



Thermal study of phenol–formaldehyde resin modified with cashew nut shell liquid

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ABSTRACT

In this study, an experimental phenol–formaldehyde resin with 20% phenol replacement by cashew nut shell liquid (CNSL) was studied and compared with a conventional phenol–formaldehyde resin synthesized totally from petrochemical raw materials. The resins were characterized with standard lab analysis for their physicochemical specifications, while their thermal properties were studied with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For comparison reasons pure CNSL and wood were also included in the TGA study. A DSC study conducted both for the neat resins and the system wood–resin as to examine the effect of wood on the curing performance of the resins in the real time conditions of their usage at the wood-based panels industry.

The adhesion strength of these resins was investigated by their application in plywood production. The plywood panels were tested for their shear strength and wood failure performance while their free formaldehyde emissions were determined with the desiccator method. It was proved that although the neat CNSL modified PF resin (PCF) cures at longer time and higher temperature than a conventional PF resin, wood affects it more significantly, resulting in the evening of their curing performance. This is a novel finding that manifests the possibility of replacing a convention PF resin by a CNSL modified one in the plywood production, without changing any of their production conditions and with improvement to their overall properties.

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1. Introduction

The current economy depends mostly on the petrochemical industry for the production of energy and materials. Nevertheless, the last decades strong efforts have been made for the replacement of fossil resources because of their limited sufficiency and the disadvantages of the fossil fuel derived products, like their volatile price and their harmful effect to the environment. Among the alternative solutions, biomass seems to be the most promising candidate as it offers both energy and a vast variety of chemical blocks suitable for the synthesis of many materials and products. Biomass from forestry and agricultural products or residues, marine and animal wastes as well as municipal solid wastes, is broadly available worldwide and its exploitation could boost the rural economies and contribute to the reduction of emissions from greenhouse gases and pollutants.

The synthesis of biomass derived products is not a new concept in the industry and especially in the industrial sector of adhesives since the first glues were from blood and casein. Nevertheless,

the glues from renewable resources were abandoned soon after 1960 because the petrochemical industry offered cheaper and more effective products. Nowadays, the new technology and the development of sciences have enlightened the synthesis processes and the causes for the performance of materials giving so optimistic prospects for a more thorough study, effective use and broad exploitation of the natural raw materials.

One of the most known biomass-derived materials in the chemical industry is the cashew nut shell liquid (CNSL). It is a liquid derived from the fruit of cashew tree. It represents about the 25% of the weight of the cashew apple and is obtained as a by-product of the cashew nut industry. Today the cashew nut shell liquid (CNSL) has many applications in paint and varnish products, foundry core oils, the automotive brake lining industry, laminating and rubber compounding resins, surface coatings, epoxy resins, wood composite adhesives and in the manufacture of anionic and non-ionic surface active agents [1]. Especially in the field of polymers, the CNSL has mostly been studied as modifier of phenol–formaldehyde resins due to its structural similarity with phenol. The CNSL reacts with formaldehyde under a variety of conditions yielding both resol and novolak resins depending on the catalyst used.

Biswas et al. describe the preparation and characterisation of a CNSL modified phenol–formaldehyde resin. The optimum settings

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disclosed are CNSL:phenol weight ratio 2:1 and their reaction with formaldehyde at a temperature of 30–40 °C [2]. Mwaikambo and Ansell describe the synthesis of a resin with CNSL and formaldehyde using NaOH as catalyst and hexamethylenetetramine (HMTA) as hardener [3]. Bisanda et al. have synthesized a resin consisting of CNSL, hydrolyzed tannin and urea–formaldehyde resin. This resin was tested in particleboard production [4].

Although the CNSL modified phenolic resins are suitable for many applications and perform improved corrosion and insulation resistance, they have the disadvantage of requiring longer till to be totally crosslinked (set) compared to their petrochemical counterparts [5]. This consideration has constrained their broad utilisation by the wood-based panels industry so far, since the manufacturers are reluctant to use a resin that is regarded to need longer pressing. This would affect their profits as would mean increase in the production costs and lowering of the economic benefits.

In this study a thermosetting resol phenol–formaldehyde resin modified with CNSL (PCF) is compared to a standard phenol–formaldehyde (PF) resin for their thermal properties and adhesion performance in plywood production. The resins are thermally studied with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), both alone and in combination with wood, as to investigate the effect of wood in their curing behavior. This has never been studied before for a CNSL modified PF resin, while it allows a comparison of the two resins under the real conditions that stand during the production of wood-based panels.

2. Experimental

2.1. Materials – characterization

Both PF and PCF resins were kindly provided by the company CHIMAR Hellas S.A. that produced them following a proprietary synthesis process suitable for industrial productions. The modified PF resin was synthesized by replacing 20% of the necessary phenol by CNSL, while the standard PF resin was synthesized by using only petrochemical raw materials.

From the chemical point of view, the CNSL is a mixture of *meta*-alkylphenols with variable degrees of insaturation attached to the benzene ring. Crude cashew nut shell liquid represents one of the major cheapest sources of naturally occurring non-isoprenoid phenolic lipids such as anacardic acids, cardols, cardanols, and methylcardols. The CNSL may react both through the phenolic group and the double bond of the side chain yielding addition, condensation and polymerisation reactions that allow the synthesis of tailor-made products and polymers of high value.

The resins were subjected to standard lab analysis for the determination of their specifications. The lab analysis included determination of their viscosity, water content, alkalinity, gel time, pH and conductivity.

The thermal behavior of the resins was studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). This thermal study revealed significant information for the critical temperatures of the resins, like their curing and decomposition temperatures. For the better understanding of the results, both pure CNSL and wood studied for their thermal decomposition, while neat resins and glued pieces of the veneers (resin–wood system) were also subjected to DSC testing.

The TGA measurements carried out with the SETSYS SETARAM TG–DTA 16/18 device while the DSC measurements conducted with the SETARAM DSC 141 device. The DSC measurements carried out with liquid resin in stainless steel sealed crucibles. In all cases of the DSC and TGA measurements the heating rate was 5 °C/min.

Table 1
Lab analysis results.

| | Phenol–formaldehyde | Phenol–CNSL–formaldehyde |
|--------------------------|---------------------|--------------------------|
| Viscosity (mPa s) | 420 | 448 |
| Water content (%) | 57.1 | 57.7 |
| Alkalinity (%) | 10 | 10 |
| Gel time at 100 °C (min) | 10 | 12 |
| pH | 11 | 11 |
| Conductivity (μS/cm) | 18 | 20 |

2.2. Production of wood-based panels

Plywood panels were produced at lab scale for the testing of the adhesion property of the resins. The plywood production and testing conducted at the premises of CHIMAR Hellas S.A. company following a process relative to the industrial practice.

The panels were of three layers from veneers that had moisture content 5.5% and dimensions 50.5 cm × 50.5 cm × 0.2 cm. For each resin a glue mixture was prepared consisting of the resin, wheat flour and water as to adjust the viscosity of the mixture to about 3000–4000 mPa s [6]. A quantity of 150 g/cm³ of the glue mixture [7] were spread on each side of the core veneer while the face veneers were placed on it, without extra gluing, at right angles. The assembled panels were initially pre-pressed without heating for 15 min and then pressed again under 130 °C temperature and 1.5 MPa pressure for 6 min for the final step of the plywood production process.

The plywood panels subjected to the most sever tests described in the European standards EN314.1 & EN314.2 for the determination of their shear strength and wood failure properties considered as of class 3 panels (non-covered panels suitable for exterior use). Their free formaldehyde emissions were determined with the desiccators' method (Japanese standard JIS A1460).

3. Results and discussion

3.1. Lab analysis

The results of the standard lab analysis of the resins are cited in the following Table 1.

It can be easily noted that the resins have comparable specifications, though the CNSL-modified PF resin has somewhat longer gel time that proclaims a later curing time compared to the standard PF resin. In general, the gel time is a measurement used by the industry as a quick indication of the pressing time requested during the plywood production, where the final hardening of the resin takes place. The prolonged curing time of the liquid PCF resin compared to the standard PF resin is in line with literature references relative to neat resins [5].

3.2. Thermal study

The TGA graphs of the CNSL as raw material and the PF and PCF resins are presented in Fig. 1 while the relative derivatives of the mass loss towards temperature (DTG) are cited in Fig. 2.

The TGA graph of CNSL in Fig. 1 shows clearly that the mass loss is implemented in two steps. The first mass loss is performed at temperatures between 168 and 392 °C, where about 63% of the initial mass is lost, while a further 31% of the mass is lost at the temperature range of 392–532 °C. The relative DTG graph in Fig. 2 signifies these mass reductions by two endothermic curves with peaks at the temperatures of 332 °C and 462 °C accordingly. The above findings are in consistency with literature references where TGA measurements show crude CNSL to perform two degradation peak temperatures at 335 °C and 522 °C accordingly. The increased

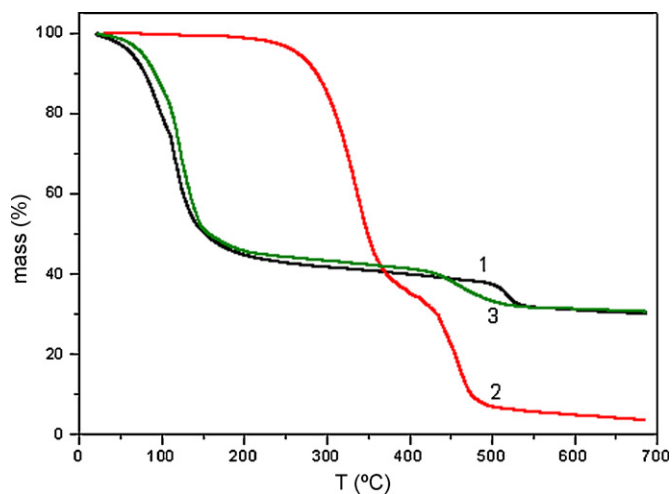


Fig. 1. Mass loss vs. temperature of (1) PF, (2) CNSL and (3) PCF.

temperature of the second degradation step compared to the values of the current studies may be due to the somewhat different composition of CNSL as not all natural products have exactly the same composition [8].

The TGA analysis of the standard PF resin (also in Fig. 1) indicates an initial mass loss from 30 to 270 °C. In the relative DTG graph in Fig. 2, this loss is expressed by a curve with a peak temperature at 118 °C. This mass reduction (58%) is attributed to its greater extent at the loss of the water content and at a minor extent to the emission of the formaldehyde that remained unbound in the resin. From the same TGA graph it is also observed that the PF adhesive starts to degrade at about 270 °C with very slow rate, while, when the temperature is raised to 475 °C, a second mass loss is observed. In the temperature range of 475–561 °C there is a mass loss of about 7% from the adhesive that is attributed to the breakdown of methylene linkages [9] to yield aldehydes and phenols. Finally, about 30% of the mass remains as a coke-like solid mass residue.

The TGA analysis of the PF–CNSL modified (PCF) resin in Fig. 1 reveals a first mass loss up to the temperature of about 237 °C. This phenomenon is attributed mostly to the loss of the water content, while according to literature references the mass loss at the temperature are of 164–237 °C is attributed also to the transformation of ether bridges to methylene bridges with simultaneous release of formaldehyde [9]. This mass loss is indicated in the relative DTG

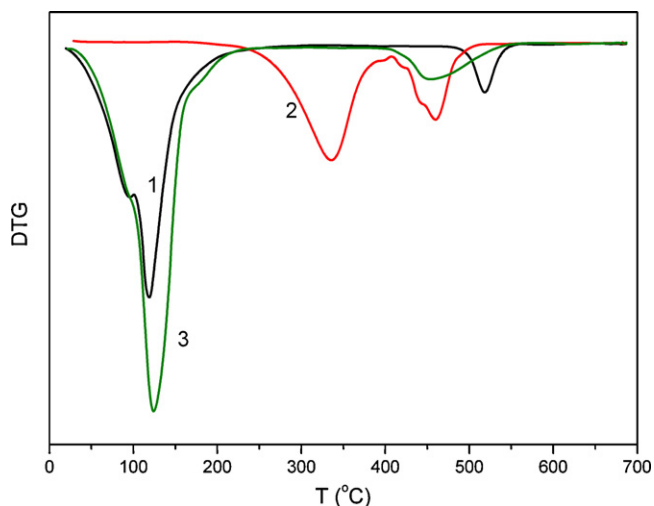


Fig. 2. Derivative mass loss vs. temperature of (1) PF, (2) CNSL and (3) PCF.

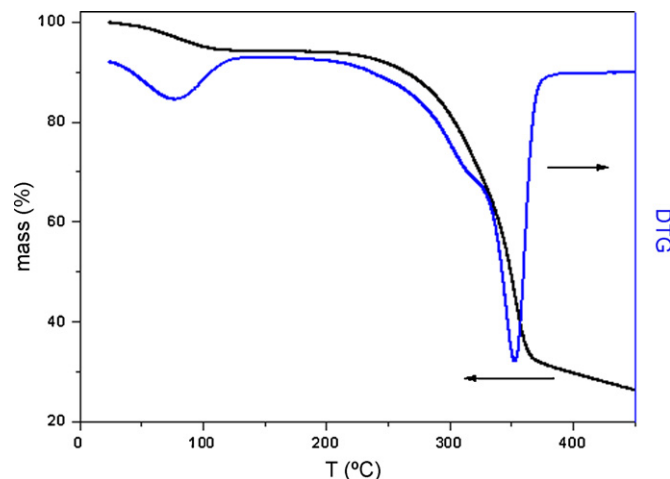


Fig. 3. Mass loss and derivative mass loss vs. temperature of pure wood.

graph of Fig. 2 with an endothermic peak at the temperature of 122 °C. Above the temperature 237 °C in the TGA graph of Fig. 1 we see the mass of the sample to be slowly reduced until the temperature is about 395 °C. Within the temperature range of 395–563 °C a massive mass loss of about 9.8% is observed due to the breakdown of methylene linkages [9]. Finally about 31% remains as solid residue.

Considering together Figs. 1 and 2 we can say that both the standard PF and experimental PCF resins perform the first mass loss, which is ought to water volatilization, at relative temperatures. The second mass loss that is attributed to the degradation of the polymer, starts earlier in the case of PCF resin (395 °C). This shift to lower temperature is explained by the participation of CNSL to the phenomenon that also performs a mass loss at this temperature area (392–532 °C). The phenomenon of mass degradation is ended at the same temperature for both resins and results almost in equal solid residue.

A sample of wood was also subjected to thermal analysis (TGA) as to investigate its decomposition performance and determine the highest temperature that can be safely applied during the pressing of wood-based panels (Fig. 3). The TGA plot of Fig. 3 shows the behavior of wood at elevated temperatures. The first mass reduction is attributed to water loss that occurs close to 100 °C. It is even more clearly indicated by the DTG endothermic peak at about 90 °C. The major mass loss of wood takes place at the temperature range of 200–390 °C as the temperature approaches the transition point. The DTG plot shows this phenomenon by a curve in this vicinity with peak at the temperature of 351.6 °C. The mass loss over the temperature of 200 °C is attributed to the evolution of various organic compounds [10]. With reference to the thermal study of wood, it was revealed that wood should not be exposed to temperatures over 200 °C because it will start to decompose.

The DSC thermographs of the standard (PF) and experimental (PCF) resins, as well as of the wood impregnated with them are presented in the following Figs. 4 and 5. The graphs manifest that in all cases the curing behavior is completed in two steps that are signified by two exothermic curves. In particular: in the case of the standard PF resin (Fig. 4), the neat resin exhibits two overlapped exothermic curves with peaks at the temperatures of 143.5 °C and 161.9 °C. According to the literature [9,11] both peaks relate to chain building condensations. In particular, the first peak at 143.5 °C is due of chain building condensation reactions involving both hydroxymethyl groups attached to various phenolic species and self-condensation reactions of 4-hydroxybenzyl alcohol, while the second peak at 161.9 °C is attributed to self-condensation reactions of 2-hydroxybenzylalcohol. The specimen of impregnated

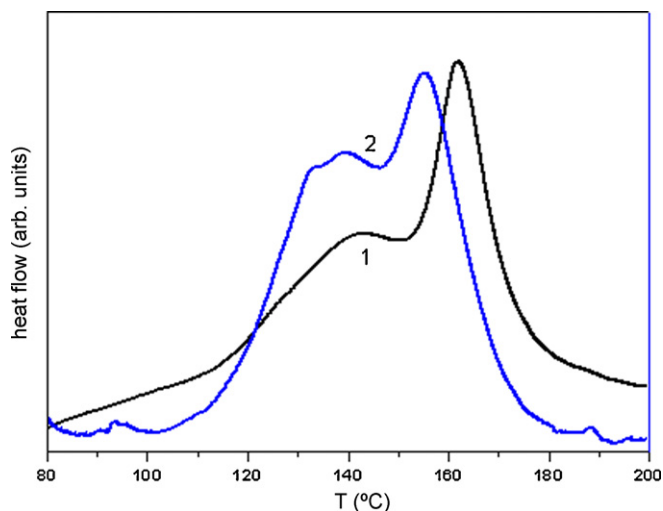


Fig. 4. Heat flow vs. temperature of (1) PF std. resin and (2) PF std. resin and wood impregnated with it.

wood shows similar curves but shifted to lower temperatures. In particular, the peak of the first curve appears at 139.9 °C and the peak of the second one at 155.4 °C. This phenomenon points to the ability of wood to accelerate the curing of the adhesive taking place during the pressing of plywood panels [12].

In the case of Fig. 5, the DSC thermograph reveals the thermal performance of the liquid PCF resin and a piece of wood impregnated with it. The liquid PCF resin exhibits two overlapped curves with peak temperatures at 153.1 °C and 168.7 °C accordingly. These curves are also attributed to self-condensation reactions of the PCF resin as in the case of the standard PF resin, although now the peaks are appeared at higher temperatures. This finding is in line with literature references [5] and the lab analysis results of this study (longer gel time). Nevertheless, the DSC graph of wood impregnated with PCF resin shows a significant reduction of these peak temperatures altering thus remarkably the curing performance of the PCF resin. Namely, the first peak is appeared at 146.1 °C and the second one at the temperature of 154.3 °C. Surprisingly, the effect of wood is so sound that moves down the final curing temperature of the PCF resin to the level of the standard PF resin (155.4 °C).

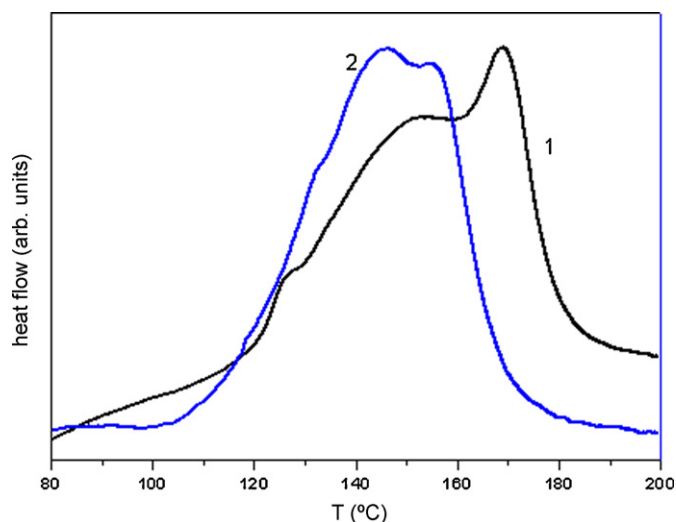


Fig. 5. Heat flow vs. temperature of (1) PCF resin and (2) PCF resin and wood impregnated with it.

Table 2
Threshold values according to EN314.2 standard.

| Mean shear strength f_v (N/mm ²) | Mean apparent cohesive wood failure w (%) |
|--|---|
| $0.2 \leq f_v < 0.4$ | ≥ 80 |
| $0.4 \leq f_v < 0.6$ | ≥ 60 |
| $0.6 \leq f_v < 1.0$ | ≥ 40 |
| $1.0 \leq f_v$ | No requirement |

Table 3
Results of plywood (PW) testing.

| Standard/property tested | Unit | PW with PF resin | PW with PCF resin |
|-------------------------------|------|------------------|-------------------|
| EN 314.1 | | | |
| Shear strength | MPa | 1.04 | 1.08 |
| Wood failure | % | 74 | 86 |
| JIS A1460-desiccators' method | | | |
| Free formaldehyde emissions | mg/l | 0.52 | 0.56 |

3.3. Plywood testing

Plywood panels subjected to the pretreatment described in the European standard EN314.2 for the exterior grade uncovered panels (class 3). The measurements carried out according to the processes described in the European standard EN314.1 while their overall evaluation based on the threshold values for the combined performance in shear strength and wood failure that are determined by the standard EN314.2 (Table 2).

The results of the testing of plywood (PW) panels are given in the following Table 3.

Studying the results we make out that the PCF resin is somewhat superior to the standard PF resin as it has improved shear strength and wood failure values while the free formaldehyde emissions have been remained at low and comparable levels. Evaluating these results as per the quality criteria of the standard EN 314.2 (Table 2), it is obvious that both the PF and PCF resins are able to be considered as of passing the prerequisites of this standard while the PCF resin is somewhat superior to the standard PF resin.

4. Conclusions

The TGA study proclaims that the second degradation step of CNSL affects the thermal stability of the PCF resin, whose decomposition starts at lower temperature than the standard PF resin. However, both PCF and PF resins start decomposing at much higher temperatures than wood. Thus, both of them may be safely used in plywood production. Any wood-based panels production has to be carried out at temperatures lower than 200 °C to prevent wood degradation.

The gel time and DSC measurements of the neat resins indicate that the standard PF resin cures in shorter time and at somewhat lower temperature than the PCF resin. Nevertheless, the DSC measurements of wood impregnated with these resins reveal that wood reduces the curing temperature of both resins, but it has greater effect on the PCF resin where it brings a reduction of 7 °C and 14.4 °C for each of the two peaks respectively. In the case of the PF standard resin this reduction corresponds to only 3.6 °C and 6.5 °C. This results to the equalization of the upper curing temperature of the PCF resin with that of the standard PF resin. That is, at real production conditions, the PCF resin has upper curing temperature similar to that of the standard PF resin. Hence, contrary to the so far consideration, a phenol–formaldehyde resin with at least 20% phenol replacement by CNSL may be used as alternative to a standard PF resin without any impair to the properties of the final product or elongation to the conventional production time. This finding is not

obvious when only the pure resins are studied while it is especially valuable for the manufacturers of plywood panels as it warrants the ability of using a CNSL modified PF resin in the plywood production applying the same pressing cycles of a standard PF resin.

More, based on the results of the plywood evaluation, the PCF resin has better mechanical strength and higher bonding quality, since it has better wood failure performance.

The free formaldehyde emissions of both resins are at extremely low levels and may be considered suitable for panels of very low free formaldehyde emissions.

Overall we conclude that a PCF resin with up to 20% phenol replacement by CNSL may be considered competitive to a standard PF resin in the production of plywood, as it enables the partial replacement of phenol by a natural material promoting thus the sustainability of our ecosystem, while it does not come behind in performance relative to the production conditions and properties of the plywood panels.

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