the same. Their intensity however increased when compared to that of the UF resin cured without a hardener. It decreased instead for a UF resin cured by addition of hardener. In the latter case, this suggested the same crystalline structure of the UF resin but at a lower level of crystallinity in the UF/NaMMT hybrid.

The influence of NaMMT on UF resins was further investigated by DSC. The DSC curves of UF + hardener and UF + hardener + 2%NaMMT are shown in Figure 2. This indicates that NaMMT accelerates hardening of a UF resin. This is shown by the earlier onset and peaking of the exotherm of UF + hardener + NaMMT (onset at 88°C, peaking at 120°C) compared to that of UF+hardener only (onset at 96°C, peaking at 128°C). Of interest is also the appearance of the peak shoulder in the range 100–118°C, which is much higher for the resin with NaMMT than for the UF resin without nanoclay. This shoulder is probably due to the elimination of water from the system, and the difference in its height for the two cases in Figure 2 means that NaMMT retards water elimination from the system. As wood panels are cured in a hot press, this is likely to give slightly different rheology characteris-
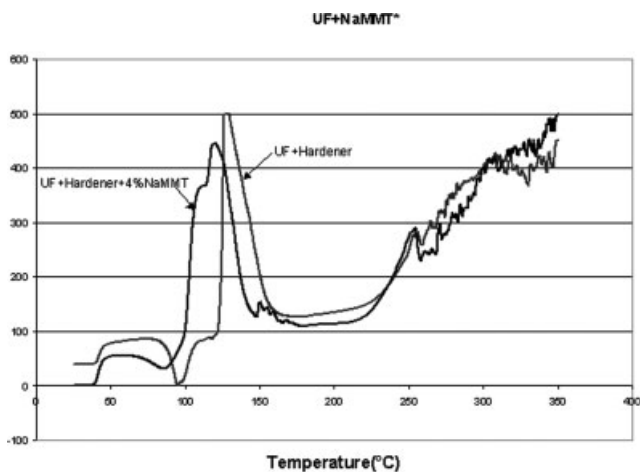
Figure 2 Differential scanning calorimetry (DSC) thermograms of UF resin+hardener and UF resin + 4%NaMMT + hardener.

Figure 4 Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximum MOE value of different percentages of Na montmorillonite (NaMMT) added to a UF resin.

tics to UF resin flow during hot curing when NaMMT is present, hence it may influence resin performance. Equally interesting is the lower intensity but greater width of the exotherm peak for the two cases in Figure 2, indicating a more controlled cross-linking, thus a more regular final network[13] when NaMMT is present.

The performance of the resin on the addition of montmorillonite nanoclays was first tested by thermomechanical analysis (TMA). In Figure 3 is shown the increase of modulus of elasticity (MOE) as a function of temperature of joints bonded with a UF resin control and with the same UF resin to which was added 10% (by weight on dry resin) of three different montmorillonite nanoclays (montmorillonite HMMT, its sodium salt Na-MMT, and OMMT an organic salt of HMMT). In all cases the resin was used without hardener. In all cases the maximum value of the MOE is
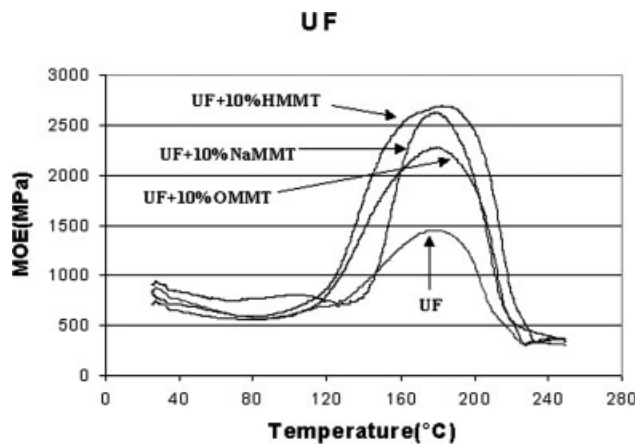
increased markedly by addition of any of the montmorillonites. The increase is particularly marked for HMMT and Na-MMT. It is this test that indicated that it was convenient to use the cheaper material Na MMT, seen its good performance. In Figure 4 is indicated the influence of different percentages of NaMMT on the maximum MOE value during curing of the UF resin, again without addition of a hardener. The maximum MOE value increases up to 4% addition of NaMMT and then decreases for higher percentage additions. This decrease is due to the considerable increase in viscosity of the mix as the percentage of NaMMT increases more than 4%, with consequent diffusion hindrance influencing negatively the curing of the resin.

Figures 5 and 6 indicate the behavior of the hardening of UF + NaMMT systems when in presence of

Figure 3 Thermomechanical analysis (TMA) curve of MOE as a function of temperature for a UF resin with or without different montmorillonite and derivatives added. HMMT = monmorillonite, NaMMT = montmorillonite sodium salt, OMMT = montmorillonite organic residue salt.
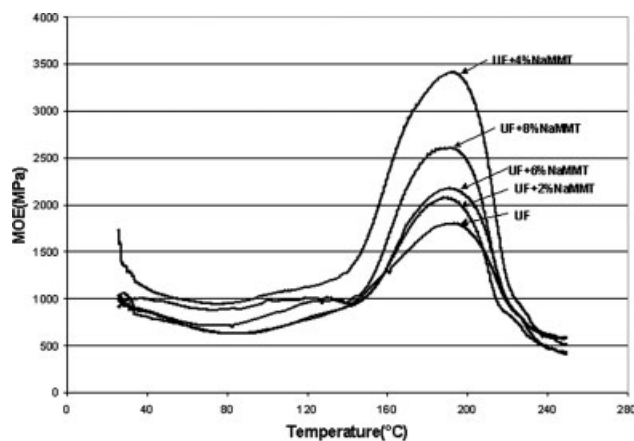

Figure 5 Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximum MOE value of different percentages of acetic acid on a UF resin + NaMMT. Acetic acid content equivalent to neutralization of alkali content of NaMMT (100%), 1.5 times more (150%), 2.5 times more (250%), 3.5 times more (350%).
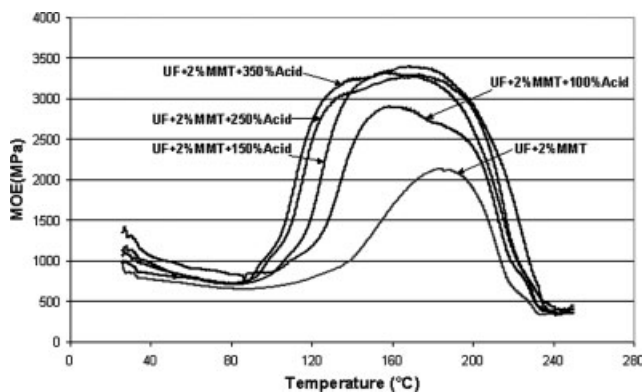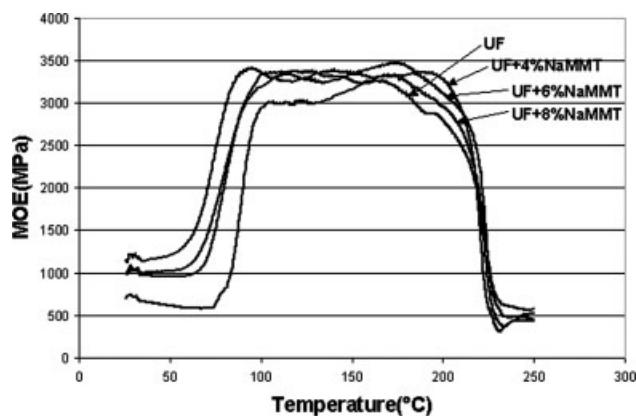
Figure 6 Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximumMOE value of different percentages of Na montmorillonite (NaMMT) added to a UF resin when both hardener and acetic acid are added.

a direct hardener, an acid (acetic acid 30%), used to partly neutralize the alkaline character of NaMMT. In the case of a direct acid hardener, the progressive increase in the acid added yields better results up to 1.5 times the acid necessary to neutralize the OH^- generated by the Na^+ of NaMMT, then the level of max MOE stabilizes. The progressive addition of higher proportions of acid also shifts the increase portion of the MOE curves to progressively lower temperatures (Fig. 5). Thus, it accelerates the rate of curing of the UF + NaMMT mix, again up to 1.5 times the acid necessary to neutralize the OH^- generated by the Na^+ of NaMMT.

The further addition, on top of the acid, of also a hidden hardener such as ammonium sulfate functioning only when the temperature increases over a certain level (Fig. 6) still shows resin curing acceleration and improved maximum MOE values when comparing UF and UF + NaMMT, but both of these are much more modest, and stop for NaMMT proportions higher than 4% on resin solids.

The applied results of two different types of wood panels bonded with UF resins to which NaMMT was added are shown in Tables I and II. In Table I results for plywood indicate that there are no signifi-

cant differences in dry tensile strength between the UF control and the UF + NaMMT panels. This is explained by the percentage wood failure being 100% in all cases, indicating that all adhesives mixes are stronger than the wood substrate and consequently the dry strength tested is that of the wood itself. The results are different and of greater interest in the case of the immersion of the panels in boiling water for an accelerated water resistance test. UF resins are not weather and water resistant. This can be noticed in Table I for the control, first by the marked decrease in wood failure observed already after 15 min in boiling water and second by the equally noticeable decrease in strength and wood failure after 25 min boiling. The behavior of the panels bonded with UF+NaMMT is different. First the decrease in strength on boiling is much less marked, the joints being stronger than the control after 25 min boiling. Second the decrease in wood failure after 15 min boiling is much less marked for the control. This indicates that NaMMT renders UF bonded plywood more water tolerant, although still far from being of exterior type. This is an interesting result as even slight improvement in water tolerance of UF-bonded joints are much appreciated by the wood panel industry, especially when these are achieved with small amounts of a relatively inexpensive material.

Table II reports the results of laboratory wood particleboard produced by adding increasing percentages of NaMMT in the UF binder used. The dry internal bond (IB) strength of the panel, which for particleboard is a direct indication of the performance of the adhesive, progressively increases with increasing proportions of NaMMT. The greatest improvement occurs with the first 2% NaMMT and then improvements are rather small up to 8% NaMMT.

The influence of nanoclay on the formaldehyde emission was evaluated by the dessicator method according to standard AS/NZS 1859.1 2004.[11] Comparison of formaldehyde emission for the control at 0.905 mg/L and for 1% addition of NaMMT at 0.827 mg/L, shows that nanoclay can decrease formaldehyde emission even if to a limited extent.

TABLE I
Results of Plywood Panels Prepared with a UF of Molar Ratio 1 : 1.5 Added of Different Percentages of Na Monymorillonite (NaMMT)

Na-montmorillonite on dry resin (%)	Dry		Boiled (15 min)		Boiled (25 min)	
	Tensile strength (N/mm^2)	Wood failure (%)	Tensile strength (N/mm^2)	Wood failure (%)	Tensile strength (N/mm^2)	Wood failure (%)
0	2.45	100	2.45	27	1.09	0
2	2.42	100	2.68	63	1.70	0
4	2.32	100	2.67	85	1.33	0
6	2.39	100	2.28	51	1.37	0
8	2.52	100	2.58	42	1.64	0

TABLE II
Results of Wood Particleboard Panels Prepared with a UF of Molar Ratio 1 : 1.1 Added of Different Percentages of Na Monymorillonite (NaMMT)

Na-montmorillonite on dry resin (%)	Density (kg/m^3)	Dry IB strength (MPa)
0	700	0.79
2	700	0.94
4	700	0.96
8	700	1.01
10	700	1.00

Figure 8 Comparison of wheat flour and NaMMT as active fillers of a UF resin. Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximum MOE value of 4% Na montmorillonite (NaMMT) and 30% wheat flour added to a UF resin when resin hardener is present.

The improvement engendered by the addition of small percentages of NaMMT as regards water resistance of UF-bonded plywood (Table I) led to consider what level of substitution by NaMMT one could have on traditional wheat flour fillers. UF resins for plywood are almost always used after addition of marked amounts of wheat flour (between 20 and 50% by weight on resin solids, with 30% being an average level of addition in industry) both to improve the consistency of the adhesive as well as to cheapen the glue-mix. The dry strength and general dry performance of UF + wheat flour filler resins is generally better than for the same UF resin alone. Unfortunately addition of flour further worsens the resistance of UF-bonded joints to water. Figure 7 reports the TMA results of a UF resin alone and to which either different percentages of wheat flour (4 and 30%) or NaMMT (2 and 4%) have been added. The maximum MOE values obtained by the addition of the small percentage of NaMMT nanoclay are considerably better than those obtained even with the higher amount of flour, when no hardener is added to the UF resin. Even when a hardener is added to the resin, UF + 4% NaMMT gives a
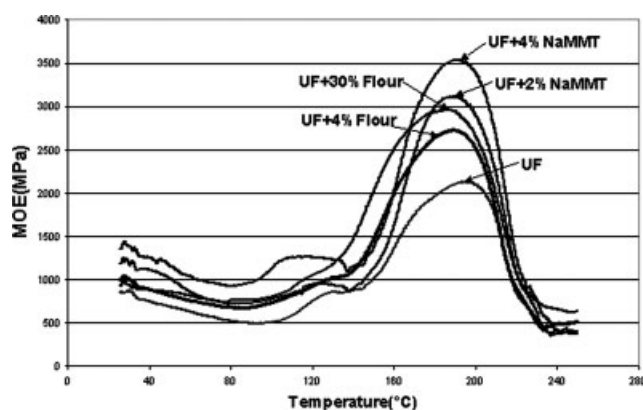
better result much faster than UF + 30% wheat flour (Fig. 8). The comparative results of plywood panels made with wheat flour filler and with much smaller percentages of NaMMT are shown in Table III. Table III shows that for both a laboratory synthesized UF resin as well as for a commercial resin the water resistance of the joint bonded with 6% NaMMT is far superior to that of the joint containing 30% wheat flour, both in strength and wood failure.

Hypothesis regarding the reason why montmorillonite nanoclays improve wet performance of UF resins

A hypothesis can be advanced as regards the improvement in water resistance of the resin due to the addition of montmorillonite nanoclay. First of all montmorillonite nanoclay itself is water repellent. Second, the observed reinforcement effect induced by the presence of filler may also be attributed to a percolation phenomenon between the nanoclay particles. The nanoclay used in the present study is a sodium montmorillonite (Na-MMT), also called bentonite. As argued below, the corresponding particles may be modeled as thin disks. When dispersed inside a continuous medium like a resin matrix, the particles are expected to touch each other, thus forming a connected infinite cluster even at low concentration. The critical amount above which a transition from a nonconnected to a connected state (i.e., a percolation transition) occurs can be calculated according to the following considerations.

First, the aspect ratio of an average typical particle should be known. The mean diameter, as seen by scanning electron microscope observation, is close to 100 nm. Applying the well known Bragg equation to the main X-ray diffraction peaks of the clay powder

Figure 7 Comparison of wheat flour and NaMMT as active fillers of a UF resin. Thermomechanical analysis (TMA) curve of MOE as a function of temperature indicating the effect on maximum MOE value of different percentages of Na montmorillonite (NaMMT) and wheat flour added to a UF resin.
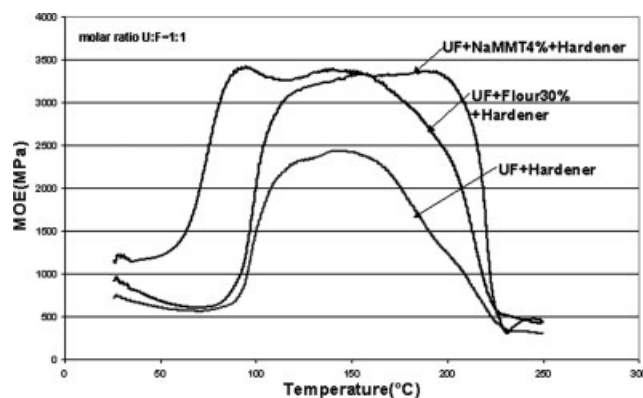
TABLE III
Comparison of Results for Plywood Prepared with 30% Wheat Flour vs. 6%
Na-Montmorillonite Using a Commercial UF and a Laboratory prepared UF

	UF (F/U = 1.5 molar)		Commercial UF	
Tensile strength	30% flour	6% Na-MMT	30% flour	6% Na-MMT
Dry (MPa)	2.09 (100)	2.39 (100)	2.16 (100)	2.32 (100)
Boil (15 min) (MPa)	1.33 (0)	2.36 (100)	0 (0)	2.65 (100)

Percentage wood failure in parenthesis.

led to an interlayer spacing of 1.27 nm. Such a result is remarkably close to what was measured for the first hydration product of bentonite, corresponding to one intercalated layer of water[14] (Ref. 13 and refs. therein), i.e., 12.4–12.6 Å. XRD diffraction of adhesive-nanoclay composites also revealed that, after dispersion inside the resin, the nanoclay is completely exfoliated. The exfoliation, which is a well-known property of Na-MMT, is caused by the reversible uptake of water by sodium ions. This gives the material a high ability to swell in one dimension, thus effectively cleaving the clay particles and causing a separation of the lamellar units in the form of extremely thin plates.[15] Given the above interlayer spacing, the thickness of the corresponding platelets should be lower than 1.3 nm. Since the stacking of the layers is close compact in the raw nanoclay, and that the intercalated sodium cation has an ionic radius of 116 pm,[16] the layer thickness after exfoliation is 1.27–2 × 0.116 = 1.04 nm, say 1 nm. This result is close to values already published for the thickness of a montmorillonite lamella, i.e., 9.1–9.2 Å.[17] Therefore, the aspect ratio diameter/thickness is assumed to be roughly 100.

The percolation threshold of systems comprising disoriented thin disks was investigated by Celzard et al. [18] and the resultant equations were successfully applied to a number of composite materials (see for example Ref. 19 and refs. therein). Briefly, the critical volume fraction Φ_c at which an infinite cluster is formed throughout a medium filled with randomly dispersed disks of radius r and thickness t reads:

$$\Phi_c = 1 - \exp\left(-\frac{\langle V_{\mathrm{exc}} \rangle V}{\langle V_e \rangle}\right) \qquad (1)$$

where $\langle V_{\mathrm{exc}} \rangle$ is the so-called total excluded volume; it is a dimensional invariant depending on the shape of the percolating objects (see Ref. 17 and refs. therein for details). V is the true volume of an average percolating object, and $\langle V_e \rangle$ is its excluded volume averaged over the orientation distribution. The excluded volume[20] is defined as the volume around an object in which the center of another similarly

shaped object is not allowed to penetrate. The underlying idea is that the percolation threshold is not linked to the true volume of the object itself, but rather to its excluded volume.[18]

The mean excluded volume of a disk of infinitely thin radius r is such that[21]:

$$\langle V_e \rangle = 4\pi r^3 \int_0^\beta \sin^2 \alpha \, d\alpha \qquad (2)$$

where α is the angle between the planes of two disks in contact with each other, as shown in Figure 9, and β represents the angle of greatest disorientation of the system of disks. In other words, $-\beta \leq \alpha \leq +\beta$. For randomly oriented disks, $\beta = \pi/2$ and such a system is isotropic. Integration of eq. (2) leads to:

$$\langle V_e \rangle = \pi r^3 [2\beta - \sin 2\beta] \qquad (3)$$

thus $\langle V_e \rangle = \pi^2 r^3$ when $\beta = \pi/2$. Consequently, the percolation threshold of a system of completely disoriented disks, reads:

$$\Phi_c = 1 - \exp\left(-\frac{\langle V_{\mathrm{exc}} \rangle t}{\pi r}\right) \qquad (4)$$

where t is the thickness of the disks. $\langle V_{\mathrm{exc}} \rangle$ is known in the extreme cases of infinitely thin disks (1.8)[22] and of spheres (2.8).[20] It is thus expected that the
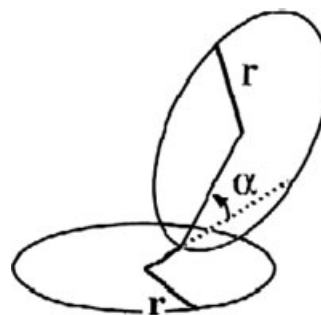

Figure 9 Excluded volume for thin discs of radius r. The objects touch and their plane make an angle α. $\langle V_e \rangle$ is calculated for any orientation such that $-\beta \leq \alpha \leq \beta$, where β is the maximum disorientation angle of the system. The latter is isotropic for $\beta = 90°$ (after Ref. 24).

value of $\langle V_{\text{exc}} \rangle$ corresponding to disks of finite thickness t lies between 1.8 and 2.8. The following double inequality is then obtained:

$$1 - \exp\left(-\frac{1.8t}{\pi r}\right) \leq \Phi_c \leq 1 - \exp\left(-\frac{2.8t}{\pi r}\right) \quad (5)$$

Since the ratio t/r of the nanoplatelets is 1/50, the percolation threshold verifies the following double inequality:

$$1.14\ \% \ \leq \Phi_c \leq 1.77\ \% \quad (6)$$

Such a result may be alternatively recovered through the use of the effective medium theory. It was demonstrated that, assuming platelets as flattened (oblate) ellipsoids, the critical volume fraction Φ_c may be written as[23]:

$$\Phi_c = \frac{9L_c(1 - L_c)}{2 + L_c(15 - 9L_c)} \quad (7)$$

where L_c is the depolarization factor, related to the eccentricity e of the ellipsoid according to the following formulas[24]:

$$e = \sqrt{\left(\frac{2r}{t}\right)^2 - 1}$$
$$L_c = \frac{1 + e^2}{e^3}[e - \arctan e] \quad (8)$$

Given the aforementioned values of radius and thickness, eqs. (7) and (8) lead to a value of 1.74% for Φ_c, which is very close to the upper limit given by eq. (5). Consequently, it can be deduced that percolation occurs in resin—nanoclay systems as soon as the concentration of nanoplatelets is in excess of 1.8 vol %.

Rather than volume fractions, Φ, the composition of filled adhesives is calculated on the basis of mass fractions, ϕ. It is easy to calculate that both concentrations are related to each other through the following equation:

$$\phi = \frac{1}{1 + \frac{\rho_R}{\rho_N} \times \frac{1 - \Phi}{\Phi}} \quad (9)$$

in which ρ_N and ρ_R are the densities of the nanoclay and of the dry, hardened, resin, respectively. Given that $\rho_N = 1.25$ and $\rho_R = 2.35$,* injecting $\Phi_c = 1.8$ vol % into eq. (9) shows that the percolation threshold corresponds to $\phi_c = 3.3$ wt %.

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*$\rho_R = 2.35$ is the average of a number of values (ranging from 2.0 to 2.7) given in the literature for sodium montmorillonite.

Now, the percolation transition is not representative of what happens from a mechanical point of view. Physical properties like elastic modulus or viscosity are not strongly affected by the onset of an incipient cluster made of randomly dispersed particles. The system indeed just undergoes a transition from a nonconnected to a connected state, but remains floppy. A second percolation transition should exist at a higher concentration such that the particles form a rigid network. This second critical volume fraction, at which the elastic modulus thus becomes nonzero for the first time, is called rigidity threshold, Φ_r. Therefore, in systems made of dispersed particles, it is obvious that $\Phi_r > \Phi_c$. This situation is met, for example, when expanded graphite particles are pressed into monolithic blocks,[25] or in wood-based composites consisting of wood fibers and phenolic resin binder.[26] In the latter case, the binder was randomly dispersed among the fiber-like particles, and its presence was shown to have no influence on the position of the rigidity threshold, thus resembling the actual nanoclay–resin systems.

The rigidity threshold may take various values, depending on the kind of elastic forces acting between the solid particles. Central forces, i.e., being normal to the surface of the particles, like in most granular systems, are the most probable and must thus be considered in priority among any others. If central forces are strictly alone, the rigidity threshold should be related to the percolation threshold according to[27]:

$$\Phi_r = 2(D - 1)\,\Phi_c \quad (10)$$

where D is the dimensionality of the system. Since $D = 3$, then $\Phi_r = 4\,\Phi_c$, so the onset of the rigidity should occur at 7.2 vol % or 13.3 wt % of nanoclay particles in the resin.

If central forces now prevail over any other kind of elastic forces, but are not alone (e.g., beam-like forces and/or angular forces are also present), the rigidity threshold is much lower and now reads[27]:

$$\Phi_r = \frac{D^2 - 1}{2D - 1}\,\Phi_c \quad (11)$$

This latter situation is likely to occur because, due to their very low thickness, the nanoclay platelets are prone to bend when forced to come closer to each other. Putting again $D = 3$ in eq. (11) leads to $\Phi_r = 8/5\,\Phi_c$, so the system should be consolidated above 2.88 vol % or 5.33 wt % of particles in the adhesive.

Before it dries and hardens, the adhesive is a liquid consisting of 65 wt % of urea-formaldehyde resin and 35 wt % of water. For reaching a given value ϕ of mass fraction after hardening, a higher weight fraction ϕ' of nanoclay has to be introduced

in the former liquid composition. The relationship between ϕ' and ϕ may be easily calculated, and reads:

$$\phi = \frac{\phi'}{0.65 + 0.35\phi'} \quad (12)$$

The various compositions that were investigated, namely $\phi' = 2, 4, 6,$ and 8 wt % of nanoclay introduced into the liquid resin, led to the following observation. At 2 wt %, the mixture flows well but, at 4 wt %, its viscosity diverges. Preparing homogeneous nanoclay—resin mixture thus becomes very difficult above 4 wt %. For $\phi' = 2$ wt %, eq. (12) shows that the corresponding weight fraction of particles in the solid resin is $\phi = 3.04$ wt %. This value is below the two rigidity thresholds that may be calculated from eqs. (10) and (11), i.e., 13.3 and 5.33 wt %, respectively. On the other hand, $\phi' = 4$ wt % corresponds, again according to eq. (12), to $\phi = 6.02$ wt %. This result is still below the rigidity threshold corresponding to purely central elastic forces, given by eq. (10), but is slightly above that obtained by eq. (11). Now, given the divergence of the viscosity at concentrations close to 4 wt % of nanoclay in the liquid resin, it is clear that the rigidity threshold is already exceeded. Such a finding strongly supports the validity of eq. (11) for describing the relationship between percolation and rigidity thresholds.

At this point of the article, it should be noticed that eq. (11) was justified theoretically[27] on the basis of the so-called Kirkwood-Keating model.[28] such a model was already confirmed by numerical simulations,[29] it is to our knowledge only the third time that it can be applied to a real three-dimensional material.

Finally, a few remarks should be added concerning the observed decrease of elastic modulus at nanoclay concentrations higher than the rigidity threshold. The higher is the concentration above ϕ'_r, the lower is the Young's modulus. Increasing the concentration above the percolation threshold naturally induces, due to the growing number of interparticle contacts, a mutual orientation of the particles. Given that the aspect ratio of the nanoplatelets is very high, such an orientation is expected to be strong, just like what happens in composites made of polymer filled with micronic graphite flakes having the same as aspect ratio.[18,30] The effect is expected to be even stronger because of the geometry of the sample, i.e., a thin film of adhesive between two flat pieces of wood. The closeness of the surface should thus prevent the particles to be fully disoriented, especially at increasingly ''high'' volume fractions.

Through the concept of excluded volume, the disorientation of the nanoclay disk-like particles may be

calculated. The excluded volume of a thin disk of radius r and thickness t is given by eq. (3), and may also be approximated as:

$$\langle V_e \rangle \approx \frac{\text{sample volume}}{\text{number of nanoplatelets}} = \frac{\pi r^2 t}{\Phi} \quad (13)$$

By identification of eqs. (3) and (13), one obtains :

$$2\beta - \sin 2\beta \approx \frac{t}{\Phi r} \quad (14)$$

It should be emphasized that eq. (14) is just an approximation, since (13) is not true at very low volume concentrations of disks (i.e., $\langle V_e \rangle$ has a constant maximum value when $\Phi \to 0$), and also eq. (3) is exact only for infinitely thin disks, which situation does not match the reality, even if t is very low indeed. However, these assumptions were already successfully applied for describing the continuous orientation of a system of disks submitted to an increasing compression.[19] A decrease of interparticle voids and an increase of particle concentration are expected to present the same behavior, so eq. (14) can be used for predicting the way the particles are misaligned throughout the system. However, rather than a maximum disorientation angle, β was experimentally shown to be the mean disorientation angle, thus corresponding to the full width at half maximum of the distribution of angles. Whatever the concentration of disks and/or the thickness of the composite sample, a fraction of nanoplatelets is indeed always misaligned almost randomly. β is thus assumed to be the same as the so-called mosaic spread.[25]

Figure 10 shows the disorientation angle of the nanoclay particles, β, as a function of their volume
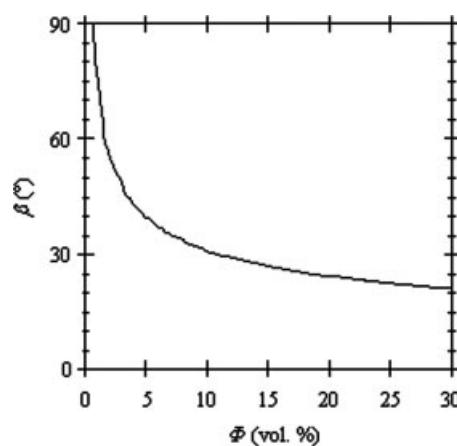

Figure 10 Mean angle of disorientation, β, of the nanoclay particles as a function of their volume concentration, Φ, in the dry hardened resin.

concentration, Φ, inside the dry, hardened, resin, calculated from eq. (14). The observed orientation, particularly fast at low volume fractions, is expected to lower the mechanical properties perpendicularly to the bedding layer, i.e., to the surface of the adhesive joint. To a lesser extent, the orientation should also lower the percolation (and hence the rigidity) thresholds. Given that disorientation is only characterized here by a single angle rather than by a distribution, quantifying both effects is not possible. The second one, dealing with the thresholds, is only expected to be weak, because of the non-negligible number of particles remaining fully disoriented, which tend to leave unchanged the values of Φ_c.[18]

CONCLUSIONS

The addition of small percentages of Na-montmorillonite (NaMMT) nanoclay appears to improve cosiderably the performance of thermosetting UF resins used as adhesives for plywood and for woood particleboard. XRD characterization indicated that NaMMT completely exfoliated when mixed with UF. The influence of NaMMT addition was particularly noted in plywood by the increase in water resistance of the UF-bonded panel. In the case of wood particleboard even the dry internal bond stength of the panel, a directy performance of the performance of the resin, improved with small additions of NaMMT. An hypothesis and modeling of the reason why such improvement to the performance of UF resins should occur has also been presented.

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