



Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: A comparative study

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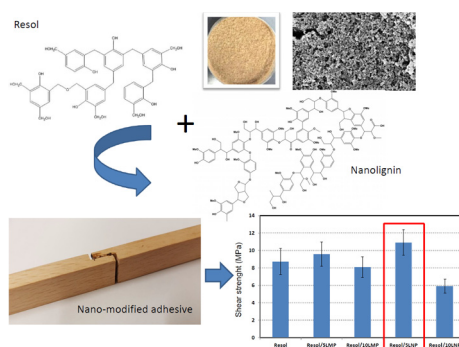
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HIGHLIGHTS

- Nanosized (LNP) and microlignin (LMP) were added to phenol–formaldehyde resol adhesive.
- Nanolignin could both favor the cure reaction, due to its abundance of phenylpropane units.
- Nanosized lignin homogeneously dispersed absorbed and inhibited dimensional changes.
- Higher specific surface area and reactivity for LNP increase the shear strength of wood joints.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigated, for the first time, the role of nanosized lignin (LNP), in comparison with microlignin (LMP), when introduced at two different weight amounts (5% and 10 wt%) in bulk phenol–formaldehyde resol as adhesive. Morphological analysis was performed to check out the dispersion and interfacial bonding of lignin in the phenolic resin. The curing process has been examined by differential scanning calorimetry (DSC), while the thermal stability of the composites has been evaluated by using thermogravimetric (TGA) and thermo-mechanical (TMA) analysis. Results exhibited that small amount of lignin could both favor the thermal cure reaction, due to its abundance of phenylpropane units, and the initial thermal resistance could be consequently improved, especially when the nano-sized lignin was used. Meanwhile, the effect of micro- and nano-modification on tensile shear strength of wood lap joints based on lignin-phenol–formaldehyde resol adhesives was also analyzed. Results showed that 5 wt% of LNP could positively increase the shear strength from 8.7 to 10.9 MPa, opening the possibility of using environmental friendly nanoscale lignin in cross linked traditional phenol wood adhesives with enhanced adhesion performance, strongly related to nanoparticles higher specific surface area and reactivity.

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1. Introduction

Lignin is the second most abundant natural biomass second to cellulose, and it can be found in the terrestrial plants on earth [1,2]. It comprises 20–30% of woody plant cell walls and, by forming a matrix

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surrounding cellulose and hemicellulose, it provides strength and protection to the plant. It is a three-dimensional, highly cross-linked macromolecule, linked mainly by two types of linkages: condensed linkages (e.g., 5–5 and β -1 linkages) and ether linkages (e.g., β -O-4 and α -O-4). The ether linkage is the dominant linkage among the three types of substituted phenols, including coniferyl, sinapyl, and p-coumaryl alcohols, yielding a vast number of functional groups (such as *ortho* aromatic hydroxyl and aliphatic hydroxyl groups) [3–6]. It is thus very attractive to many industries, since it is a potential source of bio-phenol as a substitute for the manufacture of petroleum-based phenolic resins or as an additive in biobased adhesives. The suitability of lignin for incorporation into phenolic adhesives is partly defined by the presence of chemical features that can be involved in polymerization reactions, the two most important being the phenolic hydroxyl and aliphatic hydroxyl groups. Phenolic hydroxyl groups increase the reactivity of lignin towards formaldehyde, due to activation of the aromatic ring in *o*-position and provide the possibility to form quinone methide intermediates, which could be a starting point for further condensation with other phenolic units. On the other hand, the limitations for using lignin as a wood adhesive are the lack of phenolics in the native lignin and the difficulty in isolating lignin from wood after bleaching procedures. Extensive studies have been carried out on use of lignin and lignin derivatives in phenolic resins [7–11], or as biobased wood adhesives [12–14] to be used in the wood-working industry, especially in plywood and particleboard production. Lignin-based adhesive systems have been the subject of several reviews [15–17], where the potential of lignin functionalization for the development of sustainable green adhesive materials has been reported.

Even if commercial synthetic polymer resins, based on the condensation reaction of formaldehyde with phenol, are still often used in this specific sector, it has been demonstrated that lignin modified phenolic resin exhibited comparable or higher adhesive properties for wood. Cetin and Ozmen [18] developed a phenolic resin partially replacing phenol with modified organosolv lignin in a phenol-formaldehyde resin. The effects of different substitution levels of organosolv lignin on strength properties were evaluated, highlighting that the mechanical properties of modified lignin resins impregnated paper strips were at least as good as those of neat resin. The study demonstrated that renewable resources, such as lignin, have potential as a substitute for phenol in phenolic resin systems. The same results were exhibited by the work of Jin et al. [19]: phenol formaldehyde adhesives were modified partially substituting the phenol component with enzymatic hydrolysis lignin. The adhesives were used to prepare plywoods by hot-pressing and the bonding strengths were evaluated. The results showed that the performance of the modified adhesives met the Chinese National Standard (GB/T 14732-2006) for first grade plywood when 20 wt% of the phenol was replaced by lignin, promoting a sustainable development for this type of applications. Other authors [20] demonstrated that steam explosion lignin phenol formaldehyde adhesives, in which the replacement percentage of phenol with lignin was within the range of 10–70 wt%, allowed to obtain adhesive properties in plywoods consistent with the Chinese National Standard GB/T 14732-2006]. Hussin et al. [21] succeeded to partially replace phenol in phenolic adhesive with Kraft lignin and organosolv lignin. They experienced that the higher tensile strength was obtained in the samples with 50% of Kraft lignin adhesive suggesting that the better results were due to a higher amount of crosslinking in the Kraft lignin/resin structure. A similar approach was used by Khan et al. [22] and by Moubarik et al. [23] to produce a wood adhesive using bagasse lignin. Other than mechanical performance, Aloson investigated the influence of lignin on curing reaction of phenolic resin by performing non-isothermal DSC and applying isoconversional methods (Ozawa, Kissinger–Akahira–Sunose, and Friedman) to model the process: although the variation of the activation energy at different curing degrees displayed similar tendencies in both neat and lignin containing resin, the authors found that lignin-phenol-formaldehyde resol resin showed a slightly lower average

activation energy value than that of commercial phenol-formaldehyde resin [24]. Zhang et al. concluded that the lignin could positively modify the initial thermal stability of the phenol-formaldehyde resin (in the temperature range lower than 206 °C) [25]. Furthermore, the lignin could also tremendously reduce the manufacture cost without sacrificing the mechanical properties of resins [26,27].

Lignin can be also considered as functional additive in biobased wood adhesives [28], as in case of lignin blended with soy protein [29] while, even if environmentally friendly nanocomposites show promise as wood adhesive enhancers and provide a new opportunity for the wood composite industry [30], no examples can be found, to the best of our knowledge, for use of lignin nanoparticle (LNP) reinforced adhesives. Several studies have confirmed that mechanical properties of adhesive are significantly improved with the addition of nanoscale fillers, due to the large surface area of the reinforcement and its ability to mechanically interlock with polymer [31], as in the case of biobased cellulose nanocrystals and nanofibrils [32,33].

Even though LNP have exhibited more favorable properties in different applications with improvement in mechanical and thermal behavior [34], the route of using lignin at the nanoscale in phenolic seems practically unexplored, with exception of the work of Saz-Orozco et al. [35], where the authors considered nanosized lignin (with an average diameter of 1.6 μ m) for the production of phenolic foams, by optimizing the formula using an analysis of variance approach. The results showed that the incorporation of lignin nanoparticles in phenolic foams (8.5 wt%) resulted in compressive modulus and strength up to 128% and 174% higher, respectively, than unreinforced foams. The amount of blowing agent saved to produce a reinforced foam was up to 31% of the counterpart necessary to produce an unreinforced foam of the same density.

Based on the previous research work and aiming at investigate the role of LNP in bulk phenolic samples, we studied, by means of a comparative study, the properties of phenol-formaldehyde resol resin containing lignin micro- and nanoparticles – at two different weight contents (5% and 10% wt.). Morphological analysis was performed to check out the dispersion and interfacial bonding of lignin in resin. The curing process has been examined by differential scanning calorimetry, while the thermal stability of the composites has been evaluated by using thermogravimetric (TGA) and thermo-mechanical (TMA) analysis. Moreover, we analyzed the effect of micro- and nano-modification on tensile shear strength of wood lap joints based on lignin-phenol-formaldehyde resol adhesives.

2. Experimental

2.1. Materials

A commercial resol (BAKELITE® PFS 1211, supplied by Hexion) was used as a matrix. This resin, liquid at room temperature, is an alcoholic-based phenolic resol with a viscosity of 700–900 cPs at 20 °C. It contains about 20 wt% of isopropyl alcohol and it was used as supplied by the manufacturer. Pristine lignin, obtained as bio-residue of conversion of *Arundo donax* L. biomass to bioethanol in a steam explosion pretreatment, was supplied by CRB (Centro Ricerca Biomasse, University of Perugia) [36]. Lignin nanoparticles, with an average diameter of 48.9 ± 16.4 nm, were prepared from pristine lignin by hydrochloric acidolysis, as already reported in our previous study [37,38]. In details, 4% (m/v) of alkali lignin in ethylene glycol was stirred for 2 h at 35 °C. Afterwards, hydrochloric acid (8 mL, 0.25 M) was mildly added to the solution at a rate of 3–4 drops/min, after that the suspension was stirred again for other 2 h. The product was filtered to eliminate soluble impurities from lignin. The solution was then dialyzed against deionized water up to neutrality to obtain the LNP suspension. The suspension was then diluted into a 400 mL aqueous suspension with deionized water. An ultrasonic treatment by means of a tip sonicator (Vibracell, 750) for 5 min at 40% amplitude was performed in a water-ice bath to prevent overheating. The solid LNP was collected by freeze-vacuum

dry method (lyophilizer Virtis B.T. 2 K ES). All the chemical reagents were supplied by Sigma–Aldrich® and used as received.

3. Methods

3.1. Composites preparation

Micro- and nano-composites were produced by using high shear mixing: lignin micro- and nano-particles (LMP, LNP) were added to the liquid matrix and the blends were mechanically stirred for about 30 min in cold bath in order to avoid the evaporation of alcohol. Two different amounts of micro- and nano-lignin were chosen to produce the composites: 5 and 10 wt%. The concentrations were calculated on the total weight of the resin (resol and alcohol). The following codes have been considered for the different materials: the unmodified resin was called “Neat Resol”, while the blends, containing 5 and 10% of LMP and LNP were called, respectively, Resol/5LMP, Resol/10LMP, Resol/5LNP and Resol/10LNP. After the mixing, the systems were degassed in vacuum to remove air bubbles. The curing cycle was chosen on the base of our previous works [39–41]: the resin was cured at 80 °C for about 72 h. Following this cure schedule, the development of gas bubbles, due to the formation of poly-condensation water, is reduced and the out gassing of the resin kept below the gel point is promoted. The materials were then heating up to 180 °C and post-cured at this temperature for 1 h.

4. Characterizations

4.1. X-ray photoelectron spectroscopy (XPS)

The chemical states of micro and nanolignin were examined using an AXIS-HSi XPS instrument (Shimadzu/Kratos, Ltd., Japan) equipped with an Mg K α X-ray source operated at 150 W and a charge neutralizer. Spectra were recorded using analyzer pass energy of 20 eV and a step size of 0.1 eV per step. The quantification was performed using the default relative sensitivity factor (RSF) values supplied by the XPS manufacturer. Two point energy stable referencing was made using adventitious C (284.5 eV) and valence bond energy corrections. The

percentages of individual elements detection were determined from the relative composition analysis of the peak areas of the bands.

4.2. BET analysis

The measurements of N₂ at the temperature of 77 K were carried out using the Micromeritics instrument MicroActive for TriStar II Plus. The samples (200 mg) were pretreated overnight in vacuum at room temperature before the physisorption analysis.

4.3. Microstructure

Lignin samples were examined by a field emission scanning electron microscope (FESEM, Supra 25–Zeiss) at an operating voltage of 5 kV. A drop of lignin water suspensions (pH = 7.0) was cast onto silicon substrate, dried for 24 h and gold sputtered before the analysis. Ninety measurements of nanoparticles diameters were made on FESEM images by means of Nikon NIS-Elements Basic Research (Japan) software. Microstructure of the cross-sections of the resol based samples was analyzed by using the same equipment: samples were gold coated and observed using an accelerating voltage of 5 kV. The microscope was also used to analyze the dispersion of particles in the matrix and the surface morphologies of the wood joints after the shear test.

4.4. Fourier-transform infrared (FT-IR) spectroscopy

Fourier transform infrared spectra were recorded using a Nicolet i550 FT-IR spectrometer (Thermo Scientific) equipped with attenuated total reflectance accessory (ATR). FT-IR spectra were recorded at room temperature in the wavenumbers range of 400–4000 cm⁻¹. Measurements of absorbance were taken with DTGS KBr detector with a resolution of 2 cm⁻¹ and average signal of 32 scans for each sample.

4.5. Differential scanning calorimetry (DSC)

Curing behavior of neat Resol and blend samples was tested by using a differential scanning calorimeter (DSC, Perkin Elmer mod. Pyris 1). Measurements were carried out under nitrogen flow in the temperature range from 50 °C to 300 °C at a heating rate of 10 °C/min, by using

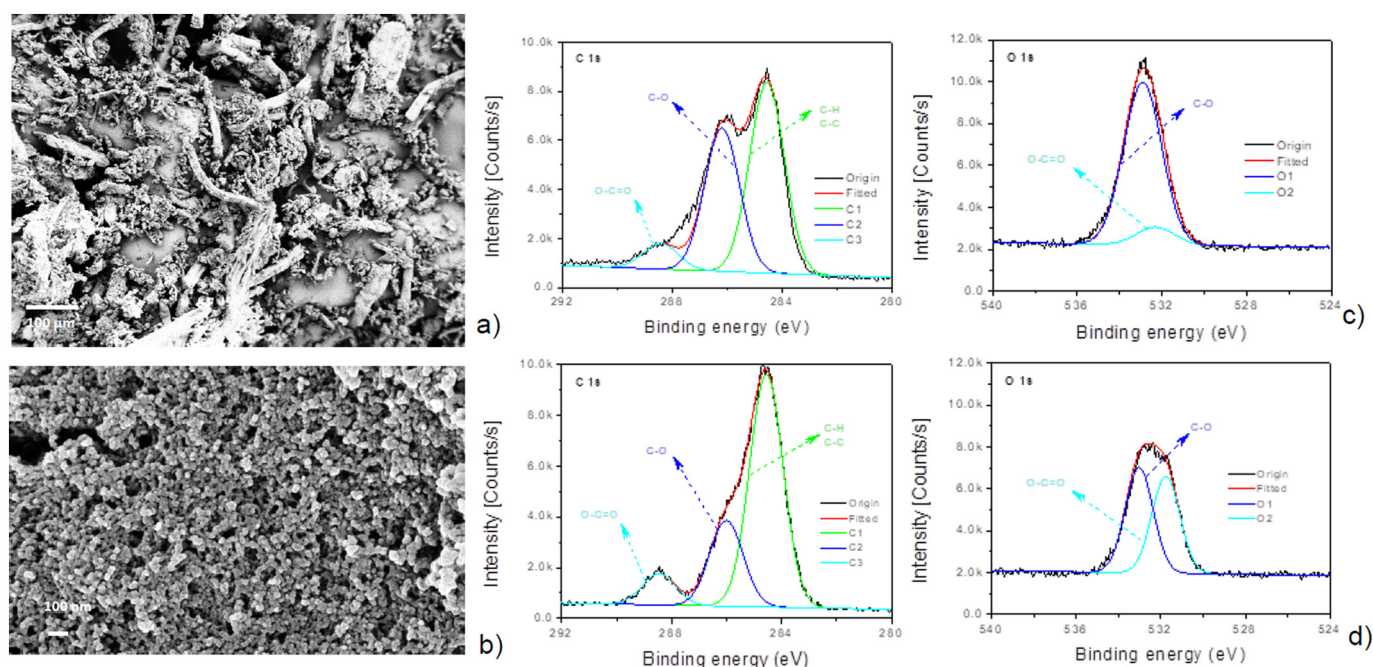


Fig. 1. FESEM images of pristine lignin (LMP) (a) and lignin nanoparticles (LNP) (b), fitting data of core level of C 1s and O 1s spectra peak area regions for LMP (c) and LNP (d).

Table 1

Results of C 1s and O 1s core levels spectra and elemental compositions calculated from spectra for LMP and LNP (Composition of C, O and C/O ratio, C1, C2, C3, O1 and O2 determined from the fitting data).

	C (%)	O (%)	S (%)	C/O ratio	C1 (%)	C2 (%)	C3 (%)	O1 (%)	O2 (%)
LMP	74.87	24.44	0.70	3.06	52.9	39.9	7.2	90.1	9.9
LNP	77.16	22.26	0.36	3.47	66.6	24.5	8.9	52.0	48.0

hermetic steel pans. A second heating was also considered for the evaluation of glass transition temperature of dynamically cured samples. The initial curing temperature (T_i), curing peak value (T_p), taken as the inflection point of the specific curing performance, and the total curing enthalpy (ΔH_1) was determined. The normalized total curing enthalpy (ΔH_2) was defined as:

$$\Delta H_2 = \Delta H_1 / W$$

where W indicates the weight fraction (%) of the resol resin in the composites.

4.6. Thermogravimetric analysis (TGA)

TGA tests were carried out using a thermogravimetric analyzer (TGA, Seiko Exstar 6300). The samples, approximately 10 mg, were heated from 30 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The weight-loss rate was obtained from derivative thermogravimetric (DTG) data. Different peak values (T_{p1} , T_{p2}) and the maximum thermal degradation temperature (T_{max}) were also collected from DTG peaks maxima, along with the residual weight percent at 900 °C.

4.7. Thermo-mechanical analysis (TMA)

TMA was carried out with a thermo-mechanical analyzer Perkin Elmer model TMA 7 on flat specimens cut in the shape of disks with a diameter of about 8 mm. Dynamic scans were performed in air at 20 °C/min from 30 °C to 300 °C using expansion probe.

4.8. Shear tests

In order to analyze the effect of the micro- and nano-modification on the tensile shear strength of lap joints of wood, we performed shear tests of the produced joints by using neat resin and lignin blends as an adhesive. The tests have been carried out according to the European Standard EN 205:2003 - Adhesives - Wood adhesives for non-structural applications - Determination of tensile shear strength of lap joints. For the mechanical tests, a dynamometer LLOYD Instrument model LR30K was considered. The amount of adhesive for each specimen was about 0.25 mL. In order to avoid the thermal degradation of wood, curing cycle for adhesives was slightly modified, by reducing time and post curing temperature: the samples were cured at 80 °C for 24 h and then post-cured at 100 °C for 3 h.

5. Results and discussion

5.1. LMP and LNP microstructure

Fig. 1a shows the morphology of pristine lignin, whose particle size mainly ranges from 50 to 100 μm in diameter, among which some bar-like objects can be seen, supposed to be hemicelluloses and some other impurities. Fig. 1b shows a FESEM image of cluster structured lignin nanoparticles: size distribution analysis revealed that, after the acidolysis, the typical diameter of the lignin nanoparticles was mainly in the range from 40 to 70 nm, no size below 20 or above 80 nm was observed and the average diameter was 49 ± 16 nm.

Elemental composition of LMP and LNP was also determined by XPS. The fitting data of core level of C 1s and O 1s spectra peak area regions for the LMP and LNP are presented, respectively, in Fig. 1c and Fig. 1d. The fitted C 1s spectra should be corresponded to C1 (C—H, C—C), C2 (C—O) and C3 (including C=O, O=C—O, Ar=O and Ar—C=O) groups bonds. The fitted O 1s spectra should be assigned to O1 (O—C), O2 (including C=O, O=C—O and Ar—C=O bonds) [42]. These bonds containing hydroxyl, methoxyl, carbonyl and carboxyl, ether and ester groups are consistent with the lignin structure [43]. Results of the composition C1, C2, C3 and O1, O2 summarized from fitting spectra peak area regions are even presented in Table 1. During the acidolysis, the carbon composition increases gradually, along with the weakening of the oxygen composition. Consequently, the C/O ratio between the

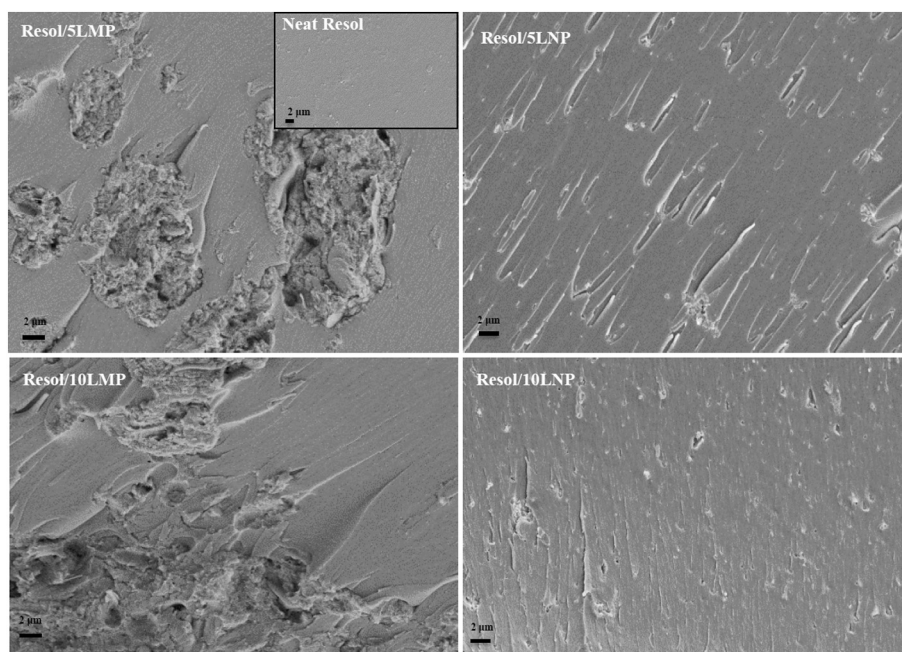


Fig. 2. FESEM micrographs (cross section morphology) of composites containing 5 wt% and 10 wt% of microlignin/nanolignin (neat resol in the insert).

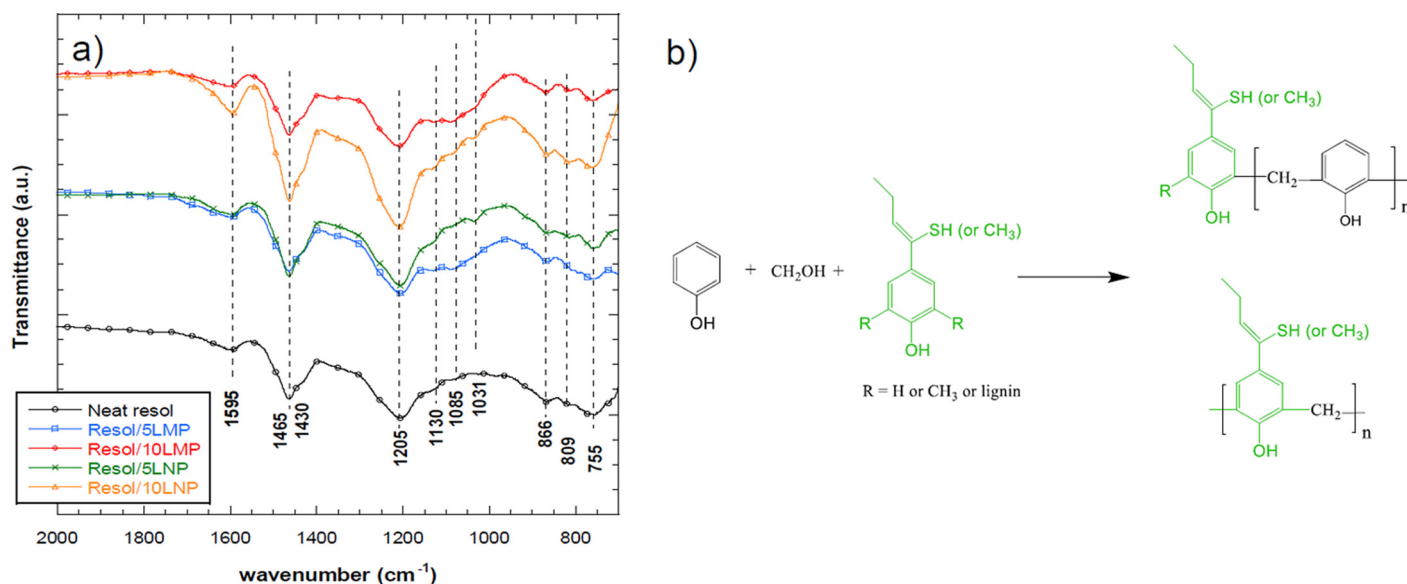


Fig. 3. FT-IR spectra of neat resol and composites containing 5 wt% and 10 wt% of micro/nanolignin (a) and possible substituted reaction of lignin in phenol formaldehyde condensation polymerization (b).

pristine lignin and acid isolated lignin increases. The spectra clearly illustrate significant changes in chemical functions between LMP and LNP. The lignin nanoparticles have lower C2 and higher C3 content (i.e. lower O1 and higher O2 content), suggesting C2 transfer to C3 bonds with formation of ester and quinone groups in the aliphatic and aromatic bonds [44]. Results from BET analysis also indicated that micro/nanolignin has a surface area of 4 m²/g, while for lignin nanoparticles we measured a surface area of 35 m²/g. Due to the higher specific surface area and reactivity of LNP, the reaction between formaldehyde and the phenolic units of the lignin should be more favorable than micro lignin particles.

Cross section morphology of neat material (insert) and composites containing 5 wt% and 10 wt% of micro/nanolignin was also analyzed and reported in Fig. 2. The neat phenolic resol shows a smooth surface, while obvious large agglomerates of micro lignin particle could be observed in the Resol/5LMP and Resol/10LMP composites. For the composite materials containing LNP, a continuous, homogeneous dispersion of LNP without an obvious aggregates phase separation between resin and lignin could be seen.

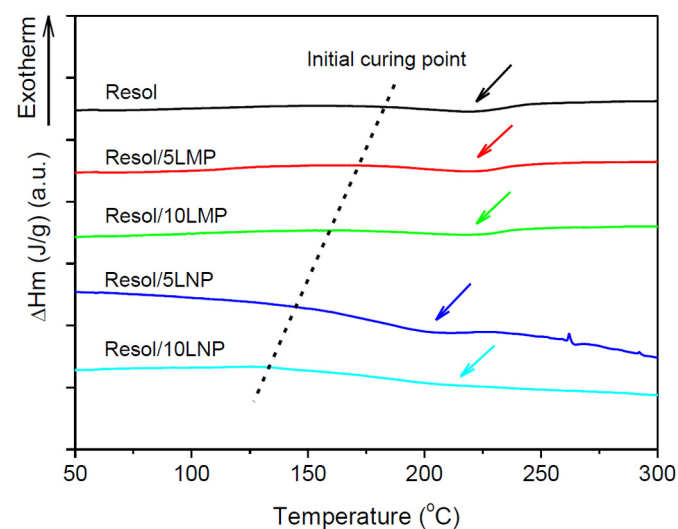


Fig. 4. DSC scan for uncured neat resol and composites containing 5 wt% and 10 wt% of micro/nanolignin.

5.2. FT-IR

The FT-IR spectra of neat material and the composites containing 5 wt% and 10 wt% of micro/nanolignin and the possible substituted reaction of lignin in phenol formaldehyde condensation polymerization are illustrated in Fig. 3a–b. It is revealed that the chemical structure for the neat resol and composites containing lignin are similar. The peaks at 1595, 1465 and 1430 cm⁻¹ should be associated with the vibration of the aromatic ring, while the new peak at 1031 cm⁻¹ for the composites containing micro/nano lignin can be assigned to the aromatic C—H deformation plus C=O stretching [45] and guaiacyl type aryl-ether bonds [7,46].

5.3. DSC

The thermal curing properties of neat resin and composites containing micro/nano lignin were evaluated by DSC and the results are summarized in Fig. 4 and Table 2. All the materials exhibited similar curing process, with a main exothermic peak (T_p) centered at 200–220 °C, depending on lignin content. Nevertheless, the initial curing temperature (T_i) significantly differs. These observations were also reported by some other studies [9,47,48] that considered the replacement of phenol with lignin at a small amount (e.g. 5–10 wt%): they observed that the cure reaction was governed by phenol reactivity and favored the thermal curing process. The lignin has two influences on the thermal cure behaviors of the resol resin depending on the loading in the formulations: 1) the small amount of lignin would favor the thermal cure, due to its abundance of phenylpropane units, while the cure process was still commanded by the phenol-formaldehyde reaction; 2) large amount of lignin would defer the thermal cure reactions, due to the lower reactivity and higher molecule weight of lignin with respect of

Table 2

DSC cure parameters for neat resol and composites containing 5 wt% and 10 wt% of micro/nanolignin.

Sample	T_i (°C)	T_p (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
Neat resol	183.2	219.1	63.1	63.1
Resol/5LMP	176.0	218.5	55.1	58.0
Resol/10LMP	168.0	218.0	51.3	57.0
Resol/5LNP	157.2	202.1	43.9	46.2
Resol/10LNP	148.7	207.0	37.6	41.7

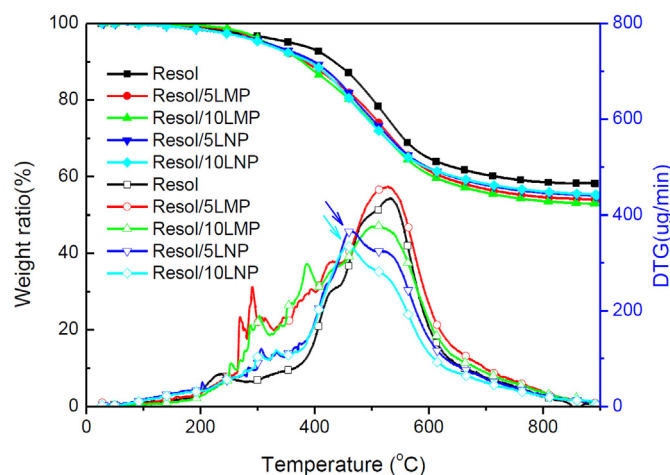


Fig. 5. TG/DTG curves of neat resol resin and composites with 5 and 10 wt% of micro- and nano- lignin.

phenol. In our case, the use of micro/nano lignin particles even decreased the heat of the curing reaction (ΔH_2). It is supposed that formaldehyde would react with the phenolic units of the lignin and form methylol substituent, which could be further condensed into methylene bridges and hence lower the curing temperature and curing heat [49]. Due to the higher specific surface area and reactivity of LNP, the reaction between formaldehyde and the phenolic units of the lignin would be more favorable than micro lignin particles, contributing to lower the curing temperature (T_i and T_p) and thermal cure heat (ΔH_2). The Resol/5LNP has the lowest T_p (202.1 °C), probably due to the optimum dispersion of LNP in the lower amount, in comparison with Resol/10LNP.

5.4. TGA

Data on TG/DTG of neat resol resin and composites with 5 and 10 wt % of micro- and nano- lignin are presented and summarized in Fig. 5 and Table 3. In our previous study [37], we showed that micro and nano sized lignin are thermally stable up to 200 °C, then the decomposition started. The degradation of phenolic resin was divided into three steps: post curing, thermal reforming and ring stripping. The first thermal decomposition occurred at 200–300 °C, due to the evaporation of the water generated from the cross-linking/condensation reactions of terminal groups [37]. In the present study, neat resol started to lose weight at ~200 °C, with a maximum of the first degradation peak at 231.1 °C. Interestingly, the addition of lignin shifted the initial decomposition peak temperature at higher values (305.4 °C for resol/5LNP). This behavior could be explained considering that the lignin enhanced the copolymerization reaction between lignin and phenol resol, resulting in an increase of the cross-linking density and decomposition temperature [50–52]. The second mass loss of phenolic resol in the range of 300–500 °C was attributed to the loss of moisture formed by the condensation reaction of methylene and phenolic-OH, as well as between two hydroxyl functional groups [53]. However, for the resol containing

Table 3

TGA parameters for neat resol and composites containing 5 wt% and 10 wt% of micro/nanolignin.

Sample	T_{p1} (°C)	T_{p2} (°C)	T_{max} (°C)	Residual mass @ 900 °C (%)
Neat resol	231.1 ± 2.1	498.1 ± 6.2	531.3 ± 0.5	57.2 ± 1.0
Resol/5LMP	287.8 ± 2.3	473.6 ± 2.5	524.6 ± 0.4	53.7 ± 0.2
Resol/10LMP	302.1 ± 0.2	458.8 ± 4.2	510.1 ± 2.7	52.7 ± 0.3
Resol/5LNP	305.4 ± 1.7	474.6 ± 6.2	524.7 ± 1.9	56.1 ± 1.1
Resol/10LNP	305.0 ± 0.0	460.2 ± 3.2	518.0 ± 3.3	54.8 ± 0.5

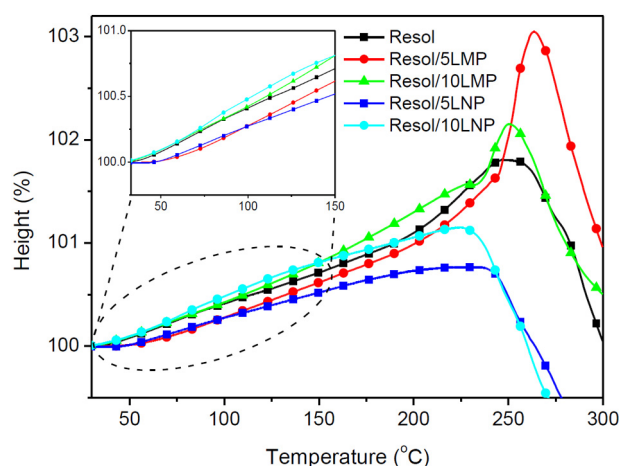


Fig. 6. TMA profiles (normalized deformation) of neat resol resin and composites with 5 and 10 wt% of micro- and nano- lignin.

micro/nanolignin, the weight loss occurred prior than that of neat resol resin, which was probably due to the rupture of lignin structure and weaker methylene bridge, resulting in the decrease of thermal stability. Consequently, the decomposition temperature of the second (T_{p2}) and third (T_{max}) weight loss process of composites were lower than that of neat resol, which is the main challenge for the replacement of lignin in phenolic resin. The third mass loss, that takes place at the range of 500–600 °C, was due to the loss of carbon monoxide and methane formed by degradation of methylene bridge [50]. The increased amount of micro/nano lignin continuously reduced the thermal resistance of the composites, as evidenced by the 5–20 °C difference in T_{max} values. However, it is worthwhile to notice that, when compared with the Resol/5LMP and Resol/10LMP composites, the DTG curves of Resol/5LNP and Resol/10LNP were less sharp and this observation confirms a more moderate thermal degradation process. Furthermore, the final char residue mass at 900 °C for Resol/5LNP and Resol/10LNP was also slightly higher than Resol/5LMP and Resol/10LMP, demonstrating higher thermal stability for LNP incorporated resol materials [48]. This behavior can be explained considering that some aliphatic structures were removed during the extraction of lignin nanoparticles, resulting in maintaining more aromatic structures than that of micro lignin, in agreement with the study by Zhang et al. [25] and Sarkar et al. [7]. In spite of some negative effects on the thermal stability after the introduction of lignin in resol, the resol/lignin composites also showed acceptable thermal resistance, especially at the initial stage.

5.5. TMA

Representative TMA profiles of the tested materials are showed in Fig. 6. Neat material and composites containing 5 wt% and 10 wt% of micro/nanolignin were characterized by volumetric expansion up to approximately 250 °C, where the matrix begins to degrade (as already reported by TGA analysis), with evolution of water, CO and CO₂ [39,40]. Beyond this temperature, the degradation of the materials was coupled with a sharp volume expansion that is more evident in the TMA profiles of microcomposites. This evident expansion was due to the sudden emission of entrapped pyrolysis gases formed during phenolic and lignin thermal degradation [50]. In the materials containing 5 wt% and 10 wt % of micro/nanolignin, it is reasonable to infer that the pyrolysis gases of lignin, that begin to degrade at lower temperatures comparing to the phenolic matrix (see also Fig. 5), remain entrapped inside the phenolic binder. It is necessary to take also into account that the humidity generated from the cross-linking/condensation reactions of terminal groups discussed above, due to the processing method [48], contribute to the formation of water vapor during the test. The volume shrinkage of the neat matrix and microcomposites was due to the formation of the

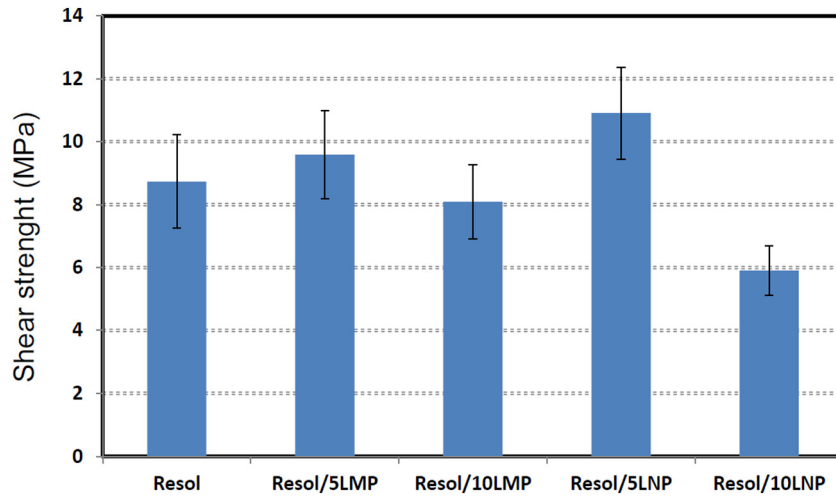


Fig. 7. Shear strength of wood lap joints containing unmodified and lignin modified adhesives.

charred residue. The TMA patterns of the nanocomposites did not exhibit the sharp volumetric expansion that are typical of neat material and microcomposites, since the presence of nanolignin allowed the materials to show a lower dependence on the temperature and a higher dimensional stability. It is reasonable to suppose that, due to the higher specific surface area of LNP as compared to LMP, the porosity of the nanocomposite systems was increased as compared to the neat matrix and as a result, the amount of trapped pyrolysis gases was reduced, minimizing the volume expansion. Moreover, the nanosized phase homogeneously dispersed in the matrix could have absorbed and inhibited the dimensional changes of the charring matrix, more effectively than the microsized counterpart.

5.6. Shear strength

The mechanical results associated to the interfacial bonding between lignin and phenolic resol were significantly influenced by the addition of different lignins, as reported in Fig. 7. Composites containing 5 wt% of both micro- and nano- lignin exhibited increased shear strength. The shear strength exceeded 9.6 and 10.9 MPa for Resol/5LMP and Resol/5LNP as compared to 8.7 MPa of neat resol. This behavior illustrates that the nanosized lignin at reduced weight contents could serve as an effective replacement for phenolic resol adhesive, in accordance with previous results on microlignin, where satisfactory

shear strength in plywood were obtained by using considerable higher amount of lignin (up to 50% wt.) [49–51]. It is well known that the crosslink density would determine the adhesive strength/shear strength. The increased shear strength in this study could be explained by the fact that substitution of small amount of micro/nano lignin enhanced the copolymerization reaction between lignin with phenol formaldehyde, inducing an increased cross-linking density and better structural alignment of lignin and phenol [54]. Actually, the lower initial curing temperature (T_i) and curing peak temperature (T_p) for composites with respect of neat resol detected from DSC measurements also evidenced the enhanced cure reaction with the addition of lignin particles, especially the nano-sized ones. However, further increase of content of micro- and nano- lignin has no enhancement effect on the shear strength, which should due to the large lignin particle aggregates.

Micrographs of tested joints have been analyzed by FESEM, results are reported in Fig. 8. The surface of the Resol/10LNP (the worst formulation in terms of adhesion properties) showed the highest level of debonding between the nanomodified matrix and the wood fibers. These zones appear as long empty channels on the analyzed surface of the sample and have been highlighted with red arrows. On the other hand, the Resol/5LNP showed the lowest level of these debonding areas, an evidence corresponding to the increased adhesion capability of this formulation. The other material formulations evidenced a mixed morphology which is then more difficult to be classified: these

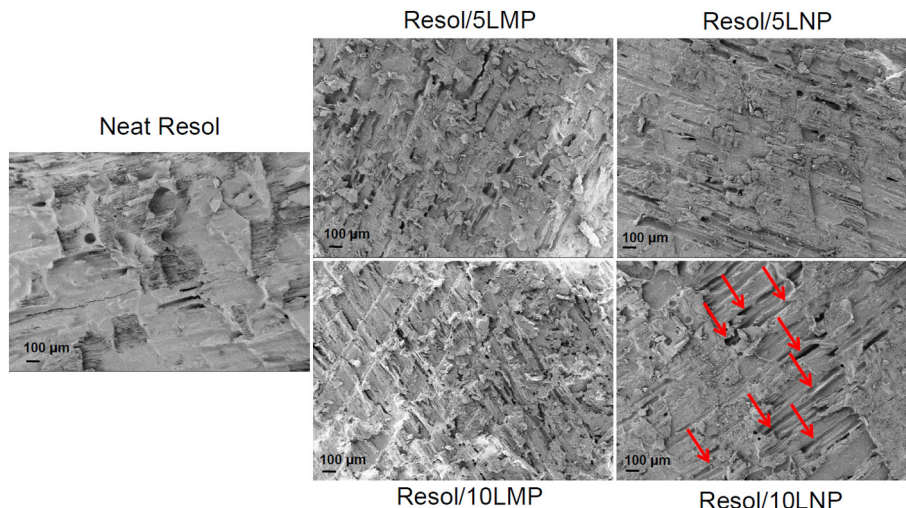


Fig. 8. FESEM micrographs of fractured surfaces for lap joints containing unmodified and lignin modified adhesives.

results reflect the experimental evidence of the mechanical properties and the related standard deviation for the Resol/5LMP and Resol/10LMP, i.e. the limited difference in terms of shear strength of these formulations when compared to the control counterpart.

6. Conclusions

In present study, the bulk phenol–formaldehyde resol resin incorporated with lignin micro (LMP) and nanoparticles (LNP) containing two weight amounts (5% and 10 wt%) were prepared. The results evidenced how LNP could be better dispersed in the resol with respect to the LMP, as confirmed by SEM analysis. Both LMP and LNP lignin would favor the thermal cure process, due to their abundance of phenylpropane units. The phenylpropane, serving as active replacement of phenol units, could react with formaldehyde to form methylol substituent, which could be further condensed into methylene bridges and hence lower the curing temperature and curing heat. Due to the higher specific surface area and reactivity of LNP, the reaction between formaldehyde and the phenolic units of the lignin would be more favorable than micro lignin particles. As a result, the crosslink density increased and the adhesive strength/shear strength was enhanced when 5 wt% of lignin was added. This work opened a gate for substituting the traditional wood adhesives by the low-cost and environmental friendly lignin residue.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Author contributions section

W.Y., M. R. did the experiments; M. N., D.P., M.R. analyzed the data; W.Y., P.M., W. D., M.R. wrote the article; J.K., L.T. contributed to reagents.

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