

Research Article

Effects of Adding Multiwall Carbon Nanotubes on Performance of Polyvinyl Acetate and Urea-Formaldehyde Adhesives in Tropical Timber Species

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Multiwall carbon nanotubes (MWCNTs) functionalized with hydroxyl groups (MWCNTs-OH) have been incorporated into polyvinyl acetate (PVAc) and urea-formaldehyde (UF) adhesives utilized in tropical wood gluing. The Raman spectroscopy, the atomic force microscopy (AFM), and transmission electron microscopy (TEM) were used to describe the MWCNTs-OH. The adhesives were evaluated in three concentrations of MWCNTs-OH: 0% (control), 0.05%, and 0.1%. The evaluation included color, the distribution of MWCNTs-OH by TEM and AFM, thermal stability and viscosity of the adhesives, and shear strength (SS) of the glue line for nine tropical woods. AFM and TEM confirmed interaction of MWCNTs-OH with adhesives. The viscosity of the PVAc adhesive increases with added MWCNTs-OH. The incorporation of MWCNTs-OH in PVAc and UF resin produces wood adhesives with less brightness, less yellowness, and increased redness. The nanotubes in the adhesive improved the thermal stability of the composites and increased the entropy factor and energy of activation in the kinetic decomposition of the resin. In relation to SS, MWCNTs-OH in any of the two concentrations had no significant effect on SS in dry condition in half of the species studied glued with PVAc adhesive, whereas, for UF-adhesive, the SS and percentage of wood failure improved in most of the 9 species studied.

1. Introduction

Adhesives play an important role in the wood industry; 75% of the products manufactured with this material are joined together by means of adhesives [1]; among those products are composites like plywood, fiberboards, and OSB [2, 3]. The employment of adhesives has also facilitated wood utilization to make good quality products [4]. Due to their importance, production of new or enhanced adhesives has incentivized the search for new methods to increase added value in the applications [1].

Application of nanotechnology to adhesive manufacturing allows the development of new characteristics and properties in these polymers that increase their performance [2, 5]. Nanoclay, aluminum oxide nanoparticles, cellulose nanocrystals, zinc oxide nanoparticles, and carbon nanotubes are among the nanofillers utilized to enhance adhesives [6].

The unique properties of carbon nanotubes have attracted great interest since their discovery in 1991. Carbon nanotubes can be used to store fuel such as hydrogen, for new compound materials, and in catalytic applications, among others [7]. Carbon nanotubes are graphene tubular structures that may be composed of a single layer (single-wall carbon nanotubes, SWNTs) or several concentric layers (multiwall carbon nanotubes, MWCNTs) [8].

The difference between SWNTs and MWCNTs is related to their properties (chemical resistance, mechanical, thermal and electrical), which are conferred by the structure thereof and also determine their applications [8]. For example, Asgari and Lohrasbi [9] compared SWNTs and MWCNTs and they conclude that MWCNTs have durability as a support for platinum electrodes for gas diffusion. Likewise, Osswald et al. [10] mention the conductive high capacity SWCNTs compared to MWCNTs; this makes the latter more suitable

for applications of mechanical reinforcement in a polymer matrix. Another important difference of the two types of nanotubes lies in production costs, with MWCNTs being the lowest cost in relation to the SWNTs [10]. These properties make many researchers, as in this work, inclined to use MWCNTs.

Another important aspect of MWCNTs is their dispersion. Despite the versatility of carbon nanotubes, dispersion into different polymer matrices has posed a challenge since they are composed only of carbon. However, a number of techniques have been developed to achieve compatibility of the nanotubes with other materials. One of these techniques consists of performing chemical modification of the nanotube surface, by adding functional groups such as hydroxyl (-OH), when polar polymer matrixes are to be used [7]. The addition of this functional group gives a polar character to MWCNTs expected to make them more compatible with polymeric matrices such as polyvinyl acetate; plus it also shows affinity to the chemical structure of the wood above giving improved dispersion [11].

Some studies have shown that adding carbon nanotubes to different polymer matrices improves the properties of the materials and the wood was not exception [11]. Similarly, Ghasemi et al. [12] showed improvement of the morphological and mechanical properties of foams based on poly(vinyl chloride)/wood flour with the dispersion of functionalized MWCNTs with -OH. However, although this approach can be easily adapted for use with current process technology, the poor dispersion of nanotubes in the matrix has been a serious drawback, resulting in a degradation of the quality of the composites. The effective utilization of polymeric composites strongly depends on the ability to disperse the MWCNT homogeneously throughout the polymeric matrix without destroying the integrity of the MWCNTs. Therefore, the elastic moduli and viscosity, namely, the rheological properties of composites, have received considerable attention over the past several years [8, 13], due to the necessity for understanding the influence of various rheological parameters on MWCNT-mixed polymeric composites.

Despite previous with functionalized MWCNT-OH in PVAc and UF wood adhesives is poorly understood and the potential importance of MWCNT improving adhesion tropical species that usually presents problems interaction between the adhesive and the wood surface.

Thus, the present work aims at showing the performance of two adhesive types—polyvinyl acetate (PVAc) and urea-formaldehyde (UF)—with added multiwall carbon nanotubes functionalized with -OH groups in two concentrations (0.05% and 0.1%, w/w) as nanofiller and the effect of this nanofiller on shear resistance (effort and percentage of wood failure) of the glue line in nine (9) tropical species: *Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyramidale*, *Tectona grandis*, and *Vochysia ferruginea*. In addition to presenting the resistance values, this study aims at characterizing the MWCNTs-OH and observes the color change of the adhesives, the variation of viscosity, thermal stability, entropy factor and activation energy in

the decomposition kinetics, the shear strength of the glue line, and the percentage of wood failure.

2. Materials and Methods

2.1. Materials. Multiwall carbon nanotubes functionalized with hydroxyl groups (MWCNTs-OH) were used, provided by Cheap Tubes Inc. (Cambridgeport, USA). In addition, multiwall carbon nonfunctionalized nanotubes from the same company were used to compare functionalization of nanotubes in Raman. Information provided by the manufacturer of both products indicates an external diameter of approximately 50 nm, 10–20 μm length, 95% pureness, and -OH groups concentration ranging from 0.5 to 1.0% in weight.

Two types of wood adhesives were employed: the water based polyvinyl acetate (PVAc) Resistol M.R. 850, produced by Henkel Capital S.A. (<http://www.resistol.com.mx/es.html>). The technical description of the product indicates that the resin is polyvinyl acetate and water, presenting 54.5–55.5% solid content and 1600–2200 cPs viscosity. The second type is water based urea-formaldehyde (UF) adhesive of the commercial brand Resina CR-560 U-F, manufactured by Química Centroamericana, Quibor, S.A. (<http://www.agroquibor.com/>). This is a three-component *in situ*-prepared adhesive: resin, wheat flour, and catalyst of sulphate type, with weight proportions of 41%, 24.8%, and 0.32%, respectively, plus 34% water. The technical description indicates that the product presents 64–65% solid content and 650–900 cPs viscosity.

The species utilized to test the modified adhesive were *Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyramidale*, *Tectona grandis*, and *Vochysia ferruginea*, all of them woods traditionally used in Costa Rica to manufacture doors and other wood products or products for engineering that demand intensive use of adhesives [14]. Some of these species have shown gluing problems [15]. The woods were obtained at different lumber stores.

2.2. MWCNTs-OH Characterization. The structure of the MWCNTs-OH was evaluated by means of the Raman spectra and the thermogravimetric analyzer. The Raman spectra of the nanotubes were collected on a DXR Raman Microscope, Thermo Scientific; the samples were excited at 532 nm from the laser line and 2.5 mW power, with a spectrograph aperture of 25 μm pinhole. Next, the analysis of the variation in the intensities of the bands characteristic in MWCNTs-OH (D, G, and G') is carried out. Measurements of TGA were carried out using 10–12 mg of MWCNTs and MWCNTs-OH in order to determine the thermal stability, at a heating rate of 50°C/min in a nitrogen atmosphere reaching a temperature of 100°C in 50 minutes. A thermogravimetric analyzer model TGA 5000, brand Instrument NBr, was used. In order to avoid unwanted oxidation, TGA measurements were conducted with the composite placed in high quality nitrogen (99.5% nitrogen and 0.5% oxygen content) atmosphere and the data analysis was made by TA Instruments Universal Analysis 2000 software. Spectra obtained with the Raman and

the curves in the TGA of the MWCNTs-OH were compared with the spectra of the MWCNTs without functionalizing.

2.3. Preparation of Adhesive with MWCNTs-OH. MWCNTs-OH were added to two types of adhesives (PVAc and UF) in three concentrations: 0% (control), 0.05%, and 0.1% (weight weight^{-1}). The addition of the MWCNTs-OH to the adhesive was carried out in two stages. Firstly, the weight of the MWCNTs-OH necessary to prepare the 0.05% and 0.1% concentrations in the adhesives was calculated. Then, the nanotubes were dispersed in a volume of water (5% weight weight^{-1} with respect to the PVAc adhesive) by sonication (dispersion A), following the method proposed by Khan et al. [16]. The second stage consisted of mixing the aqueous dispersion of functionalized nanotubes in the PVAc, which was performed mechanically. In the case of the UF adhesive, it differs from the PVAc: firstly, the mass of nanotubes corresponding to concentrations 0.05% and 1% was sonicated in the volume of water to be added in the preparation of the adhesive (54% w/w water). After that, the weight of the resin and of the other components was calculated according to the proportions indicated and then mixed.

Sonication of the MWCNTs-OH in water was performed at an amplitude of 75% for 30 minutes, at intervals of 45 seconds with 15-second breaks. For sonication the equipment ultrasonic processor model CV18 was used. To add dispersion A into the PVAc adhesive and the MWCNTs-OH mixture into the UF resin, both mixtures were stirred at 1600 rpm with the aid of four 45° inclined blade impeller for 15 minutes. During that time, the nanotube dispersion was added slowly to attain a homogeneous mixture.

2.4. Characterization of the Adhesive. First, the MWCNTs-OH were observed in the adhesive. For this, samples were observed by means of the transmission electron microscope (TEM) and the atomic force microscope (AFM). Later, the two types of adhesives (PVAc and UF) in both concentrations of MWCNTs-OH (0.05% and 0.1%) and the respective controls were evaluated for viscosity, color, and thermal behavior by means of thermogravimetric analyses (TGA).

TEM images were obtained using a Jeol JEM 2100F TEM. These images were taken with a beam current of 52 μm at 100 kV. The AFM observations performed in the wood adhesive were carried out using a Nanoscope V, an atomic force microscope (Asylum Research model MFP 3D), fitted with a Hybrid XYZ scanner. Atomic force microscope measurements were done under ambient air conditions in tapping mode. The sensitivity of the tip deviation and the scanner resolution was 0.3 nm. The resolution was set to 250 lines by 256 pixels for all observations.

Measurement of viscosity was performed using a 600 mL Low Form Griffin Beaker using 500 mL of the adhesives in the Brookfield-II+ Pro LV. 2.4.4 viscometer. Spindler number 4 for the PVAc adhesives and spindler number 3 for the UF adhesives according to the ASTM D2256-11 standard [17] were used.

As for color, a film sample (3 cm wide \times 10 cm long \times 2 mm thick) was prepared on glass with each adhesive. Once

the film was dry (approximately 72 hours later), its color was measured. Color measurement of the MWCNTs-OH in solid condition was also performed, for which purpose powder samples of the MWCNTs-OH were used. A Hunter Lab Scan XE Plus mini model spectrophotometer was used to obtain the L^* , a^* , and b^* parameters. The conditions for color measurement are detailed by Moya et al. [18]. The index of color difference (ΔE^*), according to the ASTM D2244 standard [19], was used to compare color parameters between adhesives with different concentrations of MWCNTs-OH. This index defines the color difference magnitude between two adhesives using CIELab's color systems according to (1). This index was calculated using the average color values for all samples from each adhesive:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (1)$$

where $\Delta L^* = L^{*M} - L^{*P}$, $\Delta a^* = a^{*M} - a^{*P}$, $\Delta b^* = b^{*M} - b^{*P}$, M = average value for adhesive without MWCNTs-OH, and P = average value for adhesive with MWCNTs-OH.

The thermal stability was analyzed for the two types of adhesives with the 3 concentrations. Measurements of TGA were carried out using 10–12 mg of each adhesive in each concentration, at a heating rate of 50°C/min in a nitrogen atmosphere reaching a temperature of 100°C in 50 minutes. A thermogravimetric analyzer model TGA 5000, Instrument NBr brand, was used. TGA measurement conditions are detailed by Moya et al. [18]. Two decomposition reactions were identified in the case of PVAc; in the case of UF only the second reaction was analyzed because the first one corresponds to water elimination. For each reaction, the temperature and the remnant mass at the start of the decomposition, at the maximum reaction point, and at the end of the reaction were identified. Then kinetics was calculated for each reaction (2) by means of lineation (3), according to Vyazovkin and Sbirrazzuoli [20], where the differential isoconversional method of Friedman is utilized:

$$K = K_0 * e^{(-E/RT)}, \quad (2)$$

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln K_0 + \left(\frac{-E}{RT}\right) + n \ln(1 - \alpha), \quad (3)$$

where α is degraded mass, $d\alpha/dt$ is percentage of the degraded sample in unite time, K_0 is entropy factor, E is energy of activation, T is temperature, and R is gas constant.

2.5. Bond Strength Resistance. Shear strength (SS) of glue line of PVAc and UF adhesives modified with MWCNTs-OH in both concentrations was evaluated by the shear test according to the ASTM D-905-98 standard [21]. The adhesive containing MWCNTs-OH was applied to *Acacia mangium*, *Cedrela odorata*, *Cordia alliodora*, *Enterolobium cyclocarpum*, *Gmelina arborea*, *Goethalsia meiantha*, *Ochroma pyramidale*, *Tectona grandis*, and *Vochysia ferruginea*. A total of 90 shear samples were prepared, using 3 concentrations of MWCNTs-OH (0.00, 0.05, and 0.10%), with 30 samples for each concentration. During preparation, the wood samples were stabilized at 12% moisture content for one week. The adhesive

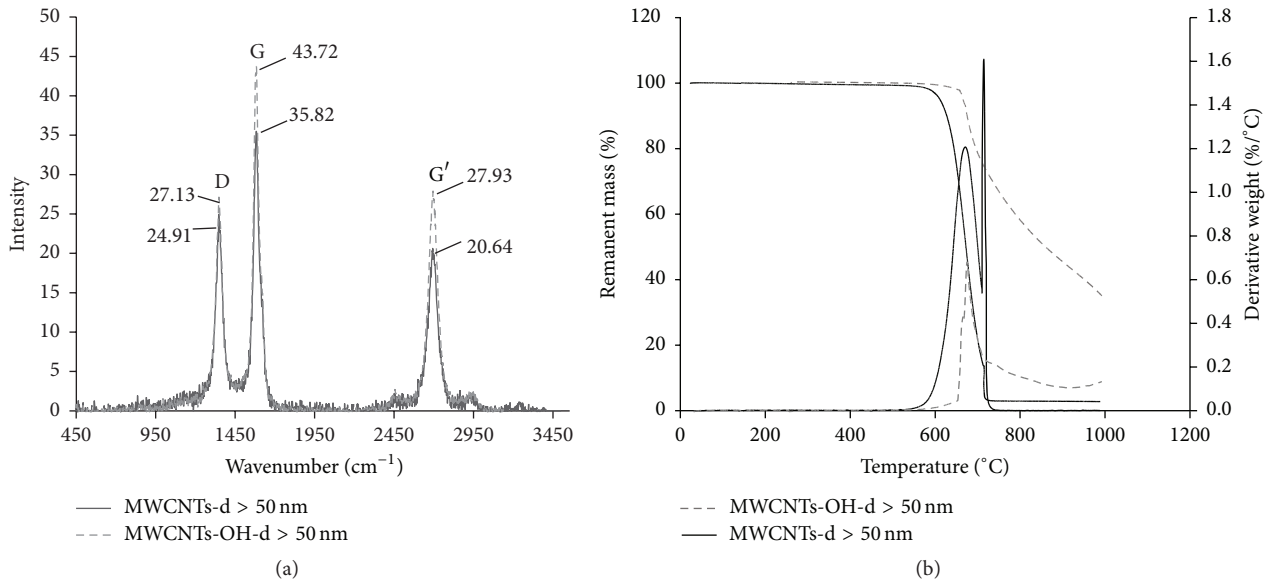


FIGURE 1: Raman spectra (532 nm excitation) (a) and TGA (b) of MWCNTs and MWCNTs-OH.

was applied according to the manufacturer's specifications, that is, an amount of 100 g m^{-2} in both types of adhesive. After applying glue on the surface of the wood, the samples were pressed in a hydraulic machine at 2.0 kg cm^{-2} pressure, maintaining the pressure for 24 hours. After pressure application, glued samples were conditioned to 20°C and 60% relative humidity for two weeks. Then 30 samples were extracted from the glued samples and tested for each set of formulation. The evaluation of shear resistance was measured in dry and wet condition. The Tinius Olsen hydraulic test machine with 10 kN capacity was used for load application and the data were entered into a computer. The percentage of wood failure and maximum load were recorded for each test. The block shear tests were carried out according to the ASTM D905-98 standard [21]. The sizes of samples for "wet condition" were the same as "dry condition tests." For "wet condition," the samples were taken directly out of the water after being immersed in water for 24 h. Before the tests, excess water was wiped off from the samples. During the water immersion period, temperature of water was maintained at 20°C . After each sample was tested in the compression test, the percentage of wood failure was evaluated according to the ASTM D-5266-13 standard [22].

2.6. Analysis of the Information. Compliance of the determined variables with the assumptions of normal distribution and homogeneity of the variances and with the presence of extreme data was verified. After that, a variance analysis was applied to verify the effect of adhesion of the MWCNTs-OH concentration (0%, 0.05%, and 0.1%) on viscosity, values of entropy factor, activation energy, function of decomposition, and temperature and remnant mass in different reactions of kinetics of decomposition and shear strength of the wood. The Tukey test at 99% confidence level was established to determine the statistical difference between the mean values.

3. Results and Discussion

3.1. MWCNT Characterization. Figure 1(a) shows the comparison between the MWCNT and MWCNTs-OH. As expected, bands D, G, and G' were detected in both types of nanotubes. However, a difference in the Raman intensity of the functionalized nanotubes in the three bands was observed. In band D, located close to 1350 cm^{-1} , the increase in the intensity represents a ring breathing mode from sp^2 carbon rings and indicates the presence of some disorder in the graphene structure in the nanotubes, attributed to other forms of carbon that contaminate the sample and to defects in the walls of the nanotubes or heteroatoms added to the structure of the nanotubes [23, 24]. Meanwhile, Datsyuk et al. [25] mention that increases in the intensities of band G, located after 1500 cm^{-1} , and band G' are produced by in-plane stretching of carbon-carbon bonds in the graphene sheets; they also point out disorders and defects of the carbon nanotubes. The above results showed that MWCNTs-OH presented an increment in all the bands with respect to MWCNT and increased defects in the walls of the nanotubes, probably due to the presence of -OH groups added to multiwall nanotubes [23, 24].

The evaluation of the thermal stability measured by TGA shows a difference between MWCNTs-OH and MWCNTs (Figure 1(b)). Two types of oxidation are observed in MWCNTs: the first one presented at 671°C and the second one occurred at 714°C , with a residual mass of 2.82%. For MWCNTs-OH, the maximum decomposition temperature occurred at 675°C and residual mass was 35% (Figure 1(b)). It is also observed that the initial decomposition temperatures differ for both CNTs, in MWCNTs being approximately 597°C and for MWCNTs-OH being 659°C .

The temperature ranges observed agree with another report of MWCNTs, which reports a range of 600°C to 750°C [7, 10, 26]. The small differences observed in this temperature

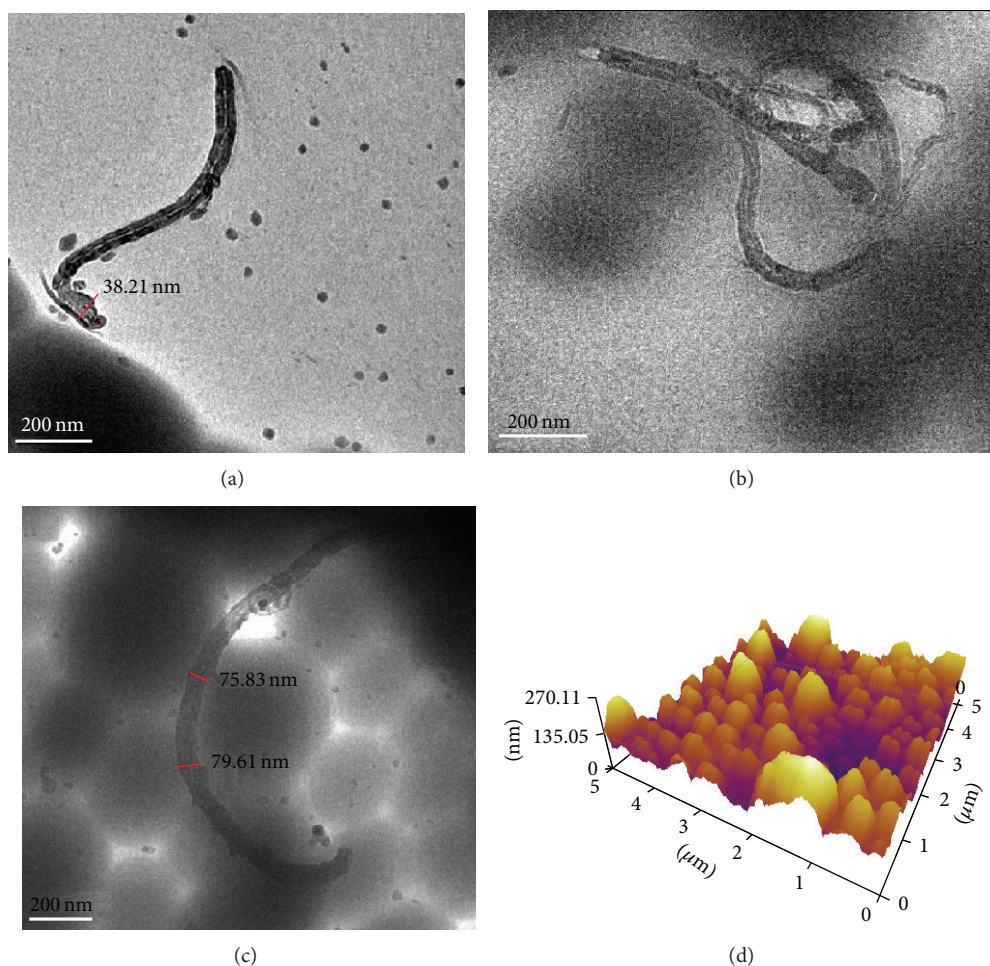


FIGURE 2: TEM micrographs ((a), (b), (c)) and AFM profil of MWCNTs-OH/PVAc films (d) of MWCNTs-OH/PVAc films.

and in decomposition temperatures can be linked to the temperatures of synthesis of the nanotubes, the presence of defect sites along the walls and at the ends of the nanotubes, the number of walls in MWCNTs and the presence of the catalyst composition, and the presence of other materials in the sample [27, 28]. The crystallinity of the nanotubes gives great stability and increases the resistance they present to oxidation; when subjected to a functionalization process, nanotubes change their size; they may lose some layers and increase the number of defects [7, 26]. These characteristics imply a loss in the crystallinity and therefore the resistance to oxidation; this should be reflected in a decrease in the maximum temperature of decomposition [7, 10, 27, 29]. However, this behavior of MWCNTs-OH does not agree with that expected. This difference could be due to two samples which do not belong to the same batch and the number of walls before functionalization differing with the MWCNTs used for this comparison.

The peak at 714°C in the MWCNTs lightly observed in MWCNTs-OH can be associated with material purity and with the presence of other types of complex materials such as fullerenes [26, 30]. Similarly, the difference between the residual masses (MWCNTs: 2.82%; MWCNTs-OH: 35%) may be associated with the metal type used for catalysis

in the synthesis process as well as oxidation products of that catalyst. This reflects a difference in the quality and homogeneity between both materials, Lehman et al. [26].

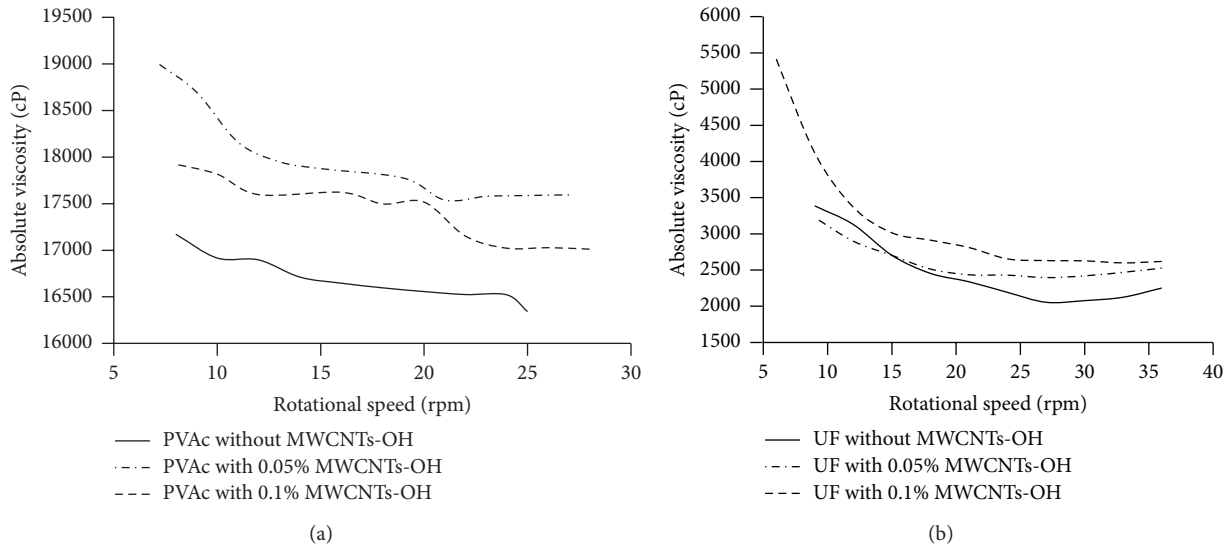
3.2. Adhesive Characterization

3.2.1. TEM and AFM. Figures 2(a) and 2(b) show MWCNTs-OH TEM images where the dimensions and irregularities of the external wall of the nanotubes can be observed. Figure 2(c) reveals the interaction of the MWCNTs-OH with the PVAc; the MWCNT-OH has a tubular structure while the PVAc can be perceived as spherical particles [28], with diameters ranging between 35.0 and 45.0 nm. Figure 2(d), meanwhile, shows the corresponding AFM image of the PVAc-MWCNTs-OH film, where zones of high and low rugosity can be observed. High rugosity zones could be associated with presence of MWCNTs-OH, while low rugosity areas could be linked to PVAc particles [2], which tend to be more homogeneous in shape and rugosity, thus coinciding with the observations from the TEM.

3.3. Viscosity. Viscosity decreases as the rotational speed increases in both types of adhesives and the 3 concentrations of MWCNTs-OH (Figure 3). This behavior is known as

TABLE 1: Viscosity and color of the adhesive modified with MWCNTs-OH.

Adhesive	Concentration (%)	L^* color parameter	a^* color parameter	b^* color parameter	ΔE^*
MWCNTs-OH	—	1.08	0.27	0.34	—
PVAc	0.00	37.40A	-3.30A	-2.06A	—
	0.05	12.75B	-0.24B	-0.68B	24.88
	0.10	12.13B	0.06C	-1.80C	25.50
UF	0.00	39.90A	7.76A	14.46A	—
	0.05	17.90B	0.15B	1.45B	26.67
	0.10	15.90C	0.44C	0.88C	28.53

FIGURE 3: (a) Absolute viscosity of PVAc with MWCNTs-OH at $22.5 \pm 0.5^\circ\text{C}$ and (b) absolute viscosity of UF with MWCNTs-OH at $21.8 \pm 0.5^\circ\text{C}$.

“shear-thinning,” which is characteristic of pseudoplastic fluids [31]. For PVAc adhesives, viscosity is greater when MWCNTs-OH are added and greater at 0.05% concentration compared to its value at 0.10% concentration (Figure 3(a)). This behavior was not observed for the UF adhesive. No differences in viscosity were observed between the adhesive without MWCNTs-OH and the adhesive with 0.05% concentration at low rotational speeds, as opposed to high speeds where differences are evidenced. Meanwhile, there was difference between the adhesive without MWCNTs-OH at 0.10% and 0.05% concentrations (Figure 3(b)).

The increase in viscosity with increasing amount of added MWCNTs-OH, especially for the UF adhesive, coincides with observations made by Pötschke et al. [32] and Du et al. [13] in polymers with MWCNTs-OH. However, the behavior found in the concentrations of the PVAc adhesive (greater viscosity at 0.05% concentration relative to 0.1% concentration) could be associated with the fact that the mixture between the PVAc and MWCNTs-OH at 0.1% concentration was not satisfactorily homogeneous [33].

3.4. Color. Relative to color parameters of the different adhesives with different proportions of MWCNTs-OH, luminosity (L^*) and yellowness (b^*) for both adhesives decreased statistically, whereas redness (a^*) increases with added

MWCNTs-OH (Table 1). However, the change in L^* differed in each resin: no differences were observed in PVAc with the proportions 0.05% and 0.1%. Parameter a^* (redness) increases in PVAc adhesive, while diminishing in UF adhesive. On the other hand, color change (ΔE^*) varied from 24.88 to 25.50 in the PVAc adhesive and from 26.67 to 28.53 in the UF adhesive as the amount of added MWCNTs-OH increases (Table 1).

According to the above results the addition of MWCNTs-OH tends to noticeably change the color parameters in both adhesives used, producing ΔE^* values above 12 [34]. This variation can be explained by the fact that unmixed MWCNTs-OH show values of L^* , a^* , and b^* close to zero, distinctive of black color. When adding the MWCNTs-OH to both resins, a suspension instead of a mixture is created, producing change in the tonality of the adhesive from white (Figure 4(a)) to gray (Figure 4(b)).

3.5. Thermal Stability of the Adhesive. TGA analysis of the PVAc modified with and without MWCNTs-OH (0.05% w/w, 0.1% w/w) shows two inflexions (Figure 5(a)). These inflexions are related to chemical reactions of decomposition that occur in each adhesive [35]. The first inflexion in PVAc adhesive, around 310°C , corresponds to the greatest weight loss and to structural decomposition of the adhesive, which

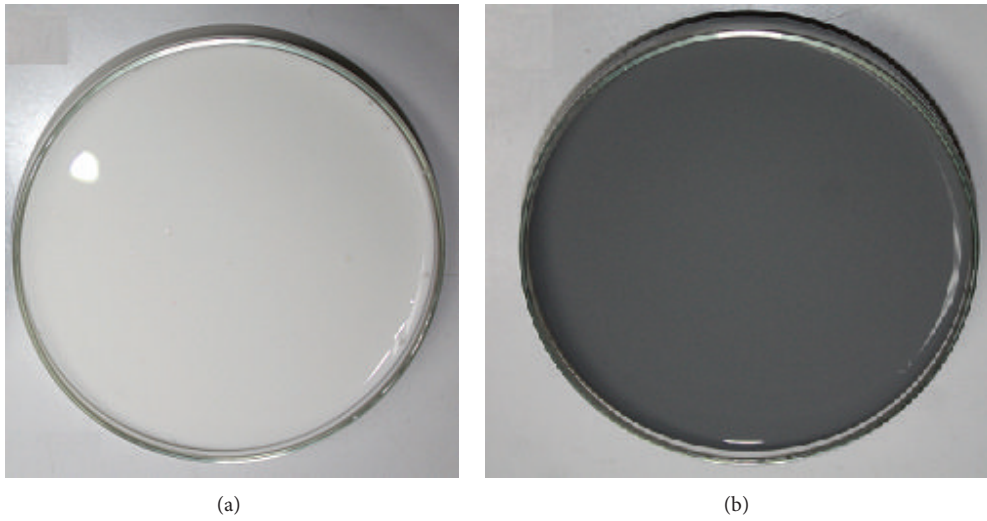


FIGURE 4: (a) PVAc sample without MWCNTs-OH and (b) PVAc with MWCNTs-OH showing color change.

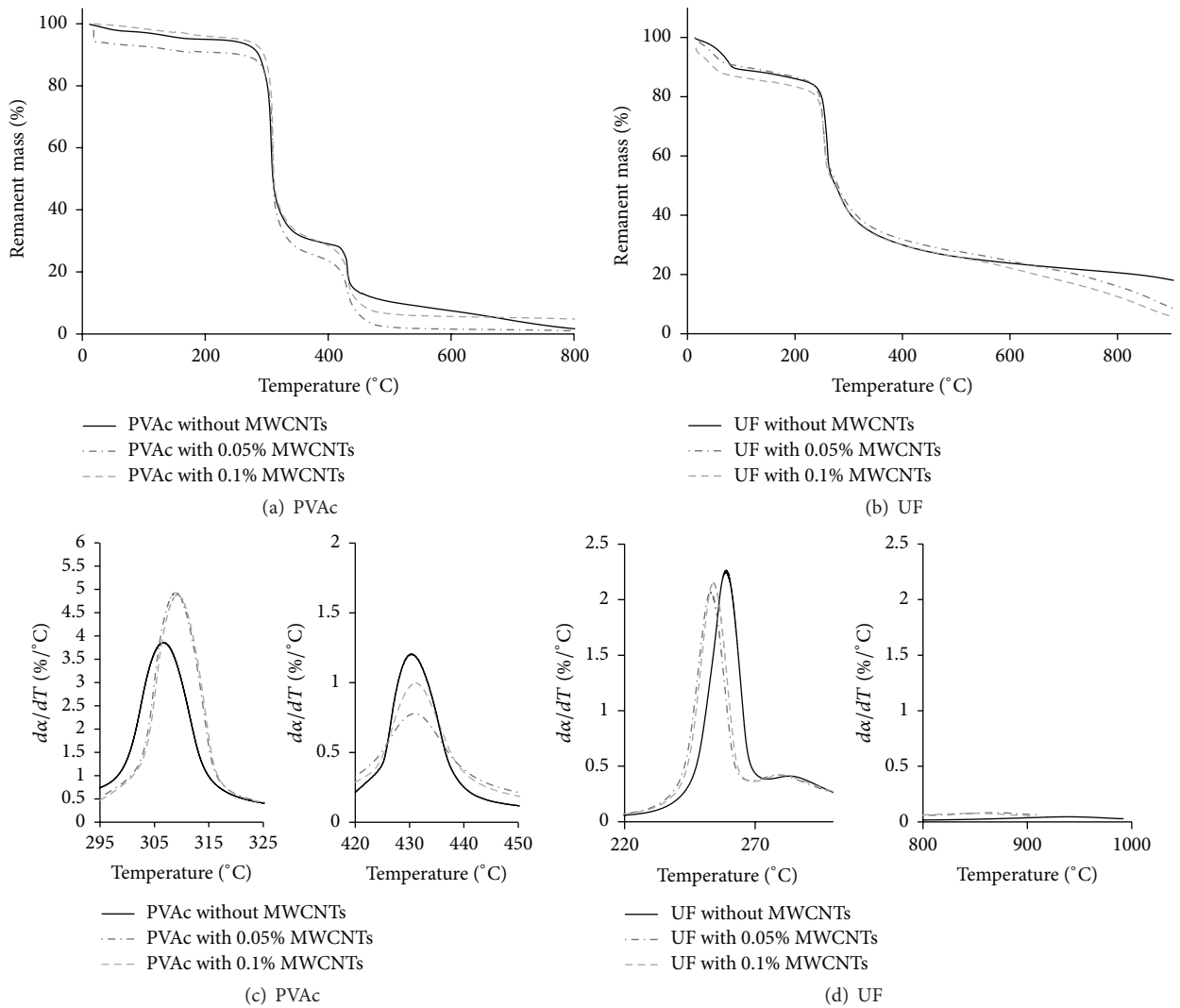


FIGURE 5: TGA (a, b) and DTG of the different reaction (c, d) curves of PVAc and UF wood adhesives adding different concentrations of MWCNTs-OH, measured under N_2 atmosphere with a heating rate of $50^\circ C/min$.

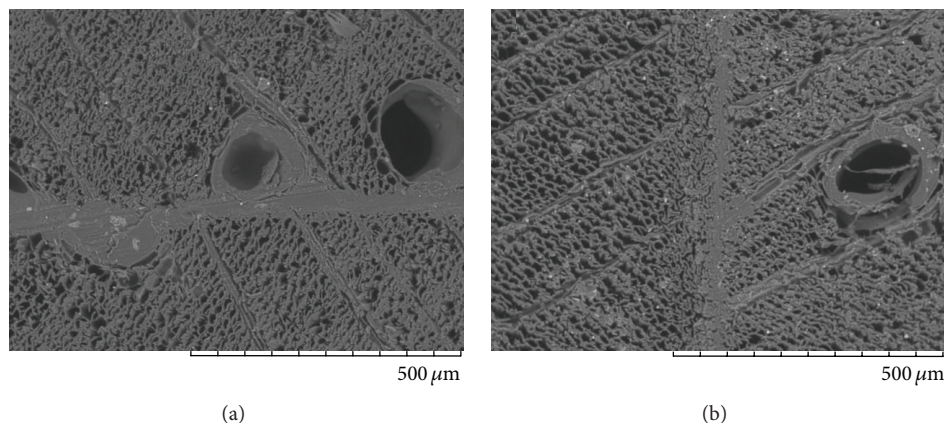


FIGURE 6: (a) Glue line in *Vochysia guatemalensis* wood glued with PVAc adhesive without (a) and with MWCNTs-OH (b).

according to McNeill et al. [36] is linked to decomposition of acetic acid. The second inflexion, close to 430°C (Figure 4(a)), could be the result of decomposition of organic additives utilized in the formulation of the PVAc emulsion [36, 37]. Regarding the UF adhesive (Figure 4(b)), small inflexion occurs before reaching 100°C, which is linked to loss of water contained in the UF adhesive [38]. A second decomposition within the range of temperature of 235°C and 262°C is also observed, resulting mainly from resin degradation. As a result, a series of components are liberated: methylene, methylol, dimethylene ethers, methylene methyl ethers, methylene glycols (formaldehyde), components with carbonyl groups, and triazine, among others [39].

The values of temperature and remnant mass at each inflexion where decomposition of each adhesive starts (Figures 5(c) and 5(d)) indicate that there is slight difference between the PVAc adhesive with MWCNTs-OH and without MWCNTs-OH in the first and second decomposition. In the first decomposition, the temperature (initial, peak maximum, and final point) presents no variation, but the remnant mass in those points is higher in adhesives containing MWCNTs-OH. A slight increase is observed with increasing concentration (Table 2). In the second reaction of the PVAc adhesive with and without MWCNTs-OH, little difference is again observed with the different temperatures. However, for remnant mass differences can be observed. The PVAc adhesive without MWCNTs-OH and the PVAc adhesive with 0.1% concentration of MWCNTs-OH presented differences in the remnant mass relative to the adhesive with 0.05% concentration of MWCNTs-OH.

The addition of any of the two concentrations of MWCNTs-OH to the UF adhesive produces noticeable alteration in temperature and increase of the remnant mass in reaction 2, with the exception of the remnant mass at the initial point (Table 2). Furthermore, no differences were found in various parameters evaluated for adhesives with 0.05% and 0.1% concentration of MWCNTs-OH (Table 2).

The analysis of the apparent combustion kinetics modelling of both types of adhesives with different concentrations of MWCNTs-OH (Table 3) showed that the activation energy in the adhesive without MWCNTs-OH is lower than that in

the adhesive with concentrations of MWCNTs-OH at 0.05% and 0.1%, increasing as the concentration of MWCNTs-OH increases (Table 3). Moreover, differences were found between the entropy factor of the combustion kinetics in the different reactions of the adhesives. The entropy factor was statistically higher in the PVAc adhesive with MWCNTs-OH in the first reaction, while the degree of the decomposition function tends to be stable for the three adhesives. Meanwhile, the entropy factor increases again with increasing concentration of MWCNTs-OH (0.05% and 0.1%) added to the UF adhesive, as what occurs with the activation energy and the degree of the decomposition function (Table 3).

With regard to the final ash content an increase was observed as concentration of MWCNTs-OH in the adhesives increased, which is attributed to the presence of MWCNTs-OH at finalization of the decomposition of the adhesive (Table 2).

TGA spectra (Figures 5(a) and 5(b)) showed that addition of MWCNTs-OH caused no modification in the decomposition reaction of any of the two types of adhesives evaluated, although modification of the thermal stability is observed (Table 3), which is due to increased activation energy and maximum temperature (Table 2). The same behavior was observed by Du et al. [13] and Fu et al. [11], although these authors added single-wall carbon nanotubes (SWCNTs). According to Fu et al. [11] thermal stability could be attributed to the barrier effects and radical-trapping effects of CNTs.

3.6. Wood Penetration. Likewise, it is important to mention that despite the increased viscosity of the glue (Figure 3), no significant effects in the penetration of the adhesive into the region near the glue line (Figure 6) are observed. Moreover, it was observed that the glue line area of *Vochysia guatemalensis* wood glued with PVAc adhesive modified with MWCNTs-OH was similar to wood glued with the unmodified adhesive (Figures 6(a) and 6(b), resp.). Even for vessels near the glue line, penetration of the adhesive was observed in glue line of wood glued with modified and unmodified adhesive.

3.7. Bond Shear Resistance. The results showed that adding MWCNTs-OH to PVAc or UF adhesives produces different

TABLE 2: Temperature and remnant mass in different reactions of decomposition kinetics of PVAc and UF adhesives adding different concentrations (weight weight⁻¹) of MWCNTs-OH.

Adhesive	MWCNTs-OH concentration (%)	Reaction 1				Reaction 2				Ash content at 900°C (%)	MWCNTs-OH weight (%)				
		Initial point Temp (°C)	Initial point RM (%)	Peak maximum Temp (°C)	Peak maximum RM (%)	Final point Temp (°C)	Final point RM (%)	Initial point Temp (°C)	Initial point RM (%)			Peak maximum Temp (°C)	Peak maximum RM (%)		
PVAc	0.00	298	85.36	309	64.50	315	44.34	414	27.63	431	21.71	450	12.47	0.97	—
	0.05	298	86.32	308	65.20	316	41.50	415	24.66	431	17.46	450	8.99	3.53	2.56
	0.10	298	87.57	309	66.73	315	43.80	415	26.59	422	19.28	449	10.40	4.40	3.43
UF	0.00	—	—	—	—	—	—	237	81.34	258	66.83	246	53.80	6.54	—
	0.05	—	—	—	—	—	—	243	81.57	253	69.60	262	57.59	10.10	3.56
	0.10	—	—	—	—	—	—	245	79.45	254	67.80	262	55.98	11.63	5.09

Temp: temperature and RM: remnant mass.

TABLE 3: Values of entropy factor, activation energy, degree of the function of decomposition, and correlation coefficient of kinetics of decomposition of PVAc and UF adhesives adding different concentrations of MWCNTs-OH.

Adhesive	Reaction	MWCNTs concentration (%)	Entropy factor (K_0 in S^{-1})	Activation energy (E in $kJ\ mol^{-1}$)	Degree of the function of decomposition (n)	Correlation coefficient (R)
PVAc	First	0.00	^A 4.33×10^{15}	^A 189.34	^A 2.0	0.77
		0.05	^B 5.35×10^{16}	^B 204.67	^A 2.1	0.83
		0.10	^C 6.53×10^{18}	^C 227.28	^A 2.3	0.82
	Second	0.00	^A 6.76×10^{37}	^A 403.94	^A 4.6	0.75
		0.05	^B 4.38×10^{20}	^B 232.27	^B 2.3	0.83
		0.10	^C 6.69×10^{23}	^C 323.01	^B 2.9	0.71
UF		0.00	^A 2.03×10^{23}	^A 237.6	^A 6.83	0.98
		0.05	^B 2.72×10^{33}	^B 333.16	^B 9.7	0.95
		0.10	^C 1.01×10^{41}	^C 414.63	^B 10.8	0.96

behaviors in the shear strength (SS) of the glue line among species (Figure 7). As expected, the highest values of SS appeared when the different types of woods were glued with the UF adhesive compared to the PVAc adhesive. The MWCNTs-OH in any of the concentrations had no significant effect on SS in the species *C. alliodora*, *E. cyclocarpum*, *G. arborea*, *O. pyramidale*, and *T. grandis* in dry condition, glued with PVAc adhesive (Figures 7(c)–7(e) and 7(g)–7(h)). *E. cyclocarpum* glued with PVAc adhesive modified with MWCNTs-OH was the only species significantly unaffected in wet condition (Figure 7(d)). The SS values for *T. grandis*, *G. meiantha*, *O. pyramidale*, and *T. grandis* glued with UF adhesive modified with MWCNTs-OH were not significantly affected in wet condition (Figures 7(f)–7(i)). For the remaining conditions and species, SS augmented significantly in at least one concentration, the adhesive with 0.1% concentration of MWCNTs-OH being the one with the highest values of SS, in many conditions and species.

In all evaluated species moisture content in dry condition was statistically equivalent for all conditions of concentration of MWCNTs-OH and species (Table 4). However, no differences were observed in this property in some species or adhesives in wet condition (MC), after the wood was immersed in water for 24 hours (Table 4). Where the PVAc adhesive is modified with MWCNTs-OH, significant decrease of the moisture absorption, that is, less MC, occurs only in *C. alliodora* and *O. pyramidale*. Meanwhile, where the UF adhesive is modified with MWCNTs-OH, moisture content decreases in the wood of *A. mangium*, *G. arborea*, and *O. pyramidale*. For the rest of the species, the value of moisture content remains statistically unaffected (Table 4).

The percentage of wood failure (PWF) in wood glued with PVAc adhesive with added MWCNTs-OH diminished significantly in the woods of *A. mangium*, *C. alliodora*, *G. arborea*, and *O. pyramidale* in dry condition (Table 4). Meanwhile, for *A. mangium*, *E. cyclocarpum*, *G. meiantha*, *T. grandis*, and *V. guatemalensis* in wet condition, the wood failure percentage increased with added MWCNTs-OH. For the rest of conditions and species, PWF was not significantly affected by the addition of MWCNTs-OH to the PVAc.

For *C. odorata* in wet condition and for *G. meiantha* in both moisture conditions (dry and wet), PWF diminished significantly with the UF adhesive with MWCNTs-OH

(Table 4). On the other hand, the PWF increased in the glue line with the UF adhesive modified with MWCNTs-OH in *A. mangium* and *E. cyclocarpum* in both moisture conditions (dry and wet); in *C. odorata* and *C. alliodora* in dry condition and 0.1% concentration of MWCNTs-OH; and in *T. grandis* and *V. guatemalensis* in dry condition.

Addition of graphene components or nanotubes (CNT or MWCNT) has proved to help improve adhesion properties of different types of adhesives [11, 12, 40–43], as observed in several of the species evaluated in the present study (Figure 5). However, few studies have utilized MWCNT in wood adhesives. One of them is the one conducted by Fu et al. [11], who found that incorporating CNTs and CNT-OH could effectively reduce the flammability of WPC, and CNT-OH conferred better flame retardancy on WPC relative to pristine CNTs due to the improved interfacial compatibilization between CNT-OH and wood flour.

Meanwhile, Pinto et al. [42] found that 50% increase of shear strength on veneer lap joints occurs by increasing concentration of graphene nanoplatelets from 0.1% to 0.3% in poly(vinyl acetate) latex. Those investigations agree with the results obtained when adding MWCNTs-OH to a base of either PVAc or UF in *A. mangium*, *C. odorata*, *C. alliodora*, and *G. meiantha* (Figures 7(a)–7(c) and 7(f)) and in *E. cyclocarpum*, *G. arborea*, and *O. pyramidale* with UF adhesive (Figures 7(d)–7(e) and 7(g)). However, an increase in SS was only observed in *G. meiantha* while changing from 0.05 to 0.1% concentration in the UF adhesive (Figure 7(c)) and in *V. ferruginea* with PVAc (Figure 7(i)), as observed by Pinto et al. [42] while changing from 0.1% to 0.3% graphene nanoplatelets in poly(vinyl acetate) latex to increase shear resistance.

Shear resistance increment occurring in most of the species when adding MWCNTs-OH, particularly in the case of UF resin in some concentrations, can be explained by the conclusions by Pinto et al. [42], who mention a significant mechanical reinforcement that can be attributed to strong interfacial interactions between polymer chains and the graphene surface. Likely, affinity of the surface of the material and good dispersion of the nanotubes inside the polymeric matrix produce cohesive reinforcement of the adhesive layer, resulting in greater joint resistance [43].

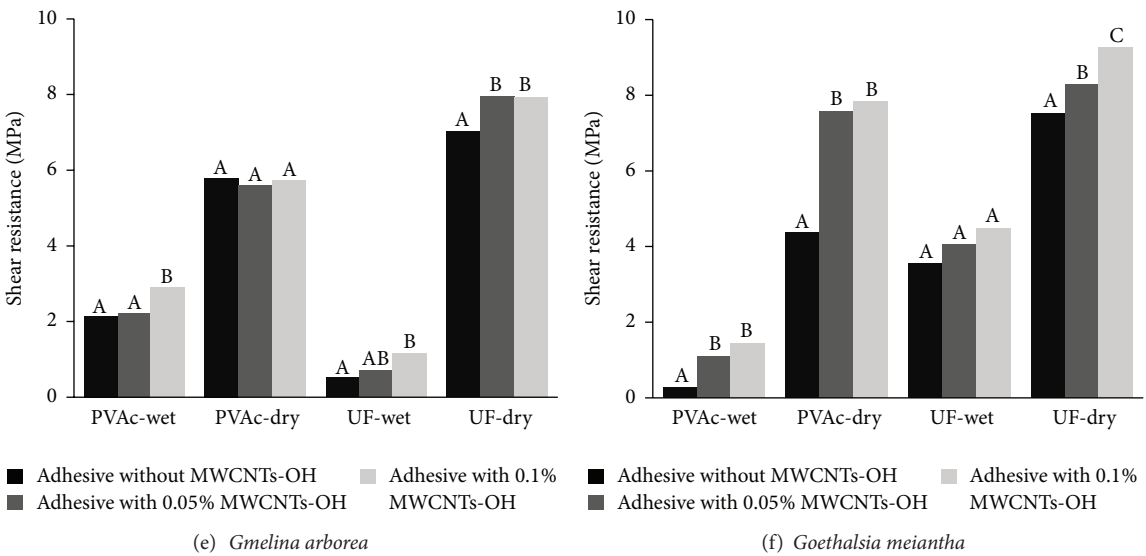
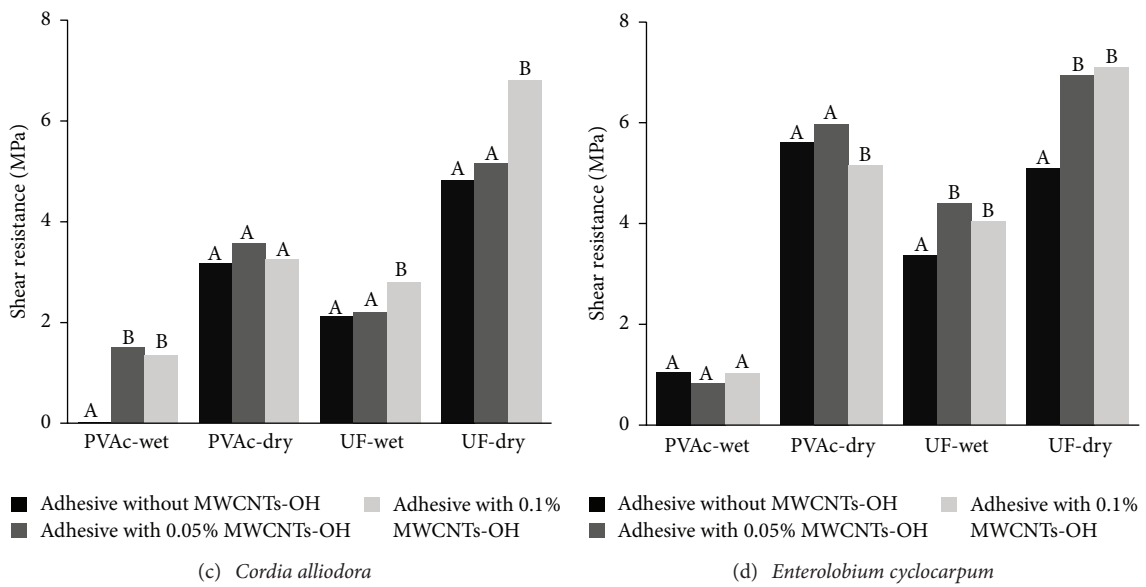
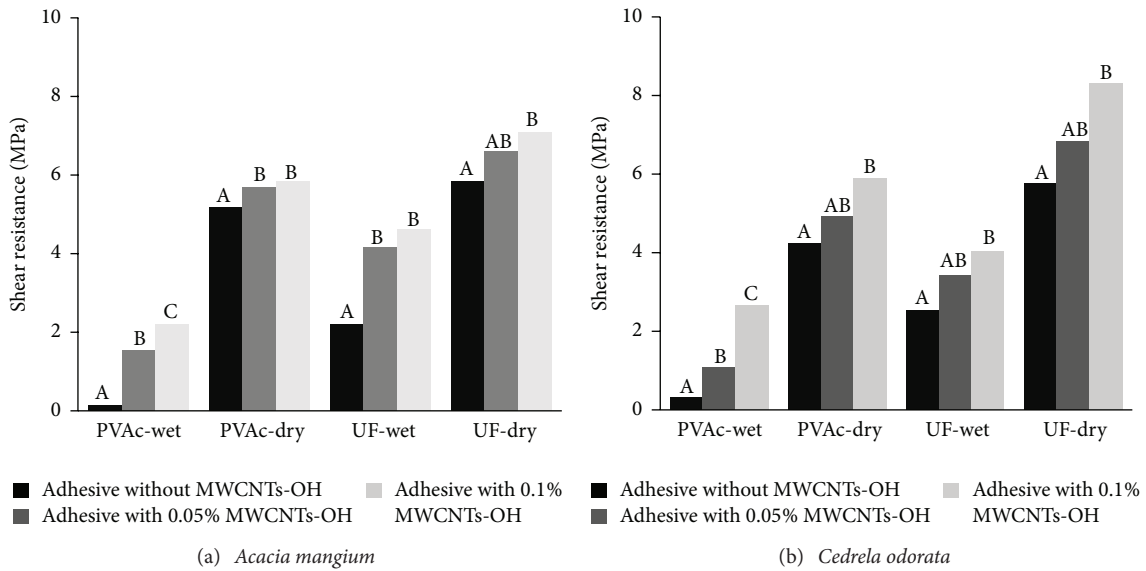


FIGURE 7: Continued.

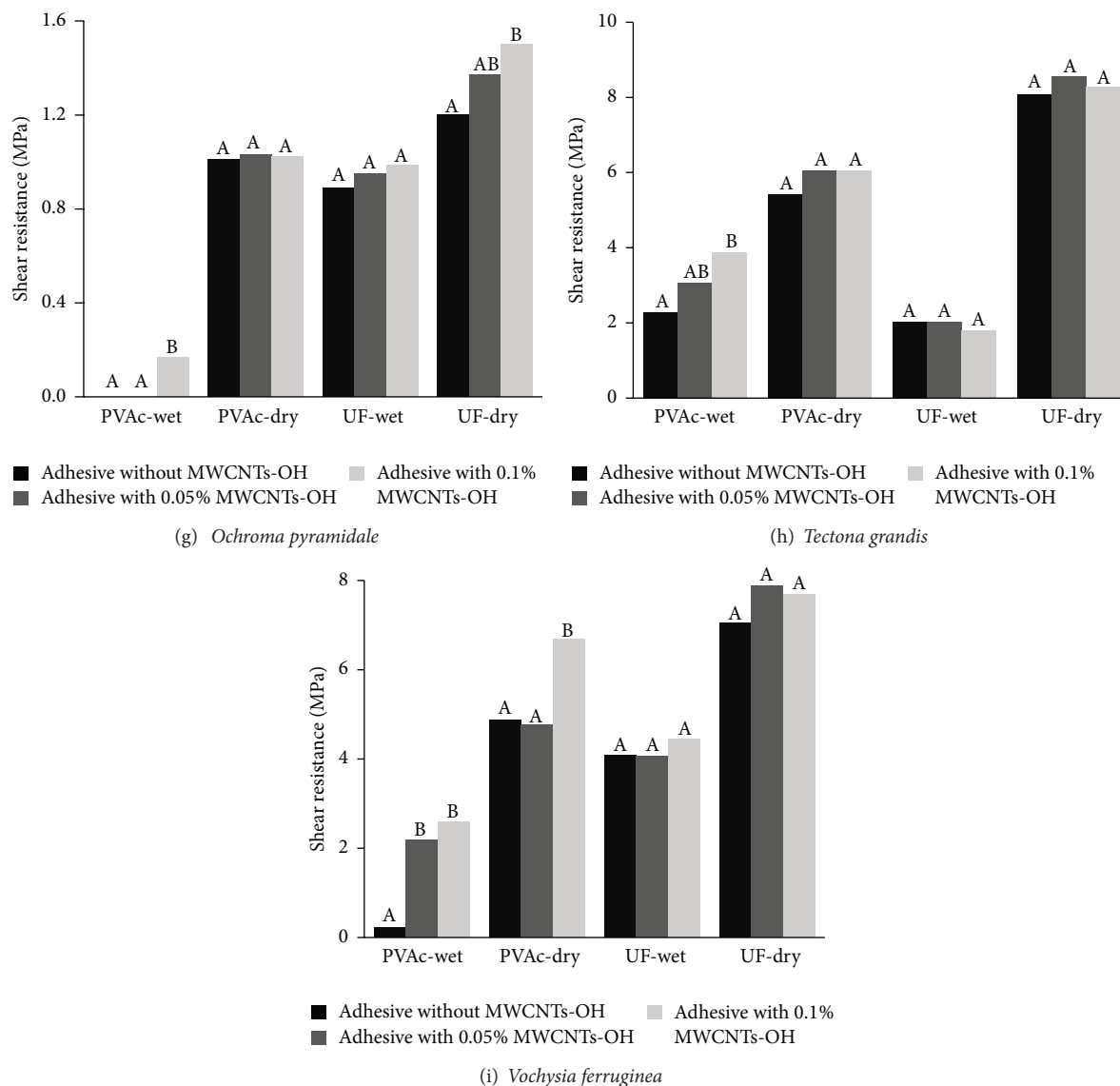


FIGURE 7: Resistance of shear strength for dry and wet condition for ten tropical species glued with PVAc and UF adhesive with and without MWCNTs-OH.

The less significant effectivity observed in the PVAc adhesive relative to the UF adhesive may be explained by agglomeration of the MWCNTs-OH in the PVAc adhesive that reduces SS, as what occurred in *C. alliodora*, *E. cyclocarpum*, *G. arborea*, *O. pyramidale*, and *T. grandis* (Figure 7), resulting in values of SS statistically equivalent between the control and the different concentrations. Therefore, according to the results, incorporating nanotubes was more effective in the UF adhesive, probably because of less agglomeration of nanotubes in this type of resin.

It is known that the performance of the PVAc and UF adhesives depends on moisture absorption by the material. Presence of water, which works as a plasticizer, increases elongation and tear strength but reduces the tensile strength, limiting the structural behavior of the adhesive [43]. This is therefore the cause for reduction of the SS in all of the species after immersing the samples in water during 24 hours (Table 3).

However, addition of MWCNTs-OH slightly increases SS or percentage of wood failure in all species; for example, an increase was obtained in *C. alliodora* and *O. pyramidale* with the PVAc adhesive and in *A. mangium*, *G. arborea*, and *O. pyramidale* with UF adhesive (Table 4). For the remaining conditions it is not possible to achieve this. These results confirm the findings for SS in dry condition: for some species the increment is achieved, whereas not for others, indicating that the adhesive modified with MWCNTs-OH fails to achieve adequate interaction between the surface of the substrate and the modifications carried out for the adhesive. Therefore, other types of functionalization of MWCNTs-OH will be necessary.

4. Conclusion

Multiwall carbon nanotubes functionalized with hydroxyl groups (MWCNTs-OH) incorporated to polyvinyl acetate

TABLE 4: Moisture content and percentage of wood failure in shear test of PVAc and UF wood adhesive adding different concentrations of MWCNTs-OH.

Species	MWCNTs (wt.%)	Moisture content (%)				Percentage of wood failure			
		PVAc adhesive		UF adhesive		PVAc adhesive		UF adhesive	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<i>Acacia mangium</i>	0.00	11.5A	32.6A	12.4A	35.7A	72.7A	4.3A	32.2A	19.5A
	0.05	11.7A	32.8A	12.4A	31.7B	26.3B	0.0A	36.5B	34.0B
	0.10	12.1A	31.6A	12.4A	31.7B	31.4B	27.3B	43.0C	34.0B
<i>Cedrela odorata</i>	0.00	10.8A	31.0A	12.7A	28.0A	66.5A	0.0A	30.7A	27.8A
	0.05	11.5A	32.0A	12.6A	29.3A	70.3A	0.0A	27.8A	6.7B
	0.10	12.5A	30.9A	12.3A	29.8A	68.3A	8.3B	49.1B	9.4B
<i>Cordia alliodora</i>	0.00	10.5A	32.5A	12.7A	32.8A	81.3A	1.5A	38.9A	31.0A
	0.05	11.4A	26.9B	11.7A	33.0A	68.5B	6.9B	41.9A	32.7A
	0.10	9.9A	25.7B	12.1A	31.3A	68.5B	15.4C	61.9B	32.6A
<i>Enterolobium cyclocarpum</i>	0.00	10.8A	40.4A	11.7A	41.4A	76.6A	84.8A	59.6A	41.0A
	0.05	10.4A	42.3A	11.4A	42.4A	97.7B	37.8B	55.7A	55.0B
	0.10	10.3A	41.6A	11.3A	42.3A	89.0C	54.8C	53.3A	52.7B
<i>Gmelina arborea</i>	0.00	10.0A	20.5A	12.3A	26.1A	52.6A	9.1A	2.6A	3.6A
	0.05	10.0A	21.6A	11.9A	23.4B	4.8B	1.0B	1.3A	2.1A
	0.10	10.7A	22.0A	11.5A	22.5B	0.0B	0.2B	0.8A	2.0A
<i>Goethalsia meiantha</i>	0.00	9.8A	38.1A	12.3A	39.1A	37.5A	15.4A	55.7A	60.6A
	0.05	9.7A	38.8A	11.8A	38.5A	93.3B	75.5B	41.8B	33.2B
	0.10	10.5A	39.2A	11.7A	37.0A	96.0B	69.2B	19.0C	52.2C
<i>Ochroma pyramidale</i>	0.00	10.8A	65.1A	12.2A	57.1A	99.6A	1.3A	68.2A	48.8A
	0.05	11.3A	58.0B	11.0A	58.8A	44.0B	44.0B	68.7A	52.4A
	0.10	11.7A	58.5B	11.8A	50.7B	69.9C	14.2B	73.2A	80.8B
<i>Tectona grandis</i>	0.00	10.9A	23.1A	12.0A	26.0A	16.7A	0.0A	8.0A	10.1A
	0.05	11.9A	25.1A	12.2A	26.1A	27.7B	0.0A	12.1B	10.0A
	0.10	11.9A	24.0A	12.0A	27.0A	21.6B	0.0A	13.5B	9.7A
<i>Vochysia ferruginea</i>	0.00	10.2A	32.7A	11.7A	32.1A	38.5A	50.0A	53.5A	37.3A
	0.05	10.5A	30.9A	10.6A	33.5A	55.0B	81.3B	79.1B	36.0A
	0.10	11.7A	32.1A	10.8A	32.5A	56.3B	78.7B	76.9B	56.6A

wood adhesives (PVAc) and urea-formaldehyde (UF) improve the thermogravimetric properties of those adhesives (increase of the initial temperature, increase of the maximum peak temperature, increase of the remnant mass in the different periods of temperature studied in the reactions of the adhesives, and increase of the entropy factor and activation energy of the kinetics of decomposition of the resin). Other physical aspects affected by the addition of MWCNTs-OH to PVAc and UF adhesives were increased resin viscosity, decreased brightness and adhesive yellowness, and increased redness, especially in the proportion of 1.5%. AFM and TEM showed that the MWCNTs-OH are appropriately distributed into the two types of adhesives and the SEM showed no penetration problems of the modified adhesives into the different types of wood.

As for the behavior of the modification of adhesives, increased shear strength of the glue line and percentage of wood failure of most tropical species occur, especially when using the UF adhesive. By increasing the moisture in the wood, the modified adhesive increases the strength of the glue line in half of the species studied, indicating that, in some species, an adequate interaction between the substrate

surface and the adhesive modified with MWCNTs-OH is not achieved.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] A. Pizzi and K. L. Mittal, *Wood Adhesives*, CRC Press. Marcel Dekker, New York, NY, USA, 2011.
- [2] A. Kaboorani, B. Riedl, and P. Blanchet, "Ultrasonication technique: a method for dispersing nanoclay in wood adhesives," *Journal of Nanomaterials*, vol. 2013, Article ID 341897, 9 pages, 2013.

- [3] F. Stoeckel, J. Konnerth, and W. Gindl-Altmutter, "Mechanical properties of adhesives for bonding wood—a review," *International Journal of Adhesion and Adhesives*, vol. 45, pp. 32–41, 2013.
- [4] L.-F. Zhao, Y. Liu, Z.-D. Xu, Y.-Z. Zhang, F. Zhao, and S.-B. Zhang, "State of research and trends in development of wood adhesives," *Forestry Studies in China*, vol. 13, no. 4, pp. 321–326, 2011.
- [5] O. V. Roussak and H. D. Gesser, "Adhesives and adhesion," in *Applied Chemistry*, vol. 2013, pp. 219–232, Springer US, 2013.
- [6] P. Mohan, "A critical review: the modification, properties, and applications of epoxy resins," *Polymer-Plastics Technology and Engineering*, vol. 52, no. 2, pp. 107–125, 2013.
- [7] R. Yudianti, H. Onggo, Sudirman, Y. Saito, T. Iwata, and J.-I. Azuma, "Analysis of functional group sited on multi-wall carbon nanotube surface," *Open Materials Science Journal*, vol. 5, pp. 242–247, 2011.
- [8] A. Fraczek, E. Menaszek, C. Paluszkiwicz, and M. Blazewicz, "Comparative in vivo biocompatibility study of single- and multi-wall carbon nanotubes," *Acta Biomaterialia*, vol. 4, no. 6, pp. 1593–1602, 2008.
- [9] M. Asgari and E. Lohrasbi, "Comparison of single-walled and multiwalled carbon nanotubes durability as Pt support in gas diffusion electrodes," *ISRN Electrochemistry*, vol. 2013, Article ID 564784, 7 pages, 2013.
- [10] S. Osswald, M. Havel, and Y. Gogotsi, "Monitoring oxidation of multiwalled carbon nanotubes by Raman spectroscopy," *Journal of Raman Spectroscopy*, vol. 38, no. 6, pp. 728–736, 2007.
- [11] S. Fu, P. Song, H. Yang et al., "Effects of carbon nanotubes and its functionalization on the thermal and flammability properties of polypropylene/wood flour composites," *Journal of Materials Science*, vol. 45, no. 13, pp. 3520–3528, 2010.
- [12] I. Ghasemi, A. T. Farsheh, and Z. Masoomi, "Effects of multi-walled carbon nanotube functionalization on the morphological and mechanical properties of nanocomposite foams based on poly(vinyl chloride)/(wood flour)/ (multi-walled carbon nanotubes)," *Journal of Vinyl and Additive Technology*, vol. 18, no. 3, pp. 161–167, 2012.
- [13] F. Du, J. E. Fischer, and K. I. Winey, "Coagulation method for preparing single-walled carbon nanotube/poly(methyl methacrylate) composites and their modulus, electrical conductivity, and thermal stability," *Journal of Polymer Science Part B: Polymer Physics*, vol. 41, no. 24, pp. 3333–3338, 2003.
- [14] B. J. Diener and H. Saklad, "Portico, S.A," *Journal of Business Research*, vol. 38, no. 1, pp. 89–96, 1997.
- [15] E. Chahud, F. A. Rocco, and R. R. Rosi, "O uso de espécies nativas comercializadas em Belo Horizonte na composição de madeira laminada colada," *Construindo*, vol. 1, pp. 42–49, 2009.
- [16] U. Khan, P. May, H. Porwal, K. Nawaz, and J. N. Coleman, "Improved adhesive strength and toughness of polyvinyl acetate glue on addition of small quantities of graphene," *ACS Applied Materials and Interfaces*, vol. 5, no. 4, pp. 1423–1428, 2013.
- [17] ASTM International, *Standard Test Method for Apparent Viscosity of Adhesives Having Shear-Rate-Dependent Flow Properties*, ASTM D2556-11, vol. 15.06 of *Book of Standards*, ASTM International, Philadelphia, Pa, USA, 2011.
- [18] R. Moya, A. Rodriguez-Zuñiga, J. Vega-Baudrit, and V. Álvarez, "Effect of silver nanoparticles on white-rot wood decay and some physical properties of three tropical wood species," *International Journal of Adhesion and Adhesives*, vol. 59, pp. 62–70, 2015.
- [19] ASTM International, *Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates*, ASTM D-2244-11, American Society for Testing and Materials, West Conshohocken, Pa, USA, 2014.
- [20] S. Vyazovkin and N. Sbirrazzuoli, "Isoconversional kinetic analysis of thermally stimulated processes in polymers," *Macromolecular Rapid Communications*, vol. 27, no. 18, pp. 1515–1532, 2006.
- [21] ASTM International, *Standard Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading*, ASTM D905-08, American Society for Testing and Materials, West Conshohocken, Pa, USA, 2013.
- [22] ASTM International, *Standard Practice for Estimating the Percentage of Wood Failure in Adhesive Bonded Joints*, ASTM D5266-13, vol. 11.06 of *Annual Book of ASTM Standards*, ASTM International, Philadelphia, Pa, USA, 2013.
- [23] J. Hodkiewicz, "Characterizing carbon materials with Raman spectroscopy," Thermo Scientific Application Note 51946, 2010.
- [24] S. P. Lonkar, O. S. Kushwaha, A. Leuteritz, G. Heinrich, and R. P. Singh, "Self photostabilizing UV-durable MWCNT/polymer nanocomposites," *RSC Advances*, vol. 2, no. 32, pp. 12255–12262, 2012.
- [25] V. Datsyuk, M. Kalyva, K. Papagelis et al., "Chemical oxidation of multiwalled carbon nanotubes," *Carbon*, vol. 46, no. 6, pp. 833–840, 2008.
- [26] J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurst, and V. Meunier, "Evaluating the characteristics of multiwall carbon nanotubes," *Carbon*, vol. 49, no. 8, pp. 2581–2602, 2011.
- [27] Y.-P. Sun, K. Fu, Y. Lin, and W. Huang, "Functionalized carbon nanotubes: properties and applications," *Accounts of Chemical Research*, vol. 35, no. 12, pp. 1096–1104, 2002.
- [28] H.-W. Cui and G.-B. Du, "Preparation and characterization of exfoliated nano-composite of polyvinyl acetate and montmorillonite," *Journal of Chemical Engineering and Materials Science*, vol. 2, no. 8, pp. 122–128, 2011.
- [29] Y. Peng and H. Liu, "Effects of oxidation by hydrogen peroxide on the structures of multiwalled carbon nanotubes," *Industrial & Engineering Chemistry Research*, vol. 45, no. 19, pp. 6483–6488, 2006.
- [30] K. E. Levine, L. Han, A. C. McWilliams et al., "Characterization of an assortment of commercially available multiwalled carbon nanotubes," *Microchimica Acta*, vol. 181, no. 1-2, pp. 171–179, 2014.
- [31] H. A. Barnes and J. F. Hutton, *An Introduction to Rheology*, vol. 3, Elsevier, 1989.
- [32] P. Pötschke, T. D. Fornes, and D. R. Paul, "Rheological behavior of multiwalled carbon nanotube/polycarbonate composites," *Polymer*, vol. 43, no. 11, pp. 3247–3255, 2002.
- [33] C. C. Sherman, *More Solutions to Sticky Problems*, Brookfield Viscometer Guide, Brookfield Engineering Laboratories, Boston, Mass, USA, 1994.
- [34] J. F. Gonnet, "CIELab measurement, a precise communication in flower colour: an example with carnation (*Dianthus caryophyllus*) cultivars," *The Journal of Horticultural Science & Biotechnology*, vol. 68, no. 4, pp. 499–510, 1993.
- [35] A. Kaboorani and B. Riedl, "Effects of adding nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive," *Composites Part A: Applied Science and Manufacturing*, vol. 42, no. 8, pp. 1031–1039, 2011.
- [36] I. C. McNeill, L. Memetea, and W. J. Cole, "A study of the products of PVC thermal degradation," *Polymer Degradation and Stability*, vol. 49, no. 1, pp. 181–191, 1995.

- [37] E. Matoso and S. Cadore, "Development of a digestion method for the determination of inorganic contaminants in polyvinyl acetate (PVAc)," *Journal of the Brazilian Chemical Society*, vol. 19, no. 7, pp. 1284–1289, 2008.
- [38] S. Samaržija-Jovanović, V. Jovanović, S. Konstantinović, G. Marković, and M. Marinović-Cincović, "Thermal behavior of modified urea-formaldehyde resins," *Journal of Thermal Analysis and Calorimetry*, vol. 104, no. 3, pp. 1159–1166, 2011.
- [39] K. Siimer, T. Kaljuvee, and P. Christjanson, "Thermal behaviour of urea-formaldehyde resins during curing," *Journal of Thermal Analysis and Calorimetry*, vol. 72, no. 2, pp. 607–617, 2003.
- [40] S. A. Sydlik, J.-H. Lee, J. J. Walish, E. L. Thomas, and T. M. Swager, "Epoxy functionalized multi-walled carbon nanotubes for improved adhesives," *Carbon*, vol. 59, pp. 109–120, 2013.
- [41] M. B. Jakubinek, B. Ashrafi, Y. Zhang et al., "Single-walled carbon nanotube-epoxy composites for structural and conductive aerospace adhesives," *Composites Part B: Engineering*, vol. 69, pp. 87–93, 2015.
- [42] A. M. Pinto, J. Martins, J. A. Moreira, A. M. Mendes, and F. D. Magalhães, "Dispersion of graphene nanoplatelets in poly(vinyl acetate) latex and effect on adhesive bond strength," *Polymer International*, vol. 62, no. 6, pp. 928–935, 2013.
- [43] J. Wang, X. Wang, C. Xu, M. Zhang, and X. Shang, "Preparation of graphene/poly (vinyl alcohol) nanocomposites with enhanced mechanical properties and water resistance," *Polymer International*, vol. 60, no. 5, pp. 816–822, 2011.



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