

Maderas. Ciencia y tecnología

ISSN: 0717-3644 ISSN: 0718-221X

Universidad del Bío-Bío

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Maderas. Ciencia y tecnología, vol. 20, no. 1, 2018, pp. 11-24

Universidad del Bío-Bío

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ISSN impresa 0717-3644 ISSN online 0718-221X

DOI: 10.4067/S0718-221X2018005001202

EFFECT OF NANOCLAY-TREATED UF RESIN ON THE PHYSICAL AND MECHANICAL PROPERTIES OF PLYWOOD MANUFACTURED WITH WOOD FROM TROPICAL FAST GROWTH PLANTATIONS

Freddy Muñoz^{1,*}, Roger Moya¹

ABSTRACT

Physical and mechanical properties were evaluated on cross-laminated panels (plywood) fabricated with three plantation species (*Cordia alliodora*, *Gmelina arborea* and *Vochysia ferruginea*) from tropical climates in Costa Rica. The panels were glued with urea-formaldehyde resin modified with nanoclay at four concentrations (0,75; 1,00; 1,50 and 2,00 %) and unmodified resin. It was determined that addition of nanoclay to urea-formaldehyde adhesive positively decreased moisture absorption and swelling of the plywood panel with statistical significance. However, nano-modification did not have a significant effect on the density and specific weight of plywood. Nano-modification of urea-formaldehyde resin with nanoclay at 0,75 % improved the Module of rupture and Modulus of elasticity in flexure parallel to surface in the three species, also increasing mechanical resistance to strains in parallel tension, shear and compression. By means of electronic microscopy, it was evidenced that the nano-modified adhesive became diffused at the inside of the cellular structure of wood in a better way, allowing for the generation of a transition zone that increased the mechanical properties at the macro level. According to the properties evaluated, it was determined that 0,75 % is the optimal percentage to use of nanoclay on urea-formaldehyde resin.

Keywords: Adhesives, Cordia alliodora, Gmelina arborea, veneers, Vochysia ferruginea.

INTRODUCTION

Cross-laminated panels of the plywood type are wood derivatives made with an odd number of veneers, each with their fibres perpendicular to the other. The veneers oriented along the fibres equate tension, reduce ruptures and minimise dimensional change and warping of the panel (Bodig and Jayne 1993). This technology makes it possible to obtain a product with good stability and mechanical strength. Resistance and rigidity of the plywood depend on the raw material, the manufacturing process, adhesive employed and conditions of use of the panel (Tenorio *et al.* 2011, Tenorio *et al.* 2012, Bayatkashkoli and Faegh 2014).

The role of bonding the various veneers with adhesive has relevance in the mechanical performance of the plywood panel. According to Frihart and Hunt (2010), an important contribution of adhesives is that they transfer and distribute strains among the veneers, increasing strength and rigidity of the plywood panels. The adhesion properties of veneers are essentially similar to those of solid wood; however, plywood panel manufacturing processes that include shearing, drying and lamination can change the physical and chemical properties of the veneer surface. These are factors to take into account in order to ensure good moistening and penetration of the adhesive (Frihart and Hunt 2010).

Various types of adhesives are employed in the manufacture of plywood panels (Stoeckel *et al.* 2013), among which the urea-formaldehyde (UF) resin is commonplace in conformation of veneer panels as well as particleboards, providing good resistance only in dry conditions service (Frihart and Hunt 2010, Kaboorani *et al.* 2013). Moreover, adhesives allow for improved use of timber by enabling the design of low density wooden products, as well as the generation of wooden pieces of greater proportions from others dimensionally lesser and the more effective exploitation of residues from other lumber industries (Zhao *et al.* 2011).

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*Corresponding author: fmunoz@tec.ac.cr Received: 19.12.2016 Accepted: 17.11.2017 Developments in nanotechnology, specifically the use of nanoparticles, have led to improvements of the properties of adhesives and the resistance at the glue line between the lumber and adhesive (Cai et al. 2007, Lei et al. 2008, Ashori and Nourbakhsh 2009, Kaboorani et al. 2011, Ates et al. 2013, Xian et al. 2013, Bardak et al. 2017). However, behaviour of nano-modified adhesives in tropical species is, as of yet, not well known (Moya et al. 2015a, Moya et al. 2015b). According the Bayatkashkoli and Faegh (2014), panels made with fast growth species treated with nanotechnology are regarded as an alternative to the increment in the demand of such engineering products.

In Costa Rica, meanwhile, lumber from reforested species has gained importance in the manufacture of engineering products (Serrano and Moya 2011). Three remarkable species in reforestation are *Gmelina arborea*, *Cordia alliodora* and *Vochysia ferruginea*. However, more research ought to be done to generate scientific and technological knowledge in order to add value to these forest species and thus successfully transform lumber from forest plantations into engineering products. As a response, so as to make complete utilisation of these reforestation species, scientific research alternatives both basic and applied have emerged globally, which have promoted the surge of high-grade development technological products such as plywood panels. This allows for competitive incursion in new markets through the use of fast growth plantations species, due to the high resistance, efficiency and structural liability that can be obtained from them (Leichti *et al.* 1990a, Leichti *et al.* 1990b).

In these products it is possible to further improve structural performance with the use of nanoparticles, as properties of all system components (veneer-adhesive-veneer) combine at the interfacial zone to provide the final properties of the composite material (Gardner 2006, Jacob *et al.* 2008, Frihart and Hunt 2010) and that ultimate performance of such composite materials depends strongly on the quality of the interface (Schultz *et al.* 1987). It is therefore of relevance to know the behaviour of this area in order to improve the mechanical performance of products using fast growth lumber species and nanomodified resins.

On this basis, the present study has the object of determining the micro- and macro-scale effects of the modification of urea-formaldehyde (UF) adhesive using nanoclay particles at four different concentrations, as well as the unmodified adhesive (0,00; 0,75; 1,00; 1,50 and 2,00 %). Evaluation of the physical-mechanical properties is done on plywood panels fabricated with three forest species from fast-growth plantations: *Cordia alliodora*, *Gmelina arborea* and *Vochysia ferruginea*.

MATERIALS AND METHODS

Raw materials

A total of 60 logs were used, 1 m long with variable diameter, of three species from forest plantations in Costa Rica with ages varying from 7 to 9 years: *Cordia alliodora* from Búfalo-Limón (latitude: 10°00'21"N and longitude: 83°10'23"W at an elevation of 25 m amsl and 9 years of age) and CATIE-Turrialba (latitude: 09°53'00"N and longitude: 83°38'01"W at an elevation of 602 m amsl and 9 years of age); *Gmelina arborea* from Bonifacio-Limón (latitude: 09°46'43"N and longitude: 82°54'59"W at an elevation of 42 m amsl and 8 years of age); and *Vochysia ferruginea* from Búfalo-Limón (latitude: 10°00'21"N and longitude: 83°10'23"W at an elevation of 25 m amsl and 7 years of age). Per species, 7 to 8 trees were felled. All logs were sawn with a rotary peeling lathe in order to obtain the veneers with dimensions of 2 and 3 mm of thickness.

Characteristics of nano-modified adhesive

Commercial nanoclay of the brand Dellite $43B^{\circ}$ -DMBHT was employed, manufactured by Laviosa-Chimica Mineraria, SpA, Livorno-Italia. The physical and chemical characteristics of the nanoclay are as follows: 3 % moisture content, < 1 % impurity content 1,6 g cm⁻³ density, 7-9 µm particle size, organically modified with dimethyl-benzyl hydrogenated tallow ammonium. The detail on the type of nanoclay and other characteristics can be consulted in Moya *et al.* (2015a). The type of adhesive used was a water-based urea-formaldehyde (UF), CR-560 UF Resin trademark, produced by

Central Chemistry Quibor SA (https://www.agroquibor.com). The technical description of the product indicates that the liquid resin is urea-formaldehyde (UF), with 64 to 65 % solids content and 650-900 cPs viscosity.

Modification of the UF adhesive with nanoclay was carried out by adding this compound at different percentages in relation to the adhesive solution (weight/weight): 0,00; 0,75; 1,00; 1,50 and 2,00 % (Kaboorani and Rield 2011, Moya *et al.* 2015a); according to the nanoclay percentage in them, treatments were then labelled as UF-0,00 (control), UF-0,75; UF-1,00; UF-1,50 and UF-2,00 respectively. The formulation of the adhesive was done according to the technical datasheet of the manufacturer, by mixing on a weight/weight ratio: UF resin at 51 %, wood flour as filler ingredient at 21 %, water at 26 % and the catalyst at 3 %, plus the percentage of nanoclay corresponding to each treatment. In order to blend the compounds, the mixture was stirred at ambient temperature for 15 minutes at 1600 rpm with a four-blade metal blender (blade inclination of 45°); the corresponding amount of the catalyst was then added, continuing with the constant stirring for another 10 minutes. Other details on the preparation of the adhesive formula can be found in Moya *et al.* (2015a). The adhesive were spread manually with a brush on the main face of the veneers, such that the adhesive coverage was approximately 250 g m⁻², methodology similar to that applied by Gao and Li (2012) and Cihad and Bektas (2014).

Pressing cycle for panels and sampling

Plywood panel fabrication was done with a hydraulic press of national craft with a total pressing capacity of 8000 kg. The press conditions for densification of the veneers were: specific pressure of 12 kg cm⁻², temperature of the plates at 160 °C to 170 °C and pressing speed of 1 min/mm (Lisperguer and Rozas 2005).

A total of 150 plywood panels were built (3 species x 5 concentrations x 10 panels), conformed in five layers with dimensions of 600 x 600 x 12 mm (Figure 1). The veneer thicknesses were set in two categories: 2 mm for outer veneers and 3 mm for inner veneers, with moisture content of the veneers at 10 to 12 %. The panels were then squared to 560 x 560 x 12 mm and sampled in order to determine the physical and mechanical properties, as shown in Figure 1. From each panel fabricated, at least one sample per test was obtained, therefore a total of 10 units were available for each test.

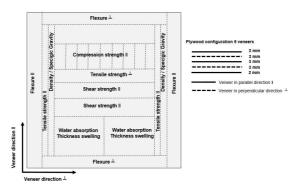


Figure 1. Distribution of samples for physical and mechanical tests on 560 x 560 x 12 mm plywood panels. Five-layer configuration for cross-laminated panels.

Physical properties

A total of 1125 samples were tested in order to determine the physical properties in accordance to the standards as follows: specific gravity at 12 % (SG_{12}) complying with method B of D-2395 standard (ASTM 2003a); moisture content according to D-4442 standard (ASTM 2003b); density at 12 % (DEN_{12}), water absorption (ABS) and thickness swelling (TS) following method B of D-1037 standard (ASTM 2003c).

Mechanical properties

To determine the mechanical properties, 1125 samples were tested in compliance to norms as follows: tension parallel to surface (T) with sample A, following method A of D-3500 standard (ASTM 2003d); compression parallel to surface (C) using method A.11 of D-3501 standard (ASTM 2000a); shear at the plane of the panel (S) using D-1037 standard (ASTM 2003c); flexure parallel and perpendicular to surface (F) and F^{\perp} respectively) as stated in method A of D-3043 standard (ASTM 2000a). All mechanical tests were carried out in a universal testing machine brand Tinius Olsen H10KT, with the exception of tension parallel to surface (T), which was tested in a Tinius Olsen Super L machine.

Electronic Microscopy

Six samples were selected of each species: 3 samples with the control treatment and other 3 samples from panels treated with UF-0,75 adhesive containing nanoclay particles brand Dellite $43B^{\$}$ -DMBHT. For each sample a cross-section measuring 5 x 5 mm was prepared, cutting off two of its corners to the shape of a truncated pyramid with a steel knife. The upper surface of the frustum was then cut using the glass edge of a Leica EM ultramicrotome, rendering a smooth surface with little roughness in order to increase quality of the microphotography. Scanning Electronic Microscopy (SEM) was carried out with working distance (WD)= 3,8 to 5,8 mm; 7,5 kv voltage and 400x magnification with an instrument brand Table Microscope TM 3000, with no gold or carbon film covering the sample.

Statistical analysis

The statistical system used was SAS® PROC UNIVARIATE. A variance analysis (ANOVA) was applied to the general statistical description (average and variation coefficient) in order to establish differences among the nano-modified adhesive treatments in panels from C. alliodora, G. arborea and V. ferruginea. Significant differences among measurements of each treatment were evaluated with the Tukey test (P < 0.01).

RESULTS

Physical properties

Density and Specific gravity

Addressing the physical properties evaluated, DEN_{12} and SG_{12} (Table 1), it was reported for the particular case of C. alliodora plywood-type panels that the effect of nanoclay is not statistically significant. For G. arborea panels, the DEN_{12} and SG_{12} values increased statistically with the addition of nanoclay to the adhesive. For panels using V. ferruginea, the effect of adding nanoclay was rather varied; for example, in UF-1,50 and UF-2,00 formulations, DEN_{12} values increased significantly in relation to the control, whereas in the UF-0,75 treatment the DEN_{12} value decreased and, finally, no effect was observed in the UF-1,00 treatment. Moreover, the effect of nanoclay in V. ferruginea panels showed a very similar behavioural pattern to the one described for the DEN_{12} , that is, UF-1,50 and UF-2,00 formulations had significantly increased SG_{12} values in relation to the control, while the UF-0,75 treatment had decreased SG_{12} values and, last, the UF-1,00 showed no positive effect.

Table 1. Density and specific gravity at 12 % in cross-laminated panels using three different plantations species, glued with UF adhesive modified with Dellite 43B*-DMBHT nanoclay particles at four different concentrations.

Physical properties	Adhesive type	Species					
Thysical properties	UF + % nanoclay	C. alliodora	G. arborea	V. ferruginea			
Density ₁₂ (kg m- ³)	UF-0,00	525 (5,56) ^a	399 (10,81) ^a	414 (5,00) ^a			
	UF-0,75	518 (7,54) ^a	446 (10,01) ^b	396 (7,18)b			
	UF-1,00	502 (6,94) ^a	447 (6,71) ^b	413 (5,56) ^a			
	UF-1,50	529 (4,25) ^a	462 (4,84) ^b	435 (4,11)°			
	UF-2,00	526 (5,88) ^a	462 (4,75) ^b	444 (3,63)°			
	UF-0,00	0,48 (5,92) ^a	0,35 (10,35) ^a	0,38 (4,93)a			
Specific Gravity ₁₂	UF-0,75	0,45 (7,29)a	0,39 (8,23)b	0,35 (7,46)b			
	UF-1,00	0,46 (7,22) ^a	0,41 (6,52)b	0,38 (5,22) ^a			
	UF-1,50	0,48 (4,67) ^a	0,42 (7,78)b	0,40 (4,14)°			
	UF-2,00	0,48 (5,80) ^a	0,42 (4,61) ^b	0,41 (3,55)°			

Average value of the physical property for each species; per cent coefficient of variation between parentheses. Different letters indicate significant statistical differences with $\alpha = 0.05$.

Change in moisture content

Figure 2A, Figure 2B and Figure 2C show the percentage of change in moisture content (ΔMC) of panels after 24-hour immersion in water. The addition of nanoclay to the adhesive formulation significantly reduced the ΔMC in all treatments for plywood panels of all species but the UF-1,00 treatment in *C. alliodora* panels (Figure 2A). Particularly for panels using *C. alliodora* and *G. arborea*, the UF-0,75 treatment showed the best significantly positive effect for reduction of ΔMC percentage in relation to the control treatment. However, UF-1,00; UF-1,50 and UF-2,00 treatments were more effective in reducing ΔMC percentage in *V. ferruginea* panels (Figure 2C). In *C. alliodora* panels, a significant statistical difference was determined in relation to the control for UF-0,75; UF-1,50 and UF-2,00 treatments, with no significant difference between UF-1,50 and UF-2,00 treatments (Figure 2B). Meanwhile in *G. arborea* panels, a significant statistical difference was determined for all treatments in relation to the plywood control, but no significant statistical difference appeared between UF-1,50 and UF-2,00 treatments (Figure 2B). Similarly, in *V. ferruginea* panels a significant statistical difference was determined for all treatments in relation to the control, while none was shown between UF-1,00; UF-1,50 and UF-2,00 treatments.

Water absorption

Figure 2D, Figure 2E and Figure 2F show the percentage of water absorption (*ABS*) of plywood panels after 24-hour immersion in water. The effect of nanoclay addition to the adhesive formulation for *ABS* reduction was more evident in *V. ferruginea* panels, particularly in UF-1,00; UF-1,50 and UF-2,00 treatments in this case, wherein *ABS* was shown to decrease significantly in relation to the control (Figure 2F) and also in comparison to panels of the other two species. For *C. alliodora* panels, the most significant reduction in *ABS* in relation to the control was achieved with the UF-0,75 treatment (Figure 2D), while for *G. arborea* panels the *ABS* was decreased with UF-0,75 and UF-1,00 treatments (Figure 2E). For *C. alliodora*, a significant statistical difference from the control was only determined in UF-0,75 and UF-1,00 treatments, as well as a difference between these two. For *G. arborea*, significant statistical difference was determined in all treatments, with no difference between UF-0,75 and UF-1,00 nor between UF-1,50 and UF-2,00.

Thickness swelling

The percentage of thickness swelling (TS) of plywood panels after 24-hour immersion in water is shown in Figure 2G, Figure 2H and Figure 2I. The addition of 2 % nanoclay concentration to the

adhesive formulation had the greatest significantly positive impact on the *TS* decrease for panels of all species. The highest statistical *TS* value was found in evaluation of *C. alliodora* panels glued with UF-1,00 while the lowest *TS* percentages in relation to the control were obtained with UF-0,75 and UF-2,00 treatments (Figure 2G), with a significant statistical difference between the two treatments. In *G. arborea* panels, meanwhile, all treatments reduced the *TS* percentage significantly in relation to the control; though no significant difference was detected between the UF-nanoclay treatments (Figure 2H). Finally, in *V. ferruginea* panels the addition of nanoclay at concentrations of 0,75 and 1,00 % did not show statistical differences in relation to control panels; the UF-1,50 and UF-2,00 treatments though, with a significant statistical difference between them, reported a statistically lower decrease in the *TS* percentage in comparison to the other concentrations (Figure 2E).

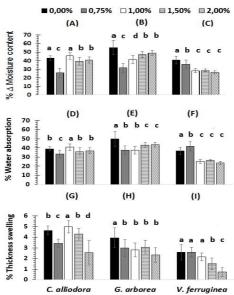


Figure 2. Physical properties: percentage of change in moisture content, percentage of water absorption and percentage of thickness swelling for plywood from 3 species glued with UF adhesive nano-modified by Dellite 43B®-DMBHT nanoclay.

Note: different letters on bars indicate significant statistical differences at $\alpha = 0.05$.

Mechanical properties

Flexure test

Mechanical strength in parallel flexure, determined through the modulus of rupture $(MOR\|)$ and modulus of elasticity $(MOE\|)$, showed that plywood panels of the three species using UF-0,75 adhesive formulation obtained the highest statistical values for mechanical strength in relation to the control treatment and the other formulations (Figure 3A, Figure 3B, Figure 3C, Figure 3D, Figure 3E, Figure 3F). Specifically, *C. alliodora* panels using UF-1,00 reported the statistically lowest $MOR\|$ and $MOE\|$ values. Results obtained for *G. arborea* panels using either UF-1,00; UF-1,50 or UF-2,00 treatments, similarly, did not show such significantly positive effect for the $MOR\|$ and $MOE\|$ values in relation to the control treatment (Figure 3B and Figure 3E). In the case of *V. ferruginea* panels, UF-1,00 and UF-1,50 treatments presented an $MOR\|$ value statistically lower in relation to the control, but it was the only species to report an increase in the $MOR\|$ value with the UF-2,00 treatment (Figure 3C).

The evaluation of mechanical strength in perpendicular flexure for C. alliodora panels showed statistically higher values for the modulus of rupture (MOR^{\perp}) and modulus of elasticity (MOE^{\perp}) in those panels treated with UF-0,75 as compared to other treatments (Figure 3G, Figure 3J), while the lowest statistical MOR^{\perp} value was obtained in UF-1,00 panels and no statistical differences were shown in the MOE^{\perp} among panels with 1,00; 1,50 and 2,00 % nanoclay concentrations in relation to the control

(Figure 3G, Figure 3J). In G. arborea panels, all nanoclay concentrations caused a significantly positive increase in MOR^{\perp} and MOE^{\perp} values in relation to the control, although no statistical difference was determined among the treatments (Figure 3H, Figure 3K). For panels from V. ferruginea, only the UF-0,75 treatment presented a significant increase, whereas the other treatments had no effect since the MOR^{\perp} value obtained with them was statistically equal to that of the control treatment (Figure 3I). In addition, UF-1,00; UF-1,50 and UF-2,00 treatments caused a significant decrease in the MOE^{\perp} of V. ferruginea panels, while in UF-0,75 the value was statistically equal to that of the control treatment (Figure 3I, Figure 3L); however, the highest value for MOE^{\perp} was reported in the UF-0,75 treatment for this species (Figure 3L).

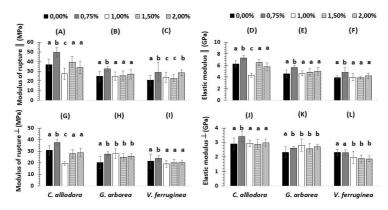


Figure 3. Mechanical properties: modulus of rupture and modulus of elasticity for flexure in parallel and perpendicular orientations for plywood from three species glued with UF adhesive nano-modified by Dellite 43B®-DMBHT nanoclay.

Note: different letters on bars indicate significant statistical differences at $\alpha = 0.05$.

Test for strength in compression, shear and tension

It was found in the test for strength in parallel compression that plywood panels using UF-0,75 treatment showed the highest statistical value in all three species studied, in comparison to control samples and the other treatments. The lowest values for strength in compression, on the other hand, were observed as follows: for UF-1,00 in *C. alliodora* panels; for UF-1,50 in *G. arborea* panels; and for UF-1,00 and UF-1,50 treatments in *V. ferruginea* (Table 2). In testing for strength in parallel shear it was found that panels of all species fabricated using the adhesive with no nanoclay (UF-0,00) showed a lower strength value when compared to nanoclay-modified UF treatments. Plywood panels glued with UF-1,50 in *C. alliodora* and *G. arborea* and those using UF-2,00 in *V. ferruginea* reported the lowest shear strength values among panels treated with nanoclay-modified UF (Table 2).

Evaluation of strength in parallel tension revealed that panels of all species manufactured with nanoclay-free adhesive also presented the least strength for this mechanical test (Table 2). Meanwhile, the maximum values for strength in tension were found in *C. alliodora* and *V. ferruginea* panels using the UF-0,75 treatment, as well as *G. arborea* panels with the UF-2,00 treatment. Last, comparing the treatments using nanoclay-modified UF, the lowest value obtained for strength in tension came from control-treated *C. alliodora* panels and from UF-1,50 panels in *G. arborea* and *V. ferruginea* (Table 2).

Table 2. Mechanical properties: compression strength, shear strength and tensile strength in parallel orientation for plywood from three species glued with UF adhesive nano-modified by Dellite 43B®-DMBHT nanoclay.

Mechanical properties	Adhesive type UF+ % nanoclay	Species and strength (MPa)					
		C. alliodora	G. arborea	V. ferruginea			
	UF-0,00	18,59 (8,44)b	12,74 (8,80)°	12,15 (7,04)°			
	UF-0,75	22,80 (5,06)ª	16,64 (3,59)ª	14,35 (4,09)a			
Strength in Parallel Compression	UF-1,00	17,00 (6,99)°	15,30 (15,34)a	12,62 (4,34)°			
	UF-1,50	19,13 (6,88)b	14,66 (6,01) ^b	12,98 (7,39)°			
	UF-2,00	18,46 (10,71)b	16,55 (8,48)ª	13,37 (4,31)b			
	UF-0,00	1,93 (20,76)b	1,38 (20,47)b	1,32 (36,58)a			
C1 . D. 11.1.C1	UF-0,75	2,54 (6,78)a	2,12 (23,67)°	1,94 (9,40)b			
Strength in Parallel Shear	UF-1,00	2,45 (8,93)a	2,75 (11,17)a	2,10 (15,96)b			
	UF-1,50	2,09 (23,40)b	2,32 (12,69)a	1,90 (17,28)b			
	UF-2,00	2,87 (10,32)a	2,55 (11,52)a	1,86 (11,90)b			
	UF-0,00	27,10 (17,23)b	18,41 (21,51)ª	15,08 (21,59)°			
C+	UF-0,75	37,63 (11,33)a	24,48 (15,70)b	20,98 (12,74) ^a			
Strength in Parallel Tension	UF-1,00	32,26 (21,66)°	24,16 (17,70)b	16,62 (13,19)			
	UF-1,50	32,24 (11,32)°	23,11 (23,46)b	16,31 (6,92)°			
	UF-2,00	30,82 (21,54)b	26,54 (13,95)b	19,06 (14,30)			

Average value of the mechanical property for each species; coefficient of variation percentage between parentheses.

Different letters indicate significant statistical differences with α = 0,05.

Glue line

No evidence of change was observed in the colour of the glue line at plain sight in the various plywood panels glued with UF and nanoclay at different concentrations, as is shown in Figure 4. The thickness of the glue line in panels using the UF-0,00 treatment, determined by means of micrometric measurements taken with electronic microscopy along a length of 200 μ m in the interfacial zone (Figure 5), revealed the following values: 90 μ m for *C. alliodora*, 46 μ m for *G. arborea* and 15 μ m for *V. ferruginea* (Figure 5A, Figure 5B, Figure 5C).

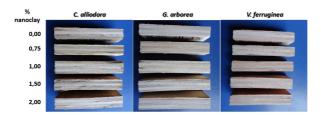


Figure 4. General view of the glue lines in plywood panels built with *C. alliodora*, *G. arborea* and *V. ferruginea* veneers, glued with urea-formaldehyde adhesive modified with nanoclay at different concentrations.

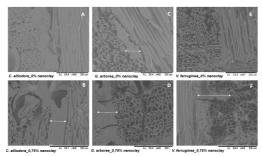


Figure 5. Microphotographs of the glue line and interfacial zone of cross-laminated panel samples, obtained at 400x electronic microscopy: (A) *C. alliodora* with UF-0,00 formulation; (B) *C. alliodora* with UF-0,75 formulation; (C) *G. arborea* with UF-0,00 formulation; (D) *G. arborea* with UF-0,75 formulation; (E) *V. ferruginea* with UF-0,00 formulation; and (F) *V. ferruginea* with UF-0,75 formulation.

DISCUSSION

Physical properties

According to Shukla and Pascal (2008), physical properties in plywood panels, such as density and specific weight, are affected by the type and conditions of each species and, in very scarce cases, by the manufacturing process of the panels. This statement agrees well with results reported in Table 1, where species with greater base specific gravity yielded higher SG_{12} and DEN_{12} values: panels built with C. alliodora veneers (SG = 0.46; Tenorio et al. 2016) obtained the highest SG_{12} and DEN_{12} values; intermediate values were obtained with G. arborea lumber panels (SG = 0.41; Tenorio et al. 2016); and the lowest values appeared in panels made with V. ferruginea lumber (SG = 0.35; Tenorio et al. 2016). Additionally, the use of nanoclay in the adhesive increased the DEN_{12} and SG_{12} values in relation to panels using UF-0.00 especially in C. alliodora and G. arborea panels (Table 1). This increase in the value of these properties is a product of the increment in mass from the added nanoclay in the adhesive. Each panel is composed of four glue lines with a greater weight percentage, attributed to nanoclay (from 0.75 to 2.00 %).

In the case of ΔMC , ABS and TS of plywood panels (Figure 2), a generalised behaviour was observed, which was the decrease in the average values of these properties in relation to the control treatment. This means that the application of nanoclay-modified UF resin improved the behaviour of panels in presence of water.

The behaviour described above is congruent with results reported by Cai *et al.* (2007), Doosthoseini and Zarea-Hosseinabadi (2010), Abdul *et al.* (2010) and Lei *et al.* (2010) for various temperate-climate species. These authors indicate that the increment of nanoclay in a polymer matrix produces a decrease of the swelling and water absorption values, resulting in augmented resistance to moisture of the plywood panel.

The general effect of modifying UF adhesive with nanoclay is the positive decrease of ΔMC , ABS and TS. In regards to this, Mansouri *et al.* (2006) indicate that urea-formaldehyde resins are the most widely employed adhesives in plywood panels for indoor use. However, a disadvantage of UF-type resins is presented at the glue line, as these resins have a high sensitivity to moisture. Therefore, treatment with the UF-type adhesive modified by Dellite $43B^{\$}$ -DMBHT nanoclay allows for improvements on the performance under moisture conditions of plywood panels of the species studied.

Lei *et al.* (2008) presented a hypothesis that all montmorillonite nanoclay itself is water-repellent. Later, Kaboorani and Riedl (2011) mentioned that nanoclay could modify the response of a polymer to a load by means of several mechanisms. Nanoclay particles have an inherently high surface area to volume ratio, leading to large interfacial area between the fillers and matrix. This condition, then, could be manifested in a decrease in moisture absorption in the glue line.

Mechanical properties

Values of the various mechanical properties reflect the characteristics of each species studied. Plywood panels made of *C. alliodora*, with a *SG* of 0,46 (Tenorio *et al.* 2016), showed the highest values for the mechanical properties and, consequently, *V. ferruginea* panels with a *SG* of 0,35 (Tenorio *et al.* 2016) presented the lowest strength values (Table 2, Figure 3). Concerning this, Shukla and Pascal (2008) indicate that the density of the timber is considered an indicator of the mechanical or strength properties of products to be fabricated from it.

The modulus of elasticity is the resistance to deflection (deformation) exerted by the plywood panel and it is considered one of the most important mechanical properties of materials, as it affects their service performance in loaded applications (Bayatkashkoli and Faegh 2014). In this way, products or conditions with greater MOE or MOR values in flexure are indicative of materials with better mechanical performance. Therefore, panels glued with UF-0,75 show the best performance in flexural strength for both parallel ($\mathbb I$) and perpendicular ($\mathcal I$) orientations, as they present the highest statistical values in all species (Figure 3).

Results obtained from the other mechanical tests, such as maximum parallel compression and tensile strengths, suggest that the use of UF resin with 0,75 % nanoclay treatment is most adequate for improvement of the mechanical properties of cross-laminated panels. However, in the case of parallel shear strength, the effect of the treatment varies more in relation to the nanoclay amount added to the resin. For example, in *C. alliodora* panels, the maximum parallel shear strength was achieved when the UF adhesive was applied at 2,00 % nanoclay, whereas in *G. arborea* and *V. ferruginea* the highest-scoring nanoclay content was 1,00 % (Table 2). It is to be noted, though, that the magnitude of the shear mechanical strength value in all panels with nanoclay treatment surpassed that of mechanical strength in control plywood panels.

The addition of nanoclay to various types of adhesive has been shown to improve mechanical properties at the glue line (Lei *et al.* 2008, Kaboorani and Riedl 2011, Kaboorani *et al.* 2012, Kaboorani *et al.* 2013, Pique *et al.* 2013, Pirayesh *et al.* 2013, Xian *et al.* 2013, Ates *et al.* 2013). A similar result was obtained in Moya *et al.* (2015b), wherein shear strength at the glue line of *Carapa guianensis* hardwood was improved by using nanoclay-modified UF resin.

The improvement of the shear strength can be explained by the work of Kaboorani and Riedl (2011). They mentioned that mechanical properties of PVAc and UF are affected by adding nanoclay. Nanoclay can modify the response of a polymer to a load by means of several mechanisms. Nanoclay particles have an inherently high surface area to volume ratio, leading to large interfacial area between the fillers and matrix. This suggests that there is an interaction zone surrounding each filler particle which substantially alters the physical properties relative to the neat polymer matrix, such as higher or lower polymer mobility, entanglement density and altered modulus. Also, the polymer-clay nanocomposites exhibit extremely strong interface with polymers due to the confinement of polymer chains within the galleries of clay platelets. It is considered that the confinement of polymer-clay interactions would affect the local chain dynamics to a certain extent.

The effects of the UF resin modification with nanoclay at different concentrations compared to those of using regular UF adhesive, for plywood panels of all three species studied, are shown in Table 3. Nanomodification of the UF was less effective in *C. alliodora* panels, whereas very effective in *G. arborea* and *V. ferruginea* panels. In general and as has been indicated, an improvement of behaviour takes place there in presence of water, as well as an important intensification of the properties in the timber. Furthermore, it is observed that the addition of nanoclay at a concentration of 0,75 % accentuates the mechanical properties in panels of the three species (Table 3).

Table 3. Increment and decrement of physical and mechanical properties in plywood panels of three plantation species glued with UF-type adhesive modified with Dellite 43B*-DMBHT nanoclay at four different concentrations.

Property	C. alliodora			G. arborea			V. ferruginea					
	UF	UF	UF	UF	UF-	UF	UF	UF	UF	UF	UF	UF
	0,75 %	1,00 %	1,50 %	2,00 %	0,75 %	1,00 %	1,50 %	2,00 %	0,75 %	1,00 %	1,50 %	2,0%
DEN ₁₂	()	()	()	()	↑ (12)	1 (12)	1 (16)	1 (16)	↓(5)	()	1 (5)	1 (7)
SG ₁₂	()	()	()	()	ft (12)	1 (17)	1 (20)	1 (20)	∜ (8)	()	1 (5)	1 (8)
ΔMC	∜ (40)	()	↓ (9)	₩ (5)	∜ (43)	₩ (25)	₩ (15)	∜ (11)	∜ (13)	₩ (31)	↓ (29)	∜ (35)
ABS	∜ (15)	()	₩ (8)	()	₩ (24)	∜ (24)	₩ (13)	∜ (13)	1 (14)	₩ (31)	₩ (29)	₩ (35)
TS	↓ (26)	1 (8)	()	↓ (45)	↓ (24)	∜ (28)	₩ (22)	∜ (41)	()	₩ (17)	₩ 41)	↓ (72)
MORI	1 (35)	↓ (26)	()	()	1 (30)	()	()	()	1 (40)	()	()	1 (37)
MOE	1 (17)	₩ (31)	()	()	1 (24)	()	()	()	1 (23)	()	()	()
MOR [⊥]	1 (21)	₩ (38)	()	()	1 (36)	1 (38)	1 (23)	1 (27)	1 (12)	()	()	()
MOE [⊥]	1 (17)	()	()	()	ft (13)	1 (21)	↑ (11)	1 (16)	()	∜ (16)	∜ (18)	∜ (19)
Cl	1 (23)	()	()	()	1 (31)	1 (20)	ft (15)	1 (29)	1 (18)	()	()	1 (10)
SI	1 (32)	1 (27)	()	1 (48)	1 (54)	1 (30)	ft (68)	1 (85)	1 (47)	ft (59)	1 (44)	1 (41)
T	1 (38)	1 (19)	1 (19)	1 (13)	1 (33)	1 (33)	1 (26)	1 (44)	1 (39)	()	1 (26)	1 (26)

Legend: $\ensuremath{\mathfrak{A}}$: significant increase of the lumber property; $\ensuremath{\mathfrak{b}}$: significant decrease of the property. The values in parentheses indicate the percentage of increase or decrease of the property.

According to the literature, there are discrepancies associated to the amount of nanoclay that is to be added to wood adhesives in order to raise the mechanical strength of plywood products. Lei *et al.* (2010), for example, reported an increase of parallel tension properties of *Pinus sylvestris* plywood panels when nanoclay was added to PUF resin at amounts less than 3 %. In another study (Lei *et al.* 2008) the *MOE* of plywood panels was increased by adding nanoclay of various types at different proportions to the UF adhesive, reaching the maximum *MOE* with around 4 % nanoclay, beyond which this value decreased, additionally increasing the viscosity of the adhesive mixture and complicating the homogenous diffusion of nanoparticles, thus negatively affecting the setting of the resin. On the other hand, Moya *et al.* (2015a) found that the optimal concentration for the shear strength at the glue line in tropical lumber species is 1 %, which is close to the percentage presented in this study. When increased to 1,50 %, however, the contrary occurs: a decrease in shear strength.

Results for the mechanical properties in this study are congruent with those of other studies, as an addition of over 1 % nanoclay particles to the adhesive causes a decrease in the properties of plywood panels (Table 3). The amount of nanoclay in an adhesive mixture must be adequate since the particles tend to agglomerate at higher concentrations, bringing about the formation of lumps in the polymeric matrix of the adhesive, in this case UF, hence a decrease in strength (Kaboorani *et al.* 2012, Kaboorani *et al.* 2013, Moya *et al.* 2015b).

Glue line

A positive aspect of modifying the UF resin with Dellite 43B®-DMBHT nanoclay is that this does not change, at least visually, the colour of the glue line (Figure 4), therefore the aesthetic quality of products fabricated with the adhesive formulations studied would not be affected.

Scanning electronic microscopy (SEM) tests and micrometric measurement taken at the interfacial zone allowed to determine the thickness of the glue line of the various nanoclay-treated plywood panels, yielding the following values: 90 μ m for *C. alliodora*, 46 μ m for *G. arborea* and 15 μ m for *V. ferruginea* (Figure 5A, Figure 5C, Figure 5E). Nano-modification of the UF adhesive with Dellite 43B*-DMBHT nanoclay particles at 0,75 % produced a significant increase of the properties in the cross-laminated panels. With this nanoclay concentration, a more uniform glue line was observed, which allowed it to transfer and distribute strains more effectively when panels underwent parallel flexure strains (Figure 5B, Figure 5D, Figure 5F). Meanwhile, in the case of Figure 5F, the generation of an interface ranging from 235 μ m to 262 μ m was determined, which indicates the adhesive became diffused at the interior of the cell structure of the wood, enabling a transition zone which favoured mechanical properties at the macro level.

It is likely that this nanoclay concentration allowed the UF resin to create the primary adhesion mechanism at the interfacial region between the adhesive and the solid wood, which is the interlocking mechanism through which the adhesive holds on to porous structures such as wood (Vick 1999). Effectivity of this interlocking mechanism is obtained when the adhesive can penetrate beyond the surface to a depth of at least 2 to 6 cells, giving place to an effective transition zone between adhesive and veneer, as happens when nanoclay concentrations of 0,75 % are present in the adhesive, which can be observed in Figure 5F. This means the interface is the region where properties of all system components are combined, thus yielding the final properties of the composite material (Pukánszky 2005, Gadner 2006, Jacob *et al.* 2008, Frihart and Hunt 2010).

CONCLUSIONS

Modification of the adhesive formulation with nanoclay did not show a significant effect on the density and specific weight of plywood panels, but it managed to significantly decrease the statistical percentage of swelling and water absorption of panels of the three species, therefore there is an improvement in the properties of this sort of tropical lumber panels in presence of water.

For all plywood panels, in general, application of the UF adhesive with nanoclay treatment at 0,75 % obtained the best mechanical performance of MOR and MOE in both parallel (\mathbb{I}) and perpendicular ($^{\perp}$)

orientations, determining a significant statistical difference relative to the control treatment. Likewise, other properties were also improved with the other treatments; nonetheless this concentration was effective for the three lumber species studied, which was not achieved with the other concentrations.

Tests at the micro-scale by means of electronic microscopy evidenced that the addition of Dellite 43B®-DMBHT nanoclay particles at 0,75 % improved the glue line and interfacial regions, allowing for distribution and transference of mechanical strains to be more homogenous.

ACKNOWLEDGEMENTS

To the Vicerrectoria de Investigación y Extensión (VIE) of the Instituto Tecnológico de Costa Rica (TEC) for funding of the project. To companies Maderas Cultivadas de Costa Rica S.A., PROGASA, Aserradero Aserrín S.A., FAPACO S.A. and Centro Agronómico Tropical de Investigación y Enseñanza (CATIE) for providing the material and logistical support for the study. To the Laboratorio Institucional de Microscopía Electrónica VIE/TEC for the scanning electronic microscopy (SEM) tests.

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