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DSC and DMA study of chestnut shell tannins for their application as wood adhesives without formaldehyde emission

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Abstract The use of chestnut (*Castanea sativa*) shell tannin extracts for the formulation of wood adhesives has been studied. The interest was centred not only on the formulation of adhesives from a renewable resource but also on the possibility of completely removing formaldehyde from the adhesive formulations. Tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamine (HEX) were used as hardeners and the results were compared with those obtained with the traditional hardener, paraformaldehyde (PAR). Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to study the chemical and mechanical cure of the formulated adhesives and the influence of the type of hardener on the curing properties. DSC curves were obtained at three heating rates and using an isoconversional method, chemical conversion vs. time at a given temperature was obtained. The curing enthalpy for the adhesive with hexamine as hardener was the highest and decreased in the order HEX $\sim$ TRIS $\gg$ GLY $>$ PAR. The highest rate of chemical cure was achieved using PAR as hardener followed by GLY $>$ HEX $>$ TRIS, that required higher curing temperatures to achieve complete chemical cure. Mechanical cure was analyzed from isothermal DMA experiments. The rate of mechanical curing decreased in the order TRIS $>$ HEX $>$ GLY, however, the rigidity after completion of curing increased in the same order. Alternative hardeners increased significantly adhesive pot-life compared to paraformaldehyde, especially tris (hydroxymethyl)nitromethane.

Keywords Chestnut shell tannins · Hexamine · Tris(hydroxymethyl)nitromethane · Glyoxal · Differential scanning calorimetry · Dynamic mechanical analysis

Introduction

Investigations on the use of renewable resources for applications up to now covered by oil-derived products have gained considerable interest in recent years for both economic and environmental concerns. The Galician (NW of Spain) food industry uses ~7,000 t/year of chestnut fruits (from the *Castanea sativa* species) for the production of different derivatives, such as marrón glacé, chestnut pureé, etc. Chestnut shell, which represents around 10% by mass of the chestnut, is removed in the peeling process and used as fuel in the factory. In previous works of the authors [1, 2] various applications for chestnut shell were analysed and the potential of chestnut shell tannins as phenol substitutes in the formulation of wood adhesives was demonstrated. Extraction process was optimised to select those conditions that lead not only high extract properties (Stiasny number, total phenols content, etc.) but also to high extraction yields [2].

Nowadays, there is a worldwide concern on the use of formaldehyde due to its suspected carcinogenic effect. For this reason, new technologies are being investigated to modify the traditional tannin–formaldehyde adhesive systems actually used, not only to prevent the use of formaldehyde but also to reduce its emission from wood panels. One of the alternatives proposed is the use of hardeners not emitting formaldehyde at all, simply because either no aldehyde has been added to the tannin or because the aldehyde cannot be liberated from the system [3]. Some examples of this alternative hardeners are methylolated nitroparaffins, in particular,

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tris(hydroxymethyl)nitromethane [4, 5], a non-volatile and non-toxic aldehyde, glyoxal [6] and hexamine, which in presence of chemical species with very reactive nucleophilic sites, such as condensed flavonoid tannins, is not at all a formaldehyde-yielding compound [7, 8].

Differential scanning calorimetry (DSC) is the most common technique used to study the chemical cure of phenolic resins [9–11] and tannin-based adhesives [12–14]. In addition, isoconversional methods [15] have been extensively used to describe complex kinetics of processes which involve multiple steps, as is the case of crosslinking reactions. However, it has been found that adhesive chemical cure, measured by DSC, might not be in agreement with the development of mechanical properties in the wood/adhesive system (or mechanical cure), measured by dynamic mechanical analysis (DMA), which normally completes before [11, 13]. Then, the simultaneous use of both techniques is recommended to optimise the process.

In this article, chestnut shell tannin adhesives were prepared using different hardeners, namely, tris(hydroxymethyl)nitromethane, glyoxal, hexamine and paraformaldehyde and their pot lifes compared. DSC was used to study the chemical cure of the adhesives, and cure kinetics was analysed by means of the Model Free Kinetics isoconversional method. In addition, the mechanical cure development was analysed using DMA and compared with chemical cure measured by DSC.

Experimental

Material

Chestnut (*C. sativa*) fruit shell (a mixture of the outer brown peel and the inner pellicle) was supplied by a food factory, Marrón Glacé, S.L. (Ourense, Spain). It was air dried till equilibrium moisture content, ground in a hammer mill, sieved, and the fraction of particle size between 0.1 and 2 mm was selected. Chemical composition of chestnut shell was determined in a previous study [16].

Extraction and concentration

Tannin extraction was carried out in a 2-L Pyrex glass reactor with mechanical stirring and temperature control. Chestnut shell and water (in the ratio 1 g shell (dry basis)/10 mL solution) were mixed at room temperature, heated and, once the selected temperature (100 °C) was attained, the alkali (4.5% sodium sulphite and 3% sodium hydroxide) was added and contact time begun to run. After 1 h the suspension was vacuum filtered, the solid residue was washed with water until a nearly colourless filtrate was obtained and the extract together with the first water washings were concentrated by spray-drying. The solid was dried at room temperature in order to calculate the extraction yield as the mass loss percentage of the starting raw material (56.5% [2]). The solid extract was characterized for its Stiasny number (80.5), total phenols content [59.1 g gallic acid equivalent/100 g oven-dried (od) extract], proanthocyanidin content (24.2 g/100 od extract), number and weight average molecular weights, 1,089 and 2,022 Da, respectively [2].

Preparation of the adhesives

A 40% (w/w) aqueous solution of the extract was prepared and a 10% (w/w, based on od extract) of the selected hardener, tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) (as a 40% aqueous solution), hexamine (HEX) or paraformaldehyde (PAR), was added and mixed at room temperature. Two different pHs were assayed, the extract natural pH (pH = 6), and a higher one (pH = 8), changed using a sodium hydroxide aqueous solution.

Pot life essay

Pot life of the chestnut shell adhesives at their natural pH was analyzed by measuring the increase of adhesive apparent viscosity with time, from 30 to 420 min since hardener addition. Measurements were performed at 25 °C with a Brookfield DV-II+ viscosimeter using the small sample adapter. Adhesive rheological behaviour was studied analysing the variation with time of the power law rheological parameters, n (the power law index) and k (the consistence index) at 25 °C.

Differential scanning calorimetry (DSC) experiments

DSC measurements were carried out in a Mettler Toledo DSC 821^{e} apparatus, equipped with a sample robot. A resin (20–30 mg) was sealed in a 120 μL medium- pressure stainless crucible with a Viton O-ring that can withstand pressures up to 2 MPa. The experiments were performed under a nitrogen atmosphere and also nitrogen was used as purge gas. The temperature range scanned was from 25 to 200 °C and three heating rates were used 5, 10 and 20 $°C\ min^{-1}$. Temperature and enthalpy calibrations were performed with indium. The results were analysed using the STAR^{e} software supplied by Mettler-Toledo. The model free kinetics isoconversional method was used to analyze chemical cure kinetics.

Dynamic mechanical analysis (DMA) experiments

The tests were carried out in a DMA/SDTA861 equipment from Mettler Toledo. A small amount of adhesive

(10–40 mg) was spread on the surface of two ash (*Fraxinus excelsior*) wood veneer samples [15 mm (length) × 6 mm (width) × 0.5 mm (thickness)] which were then piled up as a sandwich. Both ends of the sample were clamped to a rigid frame with a torque of 12 cN m and the drive shaft was clamped to the centre of the sample. The choice of a dual cantilever deformation mode was based on the fact that it favours the strain of the less stiff material, in this case, the adhesive between the more rigid supports [17]. The operating conditions used in this test were: frequency 1 Hz, maximum force 0.10 N, maximum deformation amplitude 10 µm, temperature 80 °C and total test time 20 min.

Results and discussion

Pot-life determination

The reaction of chestnut shell tannins with the different hardeners used caused the adhesive viscosity to increase with time, thus limiting the length of time during which the adhesive retained a viscosity low enough to be used in board manufacture. For this reason, the influence of the type of hardener on adhesive pot life was analysed. Table 1 shows the apparent viscosity at 25 °C of the adhesives at a fixed shear rate (10 rpm) and the power law rheological parameters for the tannin solutions and the adhesives prepared after different times at room temperature after hardener addition, 30 and 420 min, when possible.

The apparent viscosity of the adhesives in the initial period of reaction decreased with respect to that of the tannin solution, and more significantly when glyoxal was used as hardener. However, except for paraformaldehyde, whose pot life was less than 1 h, after a reaction time of 420 min, viscosity decreased in the order GLY > HEX > TRIS, as also found for the power law consistence index. Then, tris(hydroxymethyl)nitromethane provides a higher adhesive pot life at room temperature than the other hardeners essayed, as found before for quebracho and mimosa tannins by Trosa and Pizzi [4], which represents a substantial advantage for the use of this hardener.

Analyzing the rheological behaviour of the tannin solution and the adhesives, it has been found that all of them showed pseudoplastic behaviour with values of the power law index, n, lower than unity, and more pronounced with the progress of the reaction. This behaviour, previously found for pine tannin-phenol–formaldehyde adhesives [18], is of great interest because, as the adhesive is subject to stress during its application, its apparent viscosity decreases, allowing for better flow.

DSC experiments

Figure 1 shows, as an example, the DSC curves obtained at a heating rate of 10 °C min^{-1} for the chestnut shell tannin

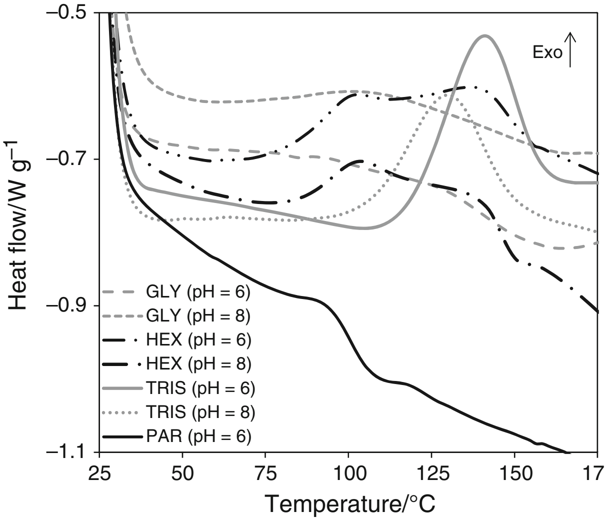

Fig. 1 DSC curves of chestnut shell tannin adhesives using paraformaldehyde (PAR), tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamine (HEX) as hardeners at pH = 6 or 8 and at a heating rate of 10 °C min^{-1}

Table 1 Rheological behaviour of chestnut shell tannin solution and adhesives at their natural pH and its variation with time

Sample	Time since mixing/min	Apparent viscosity at 10 rpm/mPa s	k/Pa s^n	n	R^2
40% tannin solution (TS)	30	2,483	3.24	0.54	0.997
TS + 10% PAR	30	2,184	2.85	0.53	0.998
TS + 10% TRIS	30	2,136	2.74	0.52	0.999
	420	4,895	8.36	0.49	0.999
TS + 10% HEX	30	2,292	2.87	0.54	0.999
	420	14,517	14.07	0.48	0.937
TS + 10% GLY	30	1,368	1.46	0.59	0.999
	420	*	24.19	0.35	0.993

* Not measurable

PAR Paraformaldehyde, *TRIS* tris(hydroxymethyl)nitromethane, *HEX* hexamine, *GLY* glyoxal

Table 2 Peak temperature and curing enthalpy for chestnut shell adhesives at heating rates of 5, 10 and 20 °C min^{-1} determined by DSC

Adhesive	pH	Heating rate/°C min^{-1}	Peak temp./°C	ΔH/J g^{-1}
TS + 10% PAR	6	5	90.4	3.51
		10	93.0	3.68
		20	104.0	3.40
TS + 10% TRIS	6	5	130.4	33.06
		10	141.0	34.28
		20	154.3	36.84
	8	5	117.5	34.56
		10	130.5	30.92
		20	143.3	32.39
TS + 10% HEX	6	5	92.6, 131.3	30.70
		10	101.3, 140.7	30.93
		20	106.9, 150.3	30.32
	8	5	91.7, 130.5	41.46
		10	103.5, 139.6	37.91
		20	113.0, 153.3	41.22
TS + 10% GLY	6	5	119.4	13.78
		10	125.8	12.41
		20	138.5	11.69
	8	5	96.5	9.96
		10	107.2	10.80
		20	117.8	9.87

TS Tannin solution, *PAR* paraformaldehyde, *TRIS* tris(hydroxymethyl)nitromethane, *HEX* hexamine, *GLY* glyoxal

adhesives prepared with the four hardeners used, and Table 2 presents the values of the curing enthalpy and the maximum temperature of the exothermic peaks corresponding to the adhesive curing reactions.

All DSC curves showed a single exothermic peak, with the exception of hexamine adhesives which showed a split peak with a second maximum at higher temperatures. The temperature of the maximum of the exothermic peak increased in the order: 90–104 °C (depending on the heating rate) for paraformaldehyde adhesives, 96–139 °C for glyoxal adhesives and 117–155 °C for the TRIS ones, which implies that increasingly higher temperatures are required to achieve complete chemical cure. TRIS was the hardener that needed the highest temperature to start the curing reaction which explains the lower reaction rate at room temperature and, hence, the higher adhesive pot-life. Regarding hexamine adhesives, the first maximum appeared in the range 91–113 °C and the second at 130–154 °C, which could be attributed to the simultaneous formation of methylene and benzylamine bridges [19, 20]. Unlike hexamine adhesives, whose peak temperatures hardly depended on pH, for TRIS and glyoxal adhesives the exothermic peak shift to lower temperatures when pH was increased from 6 to 8. As a result, at high pH chemical cure could be achieved operating at a lower temperature range.

The highest curing enthalpy corresponded to hexamine adhesives, followed by the TRIS ones, with slightly lower values, and finally the glyoxal and paraformaldehyde adhesives, in this order, with significantly lower values. Considering a proportionality between the curing enthalpy and the crosslinking created, which is related with the number of links formed, the lower the heat released the lower the crosslinking. The variation of curing enthalpy depending on the hardener used could be explained taking into account that tannin adhesive hardening by polycondensation can be coupled with simultaneous hardening by autocondensation. In addition, a low crosslinking density has been found for tannin networks obtained exclusively through autocondensation reactions [21]. Then, autocondensation seems to be favoured using paraformaldehyde as hardener, whereas hexamine or TRIS might act depressing tanning autocondensation or both condensation mechanisms occur simultaneously without interferences. As regards the influence of adhesive pH on curing enthalpy, it was more significant for hexamine adhesives. The higher value obtained at the highest pH could be explained considering that at high pH hexamine improves considerably the level of crosslinking of the hardened network [8].

Curing kinetics

The model free kinetics isoconversional method has been used for predicting the chemical conversion of the tannin adhesives prepared. It requires performing experiments at least at three heating rates (5, 10 and 20 °C min^{-1} have been used) for evaluating the dependence of activation energy on conversion, which is used for making kinetic predictions [15].

Figure 2 shows the chemical conversion predictions for the adhesives prepared using the different hardeners at both pHs essayed (6 or 8) and comparatively at two temperatures, 120 °C (Fig. 2a) and 140 °C (Fig. 2b). At both temperatures, paraformaldehyde was the hardener that provided the faster chemical cure. However, due to its extremely short pot-life, previously mentioned, it has been discarded as hardener for chestnut shell tannin adhesives. As regards the rest of the hardeners, they required higher temperatures to attain a complete chemical cure in a reasonable time. In general, the curing rate decreased in the order GLY > HEX > TRIS at a given temperature and pH. However, a distinct behaviour was observed for TRIS that showed a low curing rate at the initial stage but then increased significantly when increasing temperature. For all hardeners, except for hexamine, the rate of curing increased significantly with increasing adhesive pH as found for other tannin adhesives systems [6].

In order to complete the study of the curing kinetics of the chestnut shell tannin adhesives, the DMA technique was used to evaluate the mechanical curing rate, which characterizes the cure in terms of the rate of rigidity development, while DSC evaluates the rate and extent of chemical conversion. Figure 3 shows the variation of the storage modulus (E') with time at 80 °C for the adhesives prepared with the hardeners at pH = 8. The maximum rigidity corresponding to the finishing point of the curing reaction (E'_{max}) was achieved for the adhesives prepared using glyoxal and hexamine as hardeners, which required a higher extent of polymerization compared to TRIS. For hexamine and TRIS adhesive samples, the observed decrease of the storage modulus after reaching its maximum value (E'_{max}) could be attributed to thermal degradation reactions.

The degree of mechanical cure was calculated based on the changes of the storage modulus with time at a fixed temperature by using the following equation [13]:

$$\text{Mechanical conversion } (\%) = \left[\frac{E'_{\max} - E'(t)}{E'_{\max} - E'_{\min}}\right] \times 100 \qquad (1)$$

where $E'(t)$ is the value of the storage modulus at a given time t, E'_{min} is the value of the storage modulus when it started to increase sharply (0% of mechanical conversion)

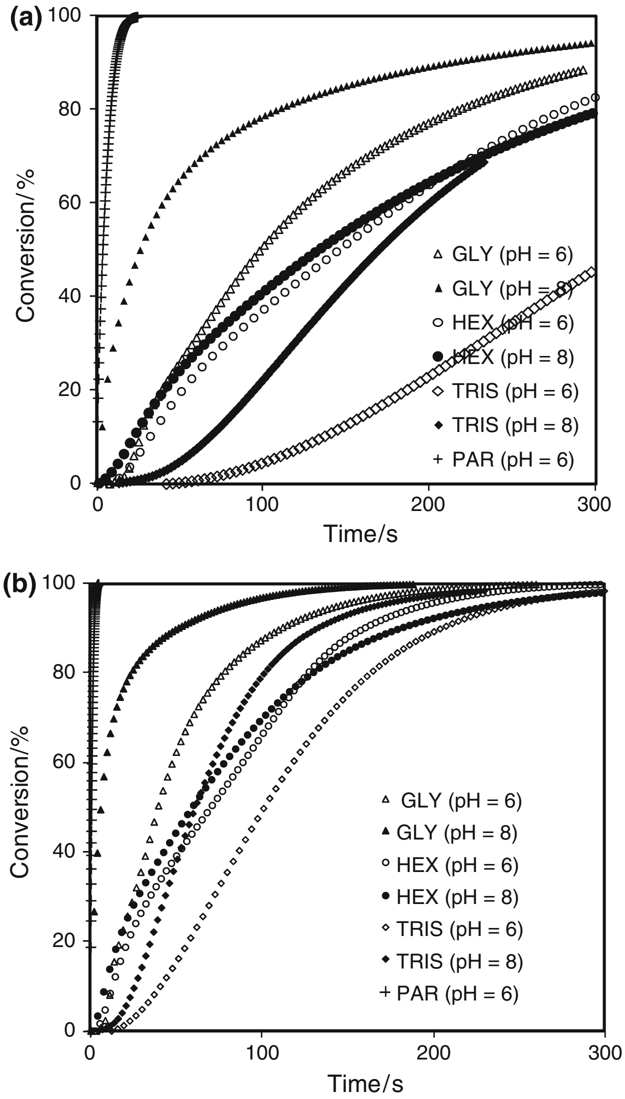

Fig. 2 Conversion versus time for chestnut shell tannin adhesives using paraformaldehyde (PAR), tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamine (HEX) as hardeners at pH = 6 or 8 and at 120 °C (**a**) 140 °C (**b**)

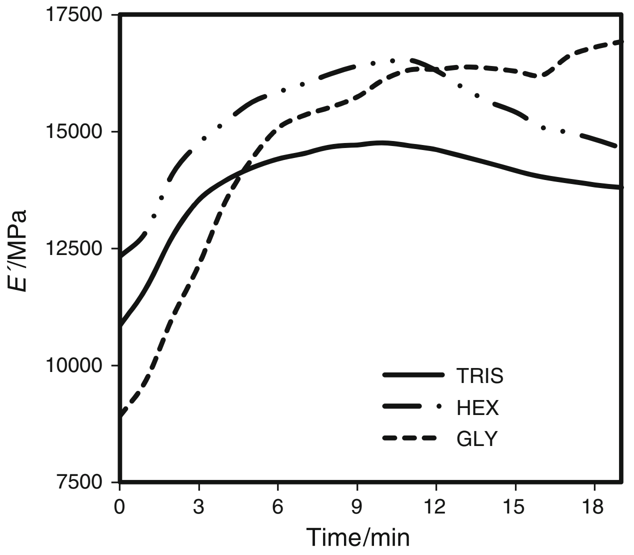

Fig. 3 Storage modulus (E') versus time for chestnut shell tannin adhesives using tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamine (HEX) as hardeners at pH = 8 and at 80 °C

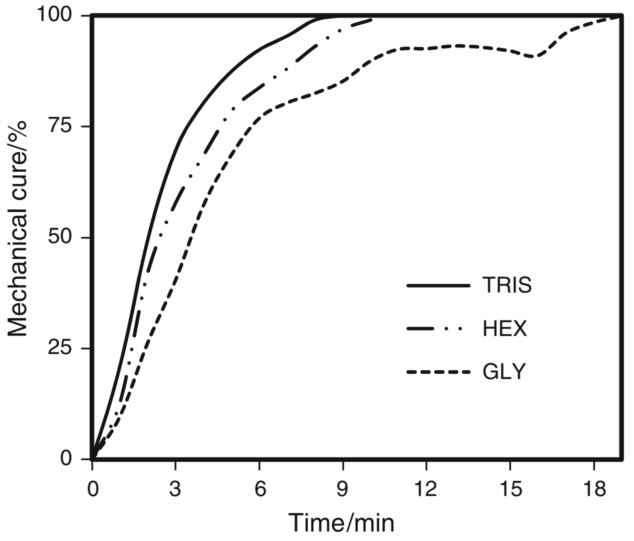

Fig. 4 Mechanical cure versus time for chestnut shell tannin adhesives using tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY) and hexamine (HEX) as hardeners at pH = 8 and at 80 °C

and $E'_{\max}$ is the maximum of the E' curve (100% of mechanical conversion). As shown in Fig. 4, where the variation of the mechanical cure with time is presented, the highest rate of mechanical cure corresponded to the TRIS adhesive, followed by the hexamine and glyoxal ones, in this order. Comparing these results with those previously obtained for the rate of chemical cure, it is observed that the adhesive with the highest rate of mechanical cure (TRIS adhesive) showed the lowest rate of chemical cure. This behaviour can be explained considering that for TRIS adhesive there is a rapid increase of the mechanical properties for low levels of chemical cure. In addition, for a given adhesive system the mechanical conversion rates were higher than the chemical conversion ones, thus, at 80 °C in 5 min around 80% of mechanical cure was achieved for the TRIS adhesive, whereas 120 °C were necessary to obtain in 5 min the same degree of chemical cure.

Conclusions

From the study on the use of different hardeners alternative to paraformaldehyde in the preparation of chestnut shell tannin base adhesives the following conclusions have been obtained:

- Tris(hydroxymethyl)nitromethane provided the highest adhesive pot life at room temperature which represents a substantial advantage for the use of this hardener in comparison with hexamine or glyoxal. On the contrary, paraformaldehyde due to its extremely short pot-life (less than 1 h) has been discarded as hardener for chestnut shell tannin adhesives.
- The curing enthalpy for the adhesive with hexamine as hardener was the highest, reflecting a higher crosslinking density, and decreased in the order HEX $\sim$ TRIS $\gg$ GLY $>$ PAR.
- The highest rate of chemical cure was achieved using paraformaldehyde as hardener followed by GLY $>$ HEX $>$ TRIS, that required higher curing temperatures to achieve complete chemical cure.
- The rate of mechanical curing, measured by DMA, decreased in the order TRIS $>$ HEX $>$ GLY, however, the rigidity after completion of curing increased in the same order.
- Mechanical conversion rates were higher than the chemical conversion ones.

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