THERMOGRAVIMETRIC ANALYSIS OF ANNINGRE TANNIN RESIN

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ABSTRACT

Three formulations of aningre tannin resins containing in order the paraformaldehyde powder, hexamethylenetetramine and aqueous glyoxal as hardeners were developed. Their thermogravimetric analysis have shown that they begin to decompose respectively from 135°C, 145°C and 140°C. About 24%, 40% and 39 % solid residues of their initial masses exist at the end of the analysis. Thermomechanical analysis has shown that the formulation containing paraformaldehyde powder as hardener has the best rigidity and the worst contains the hexamethylenetetramine. All formulations have different thermal degradation, differences were more significant between 400 and 900°C.The decomposition of hardeners become more significant from 400°C.

Keywords: Aningre tannin resins, decomposition, residues hardeners, thermogravimetric analysis, temperature, thermomechanical analysis.

INTRODUCTION

Some plants constituents such as cellulose, lignin and tannin are increasingly used today in the manufacture of bio - adhesives to replace synthetic resins such as those based on formaldehyde, epoxides. Several reviews have appeared on such a subject: The recent developments in eco - efficient bio - based adhesives for wood bonding was reviewed (Pizzi 2006). The structural beams from thick wood panels bonded industrially with formaldehyde - free tannin adhesives was presented (Pichelin *et al.* 2006) and the development and characterization of adhesives from soy protein for bonding wood (Yuan and Kaichang 2007) . The mastery of the characteristics and behaviors of tannins adhesive has become nowadays a concern for many researchers. Thermogravimetric (TGA) analysis is one of the methods most used in polymer characterization. Thus, the TGA of maritime pine tannin and maize flour adhesive has been studied (Moubarik *et al.* 2010) and identified a tannin/maize flour decomposition zone around 225 °C (Moubarik *et al.* 2010). Tannin – formaldehyde adhesive used for the manufacture of plywood and particleboards (Coppens 1980) have started to be studied already some time ago. The mechanism of the polyphenolic tannin resin and hexamethylenetetramine as hardener (Pizzi and Tekely 1995), liquefied wood as a partial substitute of melamine-urea-formaldehyde and urea-formaldehyde resins (Esteves *et al.* 2015), furanic copolymers with synthetic and natural phenolic materials for wood adhesives (Abdalla *et al.* 2015) and the thermal analysis of wood particles with low combustion (Reh *et al.* 1993) have also been studied. Equally, Blazek, has studied the reaction kinetics of the thermal degradation of polymers (Blazek 2005) and Lin *et al.* (2014) have studied the preparation and properties of phenol-formaldehyde-chinese fir liquefaction copolymer resin.

Nowadays, some problems still exist in the uses of tannin as adhesive. This is the case of viscosity, the differences in reactivity between different tannins, stiffness, cross-linking level and degradation temperature between differents tannins and adhesives formulations (Pizzi 1994, Pizzi 2006). In this paper, a new tannin extract from a plant called Aningre or Abam (superba aningre) in Cameroon is characterized for its use as an adhesive in the wood industry. It is therefore important to determine the upper limits of temperature at which the aningre tannin resin can be submitted without risks, to determine their decomposition points and rigidities.

MATERIALS AND METHODS

Resin development

Aningre is a procyanidin type tannin. To extract it, Aningre ground bark was introduced in a water solution containing 2% sodium bisulfite and 0,5% sodium bicarbonate (water: bark ratio was 6:1 based volume). All solution was introduced in a bath water, under continuous stirring at 60°C during 4 hours. Then, proceed to separation and filtration to get a reddish black liquid and a solid residue. Recovered liquid fraction was then concentrated at 60°C using a rotary evaporator, then it was frozen using liquid nitrogen and laboratory spray drier. A tannin powder, easier to use for analysis and storage was finally obtained (Sealy–Fisher and Pizzi 1992, Kireche 2012).

To develop the resin, an aqueous solution containing 40% of tannin + n % of hardener based weight tannin (n vary depending formulations) was placed into a beaker and the pH adjusted to 12 by adding NaOH. All components were mixed mechanically until the viscosity reached 750 mPa s. The viscosity was measured with a Brookfield RV viscometer.

Three formulations were developed:

Formulation 1 or PF: An aqueous solution containing 40% aningre tannin extract was mixed with 5,5% of paraformaldehyde powder based weight tannin and the pH was adjusted to 12 adding a sodium hydroxide water solution (solution concentration of NaOH was 33%).

Formulation 2 or H: An aqueous solution containing 40% aningre tannin was mixed with 6.5% of hexamethylenetetramine based weight tannin and the pH was adjusted to 12 adding a sodium hydroxide water solution (solution concentration of NaOH was 33%).

Formulation 3 or Gly: An aqueous solution containing 40% aningre tannin extract was mixed with 12% of aqueous glyoxal based weight tannin and the pH was adjusted to 12 adding a sodium hydroxide water solution (solution concentration of NaOH was 33%).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was done using NETZSCH STA 449F3 Jupiter (Germany) equipment. About 100 mg of each cured samples was placed on a balance located in the furnace and heat was applied over the temperature range from 20 to 900°C at a heating rate of 5°C/min during 30 min in argon gas. Weight gain (TG curves) and rate of mass loss (DTG curves) of each formulations were determined.
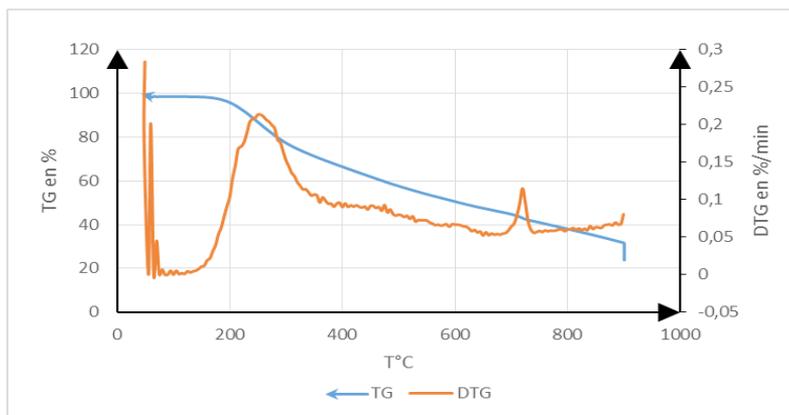
Rigidity of aningre tannin resins

The rigidity of different formulations of resin was compare using thermomechanical analysis (Navarrete *et al.* 2011).The maximum of the curve (MOE depending temperature) was considered as the peak in Modulus of Elasticity (MOE). A METTLER TOLEDO TMA 40 (Orangeburg NY, USA) equipment was used for the analysis.

RESULTS AND DISCUSSION
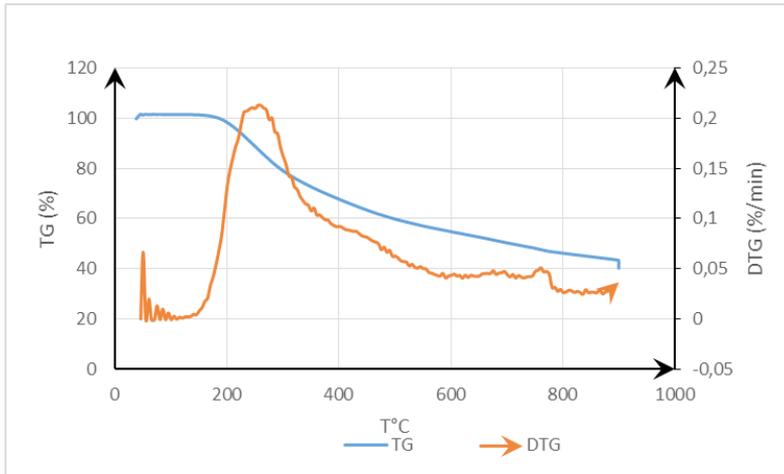
Pyrolysis of formulation 1 resin

Figure 1 shows the TG and DTG curves of the aningre tannin resin (formulation 1). The pyrolysis of this resin (formulation 1) shows three main regions of mass losses: The first region between 40°C and 135°C with the peak at 49°C due mainly to loss of absorbed water and trace formation of volatile compounds such as CO and CO_2 released by the resin. The second region between 135°C and 675°C with the peak around 255°C is due to the degradation of laterals resin chains (Zhang *et al*. 2011). In fact, between 135°C and 255°C, tannin starts to decompose and releases CO_2 and CO at 215°C. The decomposition which occurs around 299°C is due to the auto - inflammation of paraformaldehyde releasing CO, CO_2 and hydrogen (Anachemia 2012). Around 480°C, paraformaldehyde releases CO and CO_2 also. The third region of mass loss between 675°C and 765°C with the peak around 720°C is due to the decomposition of rigid segments in the resin (Yoshio *et al*. 2003) with a release of CO, CO_2, CH_4 and carbon formation. It should be noted that the decomposition was not total, about 24,01% of initial mass stays there.

Figure 1. TG and DTG curves of pyrolysis analysis of aningre tannin resin under formulation 1.
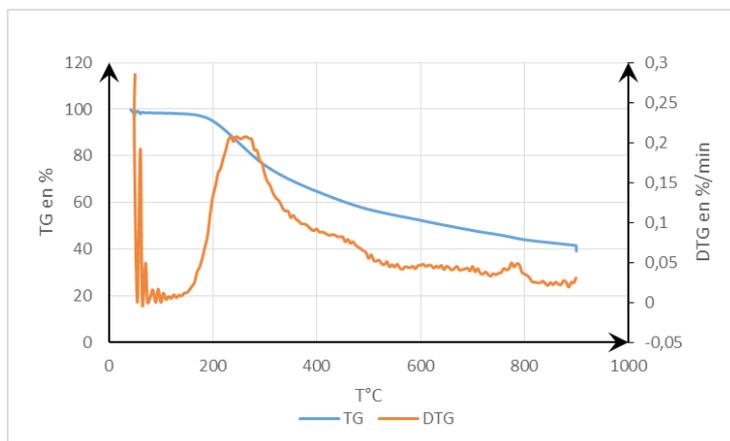
Pyrolysis of formulation 2

Figure 2 shows the TG and DTG curves of formulation 2 of aningre tannin resin. The first region of weight loss (formulation 2) occurs between 40°C and 145°C with the peak around 49°C. This loss is due to the evaporation of absorbed water and the formation of small volatile combustible compounds (H, CO, CO_2) released by the resin (formulation 2). The second region between 145°C and 590°C with the peak around 250°C is due to the degradation of laterals chains of the resin (Zhang *et al*. 2011, Petrovich *et al*. 1994) and to the formation of volatile combustible compounds released by hexatramethylenetetramine. The mass loss registered in the region between 590°C and 800°C whith the peak around 770°C is due to the total decomposition of elements which began their decomposition during previous phases (Yoshio *et al*. 2003). At the end of pyrolysis analysis around 40,21% of initial mass is not decomposed, this can correspond to the mass of rigid segment in the resin (formulation 2), all bonds within molecular rings are treated as rigid.

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Figure 2. TG and DTG curves of pyrolysis analysis of aningre tannin resin under formulation 2.

Pyrolysis of formulation 3

Figure 3 shows TG and DTG curves of formulation 3 resin. Three main regions of mass loss are observed: In the first region between 40 and 140°C with the peak at 48°C, we note the loss of water and small formation of volatile compounds (CO, H, CO_2) released by the resin and particularly by glyoxal. The second region of mass loss which occurs between 140 and 565 °C with the peak at 245°C is due to the degradation of the laterals chains of the resin (Zhang *et al.* 2011) and the formation of volatile coumpounds (Lu 2008), it is in this region that the decomposition of glyoxal is observable. Around 470°C, there is cleavage of C-C bonds to form carbon and hydrogen as CH_4, CO or CO_2 (Gunes *et al.* 2009, Petrovich *et al.* 1994, Zhang *et al.* 2011). The third region between 735 and 845°C with the peak at 790°C is due to the decomposition of A and B ring flavonoid to form carbon skeleton. About 39,12% of initial mass is not total decomposed, this can correspond to the mass of rigid segment in the resin (formulation 3).

Figure 3. TG and DTG curves of pyrolysis analysis of aningre tannin resin under formulation 3.

Comparative study

Table 1 compares data of the resins analyzed. Residues obtained show that sample H (formulation 2) has lost less energy than GLY (formulation 3) and PF (formulation 1) samples; GLY sample loses less than PF (40,21>39,12> 24,01%). The different slopes of the TG curves (series1) confirm these different degrees of weight loss. From these residues, it is appropriate to conclude that in resin H (formulation 1), there are more resistant segments to heat than in the GLY (formulation 3) and PF (formulation 1) samples. The molecular weight of hardeners confirms this [hexamethylenetetramine molecular weight (140,18 g/mol) > glyoxal molecular weight (58,03 g/mol) > paraformaldehyde molecular weight (30,03 g/mol)]. The beginning of the degradation of the H sample (145 °C) is higher than those of PF (135 °C) and Gly (140 °C); the low molecular weight of formaldehyde and its earlier decomposition than the others formulation (135<140<145°C) explains the higher decomposition recorded by PF than the others formulations (2 and 3).

Table 1. Thermoanalytical data of samples.

Analysis type	Samples	Temperature range (°C)	Temperature peak (°C)	Residue samples (%)
Pyrolysis	Gly (formulation 3)	40 – 140	48	39,12
		145 – 565	245	
		735 – 845	790	
	H (formulation 2)	40 – 145	49	40,21
		145 – 590	250	
		590 – 800	770	
	PF (formulation 1)	40 – 135	49	24,01
		135 – 675	255	
		675- 765	720	

According to Figure 4 and 5 which recapitulate respectively the TG (H_ pyro, PF_ pyro, Gly_ pyro) and DTG curves (H_ pyro, PF_ pyro, Gly_ pyro), the biggest difference between these formulations occurs from 400°C, it means that, the decomposition of the hardeners used (paraformaldehyde, aqueous glyoxal, hexamethylenetetramine) become more significant from 400 °C onward.(H_pyro, P_pyro, Gly_pyro mean respectively pyrolysis of H, PF and Gly samples).
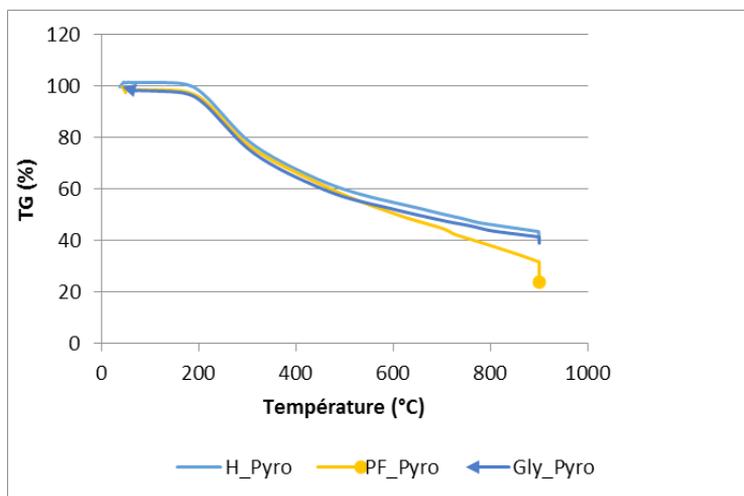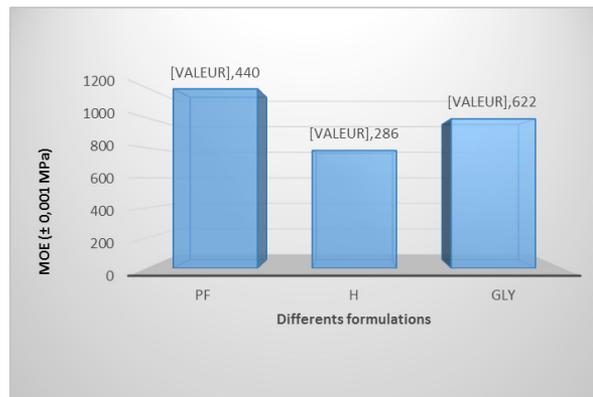

Figure 4. Recapitulation of TG curves.
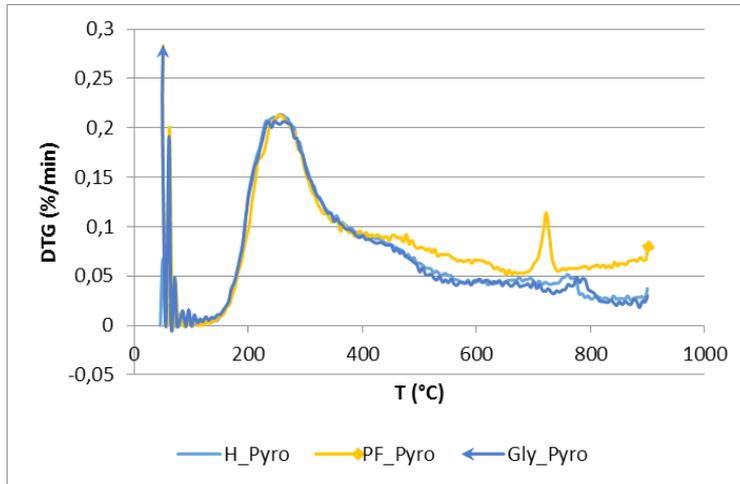
Figure 5. Recapitulation of DTG curves.

According to the Figure 6, PF, Gly and H formulations have respectively for rigidity 1190, 991 and 781 MPa. PF which has the smaller residues (20%) after pyrolysis presents the best rigidity, the H formulation with its highest residues (40%) has the worst rigidity (1190>991>781 MPa).

Figure 6. Comparison of resins rigidities.

CONCLUSIONS

Aningre tannin-based resins present a good future alternative for the wood industry, the heat resistance of various formulations being encouraging. The biggest difference between these formulations occurs from 400°C onward, the decomposition of hardeners used (paraformaldehyde, aqueous glyoxal, hexamethylenetetramine) become more significant from 400°C onward.

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