Thermal characterization and comparisons of lignin-formaldehyde and lignin-glyoxal adhesives

Mohamed Ammar[1],*, Ramzi Khiari[2,3], Mohamed Naceur Belgacem[3], Elimame Elaloui[1]

[1]Materials, Environment and Energy Laboratory, Faculty of Sciences of Gafsa, University Gafsa -Tunisia

[2]Research Unity of Applied Chemistry & Environment, Department of Chemistry, Faculty of Sciences, University of Monastir, 5019 Tunisia.

[3]Laboratoire de Génie des Procédés Papetiers (LGP2), UMR CNRS 5518, Grenoble INP-Pagora – 461, rue de la papeterie – 38402 Saint-Martin-d'Hères, France.

Abstract: In the present study, the main focus was the use of lignin isolated through an industrial waste (black liquor) to prepare phenolic-type resins. Thermal properties of control lignin-formaldehyde adhesive (RLF) and lignin –glyoxal adhesive (RLG) have been investigated in detail. The effect of methylolation of lignin by formaldehyde and glyoxal have been studied using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Methylolation has significant effect on the structure and the thermal stability of lignin. Rate of curing is enhanced by the type of curing agent and temperature.

Key word: Lignin, glyoxal; formaldehyde; resin; thermal stability.

Introduction

Recent environmental concerns led to increasing uses of materials obtained from biomass as raw materials for the production of biofuels, bioenergy, biomolecules, and biobased product[1,2,16,17]. A number of different approaches have been investigated, namely, the use of soy protein adhesives to formulation without aldehydes or even without hardeners, synthesis of clay-nanocomposite solvent-based polyurethane adhesives[15] and more recently, the development of polycondensation products of lignin with phenol-formaldehyde (*PF*) resins[3]. Lignin is of special interest since it is the second most abundant biopolymer after cellulose and given its extremely low cost phenolic nature is one of the leading candidates for preparing wood adhesives to replace those derived from oil. Lignin has a complex structure, composed of a highly branched phenylpropanoid network. Especially three repeat units, namely methoxylated coumaryl, coniferyl, and sinapyl alcohols are very abundant in the polymer[4,5].

In the approach of adhesive formulations based on the polycodensation products of lignin with glyoxal, up 50-60% of lignin was used on total resin solids. Lignin-based wood adhesives satisfying the requirements of relevant international standards for the manufacture of interior-grade and exterior-grade wood particleboard, in which formaldehyde was not used in the preparation (it was substituted by a non-volatile nontoxic aldehyde, namely glyoxal).

Glyoxal is a nontoxic aldehyde and is nonvolatile but less reactive than formaldehyde, which is toxic[6]. In the search to further increase the proportion of natural, environmentally friendly materials in these formulations, we tried to eliminate the formaldehyde from formulation and to substitute these with glyoxal.

In this study, we first dealt with the optimization of lignin-based adhesives for wood by attempting to eliminate the addition of formaldehyde, substituting it with glyoxal. The results have been compared the resin-lignin-glyoxal (*RLG*) to those prepared from lignin-formaldehyde *(RLF)*.

Experimental Section

Extraction of lignin
The black liquor use for obtaining lignin was kindly supplied by *SNCPA* –National Company of Cellulose and Alfa Pulping (Kasserine, Tunisia); the lignin was precipitated by decreasing black liquor pH from 12.5 to 1.5 and by adding sulfuric acid.

Before use, the lignin was washed with hot water (70°*C*) for 30 *min* under mechanical stirring to remove residual sugars and impurities. Then, the lignin was filtrated and dried in an air circulation stove at 40°*C* to a constant weight.

Resin synthesis
Resin-Lignin-Glyoxal (*RLG*)
In this study, resins were condensed in a 6-*dm³* glass reactor equipped with a stirrer, a condenser, and external cooling and internal heating units. Modified resins were synthesized according to the preparation method of the reference[7]. The amounts of the glyoxal were 50% of the amounts of lignin, which is twenty grams for all samples. In the meantime, 4.5 *g* of sodium hydroxide (on dry basis) was added very progressively in the form of 30 wt.% aqueous solution until the final *pH* between 12 and 13.

Resin-Lignin-Formaldehyde *(RLF)*
20 g of lignin, 20 g of formaldehyde solution (0.518 *moles*), were mixed and heated at 80°*C*. 4.5 *g* of sodium hydroxide (on dry basis) was added very progressively in the form of 30 *wt.%* aqueous solution until the final pH between 12 and 13, and reaction was maintained at 80 °*C* for 4 *hours*[8].

Gel point measurements:
The gelation was studied by means of rheological measurements performed in an MCR 301 rheometer with parallel plates of 25 *mm* diameter and samples of approximately 5mm diameter and 1 mm thickness. A shear rate of 1 *s⁻¹* was used at 80 °C, the gelation point was determined by the divergence of viscosity[9]. Gelled resin was rapidly cooled and experiments were carried out at 10°C/min from 50 to 900°C to study thermal degradation.

TGA thermo-degradation of gelled resins:
For thermal gravimetric analysis (*TGA*; Perkin-Elmer Pyris 1 TGA-7), about 8 *mg* of gelled *RLG* or *RLF* resins was put into a platinum sample pan and heated from 50 to 900 °*C* at a heating rate of 10°*C/min* under a nitrogen atmosphere with a flow rate of 20 *ml/min*. Curves of weight loss and derivative weight loss (*DTG*) were plotted.

DSC measurements
The calorimetric measurements were performed with a differential scanning calorimeter (DSC Q100 TA Instrument) under an atmosphere of N₂ (flow rate = 50 *ml/min*). Pans utilized

were pressure medium (ME-26929) and samples size was 8–10 *mg*. The pans, with a volume of 120 μl, can withstand vapor pressures up to 10*MPa*. Since it was difficult to weigh the same amount of sample in all cases, different thermograms were normalized, by the calorimeter software, at 1 *g*. Later, the baseline "spline" was subtracted from the original thermogram.

UV-spectroscopy

UV-spectroscopy offers a simple and rapid way of determining phenolic hydroxyl groups. The method is based on the difference in absorption between lignin in alkaline solution and lignin in neutral or acid solution[10]. After being dried overnight in vacuum at 40°*C*, about 10 *mg* of the resin was dissolved in 5 mL of dioxane and 5 *mL* 0.2 *M* NaOH. From each resin solution, 2 mL was further diluted to 25 mL using either a pH = 6 buffer solution (citrate-NaOH, Merck), a 0.2 *M* NaOH solution or a pH=12 buffer solution (prepared by adding 12.4*g* of H_3PO_4 to 2 *L* of 0.1*M* NaOH). This gave each solution a final concentration of resin of about 0.08 *g/L*. UV-spectra were recorded on a Shimadzu double-beam spectrophotometer, with the pH=6 resin solution as a reference and the two alkaline solutions measured against it. Hydroxyl value can be expressed as follows[10]:

$$\textbf{Hydroxyl value} = \{\mathbf{0.250} \times A_{300nm}(NaOH) + \mathbf{0.107} \times A_{350nm}(NaOH\} \times \frac{1}{c \times l} mmoles/g$$

Where A=Absorbance;
c =concentration in g/l;
l = path length through the sample in cm

FTIR spectra

FTIR spectra of the different samples *were* collected on a FTIR spectrophotometer (Bruker) by preparing KBr pellets using a resins concentration of 1% (w/w). Spectra were recorded between 600 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding forty sixteen scans.

Results and discussion

Characterization of resins

The hydroxyl value of lignin, *RLG* and *RLF* are given in Table 1. The result obtained show that hydroxyl value of lignin is higher that's of *RLG* and *RLF*. It can be inferred that metylolation reduce the free OH group of lignin and formaldehyde is more reactive than glyoxal, this result is confirmed by the gel time and viscosity measurement. When the resin temperature is increased, the gel time decreases lead to generate more methylol groups, thus, the cross-linking processes occur.

Table 1. Physical properties of Lignin, RLG and RLF.

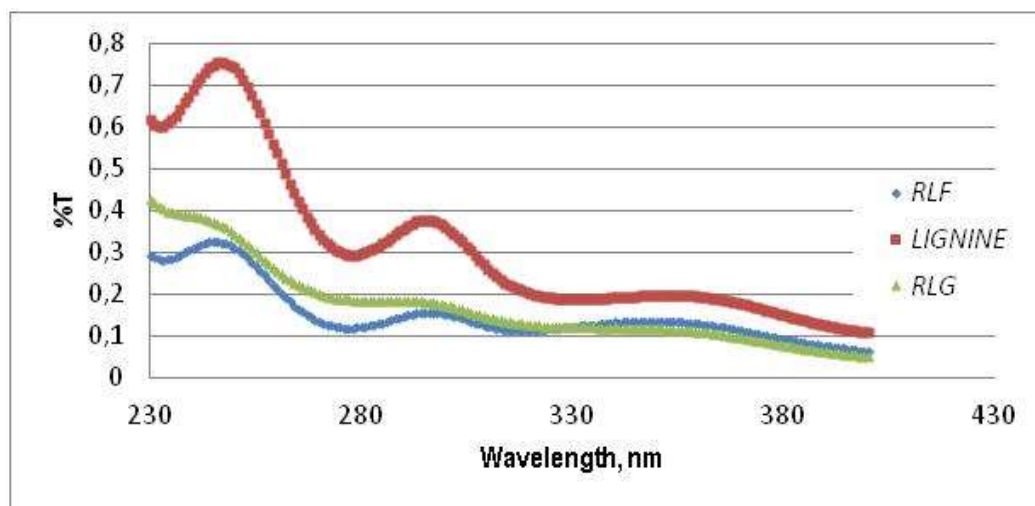| Samples	Lignin	RLG	RLF
Hydroxyl value mmol/g	1.13	0.54	0.47
Gel Time at 60°C (min)	-	70	41
Gel Time at 100°C (min)	-	40	26
Viscosity [Pa·s]	-	1.08	0.8

Figure 1. UV-spectra of lignine, RLF and RLG
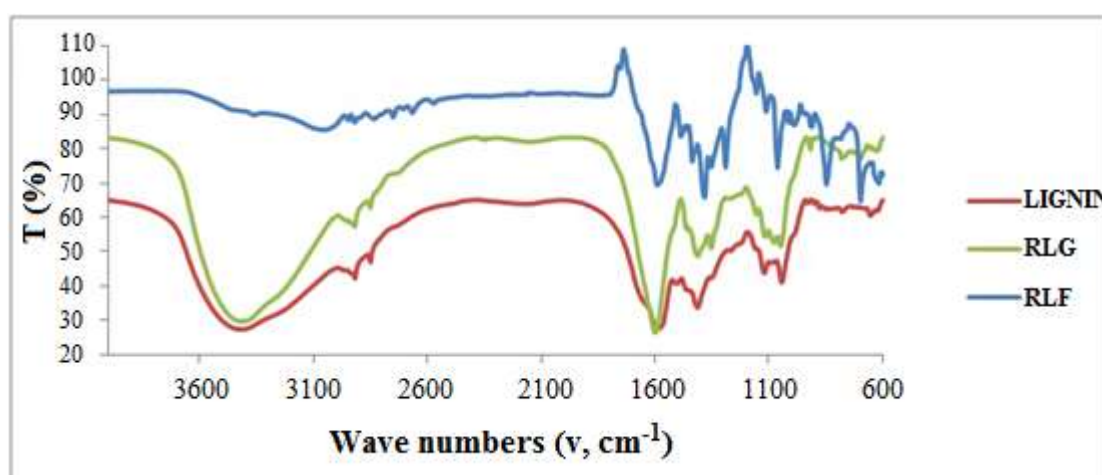

Figure 2. FTIR Spectra of Lignin, RLG and RLF

Figure 2 shows the spectra of original lignin, RLG and RLF, the three spectra presented a broad band attributed to OH stretching (3412 – 3460 cm^{-1}). This band became very weak in the RLF spectra which confirm the low hydroxyl value seen in table 1.

The dominance and relative increase of the band at 1192 cm^{-1} and 1360 cm^{-1} in the RLG and RLF spectra, indicated the increase of -CH2-, or better -CH2-CH2- bridges due to the condensation reaction of glyoxal and formaldehyde with the aromatic groups of lignin. This band is more intense in the RLF spectra which indicate that formaldehyde is more reactive than glyoxal.

The decrease of the 1130 cm-1 band confirms the cleavage of some β-O-4 and α-O-4 bridges of lignin and to its demethoxylation. Besides, the band at 1065 cm-1 is indicative of aromatic C-H in plane deformation, the relative increase of this band in RLG and RLF spectra which indicated that aldehyde groups reacted with phenolic C-H in lignin, this band is more intense in the RLF spectra. The 920 cm^{-1} band of C_1-β groups confirm the polymerization of lignin by glyoxal and formaldehyde.

TGA thermo-degradation analysis of gelled *RLG* and *RLF*

Figure 3 shows the TGA and DTG curves of cured RLG and RLF resins. The normal RLG resin had better heat resistance than that of RLF, less weight loss during the period of heating, and higher char content at 700°C. The thermo-degradation of these resins can be divided into three temperature regions, lower than 300 °C, 300–450 °C, and higher than 600 °C. For temperatures below 300 °C, the weight loss included the evaporation of formaldehyde (RLF) or Glyoxal (RLG), water, and cresol those formed by the breaking of methylol groups, the condensation reaction between methylol groups, and the methylene bridge breakdown[11].

The peak at 78 ° C in DTG curve of RLG is related to the evaporation of free glyoxal, this peak does not exist in the RLF spectra, it indicate that glyoxal is less reactive than formaldehyde. For temperatures higher than 300°C, the weigth loss might be due to crosslinking of methylene with carbon-hydrogen crosslink causes hydrogen elimination.

Furthermore, the water and the hydrogen produced would react with the methylene group, which would release carbon monoxide and methane, respectively. When the temperature exceeded 600 °C, the continuous weight loss is mainly caused by the dehydrogenation of the benzene ring structure. The area of this region is greater for RLG than RLF indicating that the polycodensation of RLG is at higher temperature.
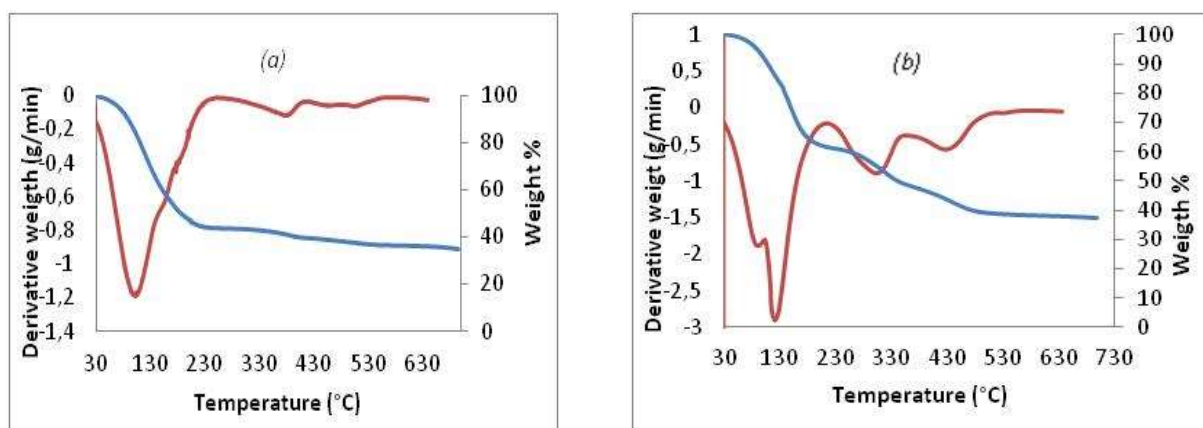

Fig. 3: TGA and DTG curves of RLF *(a)* and RLG *(b)* resins

Figure 4 shows TGA and DTG curves of lignin before methylolation, comparing it to RLG and RLF curves we can seen that methylolation by glyoxal or formaldehyde reduce the heat-resistance of lignin[12-14].
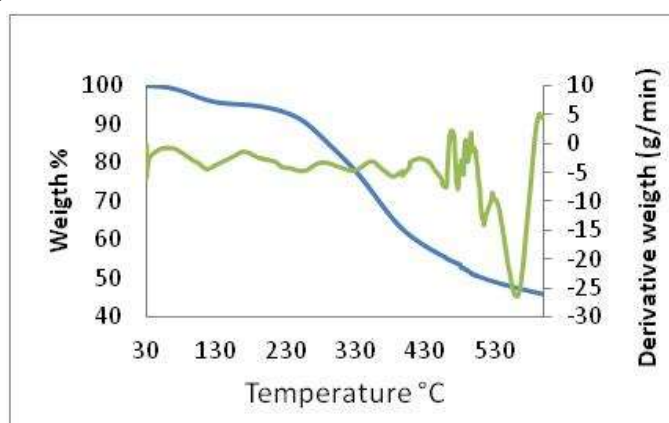

Figure 4. TGA and DTG curves of lignin before methylolation

DSC thermosetting analysis of *RLG* and *RLF*

To observe the curing behavior of RLG and RLF adhesive, DSC analysis was carried out. Figure 5 shows the DSC curves of RLG and RLF adhesives. Thermal transition in the temperature range of 170 to $260°C$ shows an endotherm, which is a consequence of curing in the system.
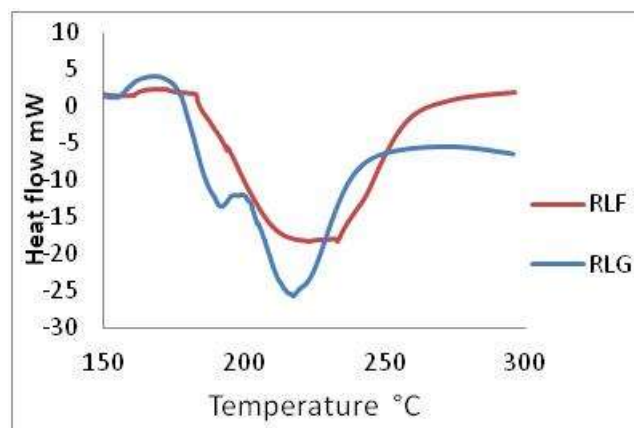

Figure 5. DSC curve of RLG and RLF adhesive

The reaction rate α_{gel} (conversion at gel time) of resin at gel time is obtained by dividing the peak height ΔHp by the total heat of curing reaction, ΔH_0.

The reaction rate equation can be expressed as follows: $$\alpha = 1 - \frac{\Delta Hp}{\Delta H0}$$

Table 2. DSC analysis of RLG and RLF adhesives

Resin Type	ΔH_0	ΔHp	α_{gel}
RLG	820	305	0.62
RLF	880	544	0.38

The value obtained for α gel is of 0.61 and 0.39 for the RLG and RLF, respectively, as shown in Table 2. The conversion at the gel point is lower for RLF than RLG indicating it had higher reactivity. The endothermic peak of RLG is sharper than RLF peak's; it might because it had higher free glyoxal content, which causes a drastic crosslinking reaction during DSC heat scanning at early time.

Conclusion

- The FTIR spectra confirm the condensation reaction of glyoxal and formaldehyde with the aromatic groups of lignin.
- The RLF resins had higher reactivity than the RLG resins; they had shorter gel time and higher viscosity.
- The methylolation of lignin by glyoxal or formaldehyde affects its thermal stability.
- RLF has a low conversion at the gel point.

Acknowledgements

References

1- L. Hong, A. Pizzi, Journal of Applied Polymers Science, **2008**, 107, 203–209.

2- A. Hüttermann, C. Mai, A. Kharazipour, Applied Microbiology and Biotechnology. **2001**, 55, 387–394.

3- L. I. Crishechko, G. Amaral-Labat, A. Szczurek, V. Fierro, B. N. Kuznetsov, A.Celzard, Microporous and Mesoporous Materials. **2013**, 168, 19-29.

4- Y. Tingting, X. Yingqi, Y.Chongwen, Journal of Applied Polymers Science. **2009**, 114, 1896–1901.

5- Z. Xuebing, D. Lingmei, L. Dehua, Journal of Applied Polymers Science. **2009**, 114, 1295–1302.

6- G. A. Amaral-Labat, A. Pizzi, A. Gonc, R. Alves, A. Celzard, S. Rigolet, G. J. M. Rocha, Journal of Applied Polymers Science. **2008**, 108, 624–632.

7- N.-E. El Mansouri, A. Pizzi, J. Salvado, Journal of Applied Polymers Science, **2007**, 103, 1690–1699.

8- A. K. Mozaffar, M. Sayed, M. Ashraf, P. Ved, Journal of Applied Polymers Science. **2004**, 92, 3514–3523.

9- S. Pingan, C. Zhenhu, M. Qingrong, F. Shenyuan, F. Zhengping, W. Qiang, Y. Jiewang, Journal of Macromolecular Science, Part B: Physics. **2012**, 51, 720–735.

10- G. Anna, G. Goran, Nordic Pulp and Paper Research Journal. **1999**, 14, 163-170

11- M. A. Khan, S. M. Ashraf, Journal of Thermal Analysis and Calorimetry. **2007**, 89, 3, 993–1000.

12- Y. N. Sazanov, E. N. Popova, G. N. Fedorova, V. E. Yudin, Russian Journal of Applied Chemistry. **2011**, 84, 1233-1237.

13- H.R. Mansouri, P. Navarrete, A. Pizzi, S. Tapin-Lingua, B. Benjelloun-Mlayah, H. Pasch, S. Rigolet, European Journal of Wood and Wood Products. **2011**, 69, 221-229.

14-H. William, B. O. Francielli, G. Stephane, S. Bernard, F. Elisabete, C. Alain, Macromolecular Materials and Engineering. **2006**, 291, 829–839.

15- C. Esposito Corcione, P. Prinari, D. Cannoletta, G. Mensitieri, A. Maffezzoli, International Journal of adhesives and adhesion. **2008**, 28,91-100.

16- C. Esposito Corcione, G. Mensitieri, Polymer Engineering and Science. 2009, 49, 1708-1718**.**

17- C. Esposito Corcione, A. Maffezzoli, Thermochimica Acta. **2009**, 485, 43-48.