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MIMOSA AND CHESTNUT TANNIN EXTRACTS REACTED WITH HEXAMINE IN SOLUTION

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Autocondensation reactions of mimosa and chestnut tannin extracts solutions have been analysed at several pH by differential scanning calorimetry (DSC). Alkaline pH promotes autocondensation reaction of these tannins. Curing reactions between these tannins and hexamine at acid and not strongly alkaline pH have been proved by DSC. Thermal analysis gives insights not only on reactions between tannin and hexamine, but also about water presence on solutions and degradation reactions of tannins. Products obtained from reactions between tannins and hexamine have been analysed by Fourier transform infrared spectroscopy (FTIR). The obtained chemical structures are influenced by both chemical structure of tannin and pH of solution. For mimosa tannin amine and ether groups are obtained while for hydrolysable chestnut tannin amide groups have been detected.

Keywords: *autocondensation, hexamine, pH, polycondensation, tannin*

Introduction

Phenol and formaldehyde toxicity and the new requirements for increasing recycling and re-use of wastes prompted the use of renewable resources such as wood [1]. Amongst the possible alternatives, tannin is an excellent renewable resource which can be used for replacing all or part of the petroleum-derived phenolic compounds of adhesives [2–5].

Hexamethylenetetramine (hexamine) has been used for a long time as a hardener of tannin adhesives [6]. The reaction of hexamine with tannins in aqueous solutions was analysed by Pizzi, who showed that hexamine is not a formaldehyde-yielding hardener and thus it leads to cured products with low formaldehyde emissions [7, 8]. On the other hand, some works are focused on the manufacture of adhesives composed of polyphenolic tannin and hexamine. Indeed, Theis and Grohe [9] have reported the manufacture of biocomposites based in hemp and biodegradable mimosa tannin adhesive cured with hexamine. Mosiewicki *et al.* [10] have shown that composites based in pine woodflour as filler and pine tannin-hexamine adhesive have thermal and mechanical properties adequate for using in some industrial applications.

For the analysis of reactions between tannin and hexamine it must be considered that different pH can influence in chemical pathways. As it is well know, hexamine decomposition occurs easily at acid pH [11]; in these conditions tannin-hexamine solutions result in an instantaneous 'gel' formation [8–12]. At basic pH deprotonation of hydroxyl groups of flavonoid molecule occurs more easily.

In this work, autocondensation and polycondensation reactions of mimosa and chestnut tannin extracts solutions with hexamine have been evaluated by DSC. Fourier transform infrared spectroscopy (FTIR) has also been employed for the determination of the chemical structure of crosslinked materials.

Experimental

Materials and methods

Commercial powders of chestnut (*Castanea sativa*) and mimosa (*Acacia mearnsii*), wood extracts were used without purification. Fine hexamine (without stabilization) was gently provided by Hexion Specialty Chemicals (Spain). Analysed samples have been obtained by mixing water solution of every tannin at 40 mass/mass% with 10 mass/mass% of hexamine. Sodium hydroxide and clorhydric acid have been employed to control pH of solutions.

FTIR spectra of the resins were obtained in a Nicolet spectrophotometer. The acquisition conditions were 400–4000 $\mathrm{cm^{-1}}$ spectral range, 10 scans and a resolution of 4 $\mathrm{cm^{-1}}$. Analysis was performed on KBr pellets.

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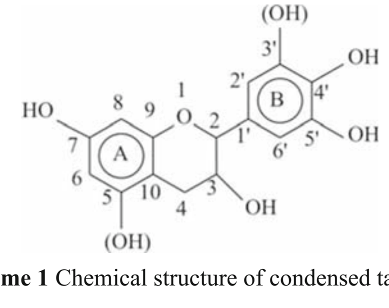
Thermal analysis was carried out using a differential scanning calorimeter (DSC) Mettler DSC20 linked to a TC 15 TA Processor. 2 to 6 mg samples were sealed in a medium pressure pan which could withstand up to 20 bar. The capsule containing the sample and the reference capsule were transferred to the DSC sample holder assembly which had been set at 25°C. A scanning temperature range from 25 to 250°C was employed for thermal characterization. The sample crucibles were heated at 10°C min^{-1}.

Thermal degradation studies of cured materials were performed in a Setaram 92-12 thermal balance linked to a Setaram CS9212 Processor. Scans were performed from 30 to 500°C in helium atmosphere.

Results and discussion

Autocondensation reaction is based on the opening, under alkaline conditions, of the O_1–C_2 bond of the catechin repeating unit (Scheme 1) and subsequent autocondensation between the carbocation at C_2 of the open unit with the free C_6 or C_8 sites on a catechin unit of another polymer chain. Although this reaction leads to noticeable increases in viscosity, gelling does not occur [14].

In order to analyse autocondensation reactions DSC scans of solutions of mimosa tannin extract have been performed at several pH (Fig. 1a). As can be seen in curves obtained at pH 10 and 12, some baseline deviation between 50 and 150°C takes place. On the contrary, at lower pH this deviation does not occur. On the other hand, curves obtained for mimosa tannin solutions containing 10 mass/mass% of hexamine have also been performed. It is clear from Fig. 1b that at pH 4 and 8 exothermic peaks at 100 and 130°C are present. These ones are not visible in curves obtained for mimosa tannin solutions without hexamine. At pH 10 and particularly at pH 12, curves obtained with and without hexamine are similar. Then, according with these observations it can be concluded that at pH lower than 10 autocondensation reaction does not occur. Only when strongly alkaline conditions are employed autocondensation reactions are present.



Scheme 1 Chemical structure of condensed tannins

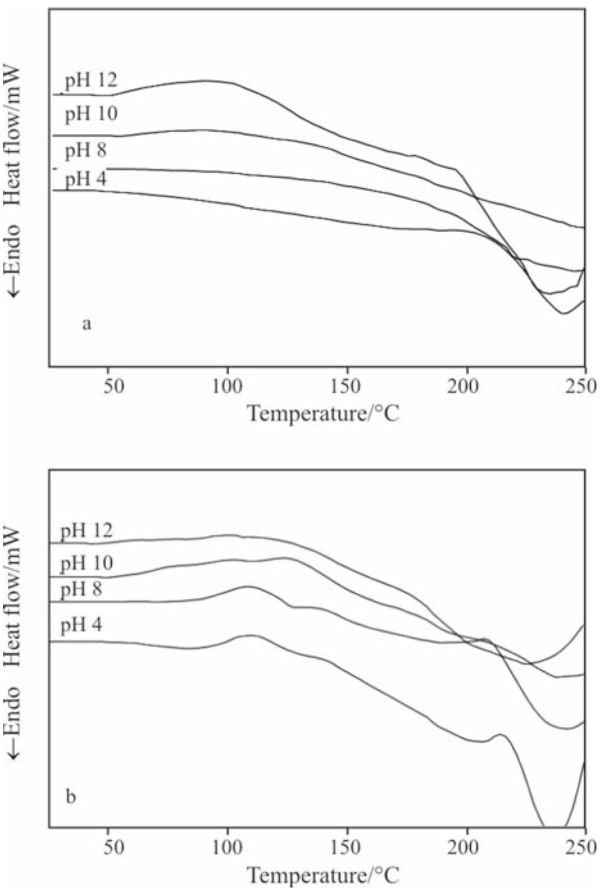


Fig. 1 DSC curves of mimosa and mimosa–hexamine water solutions at several pH (a – mimosa; b – mimosa–10% hexamine)

Solubility analysis of obtained products has also been performed. Samples obtained from mimosa tannin solutions after DSC scans are water soluble. On the contrary, the ones obtained from systems tannin–hexamine at pH 2–8 are insoluble, but the ones at pH 10–12 are soluble. According with these observations it can be concluded that at pH 2–8 mainly crosslinking reactions between tannin and hexamine occur. Whereas, at alkaline pH autocondensation reactions occur, which increase viscosity but crosslinked products are not obtained, as Pizzi and Stephanou have reported [15, 16].

A similar analysis has been performed with chestnut tannin extract solutions (Fig. 2). The behaviour of this tannin is similar to the one observed for mimosa tannin. It must be noted the displacement of the exothermic peak to higher temperatures when pH of solutions increases. This difference of the behaviour between mimosa and chestnut tannin extracts solutions curing with hexamine will be analyzed in a next work in which kinetic analysis of these reactions will be performed. Moreover, curves obtained for systems with and without hexamine at pH 12 are similar at low temperatures but when temperature increases an

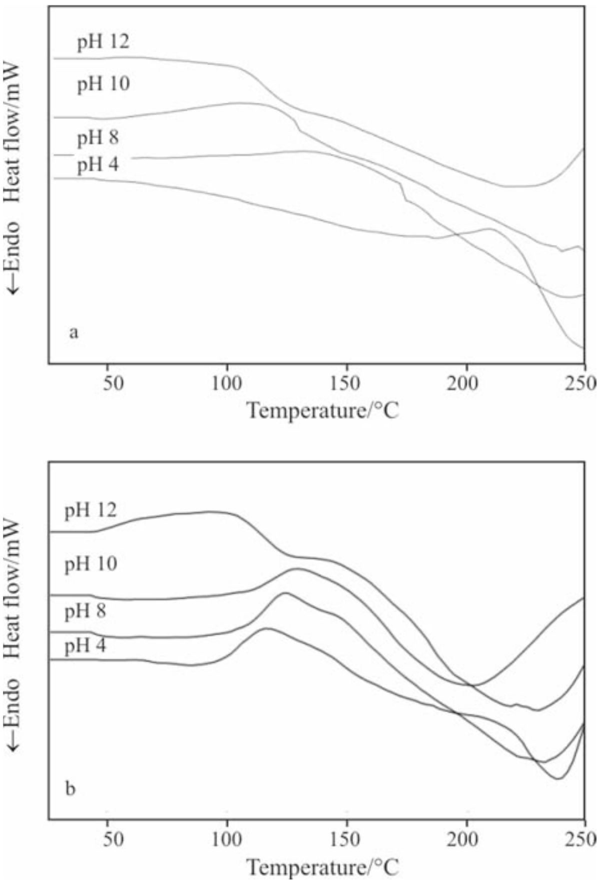


Fig. 2 DSC curves of chestnut and chestnut-hexamine water solutions at several pH, (a – chestnut; b – chestnut–10% hexamine)

exothermic peak is present in system which contains hexamine. In addition, solutions at pH 8 and 10 have exothermic peaks which are not present in the ones with hexamine. These differences can be attributed to the autocondensation reaction as above have been discussed for mimosa solutions. Therefore, autocondensation reactions of chestnut tannin solutions in alkaline conditions occur, but they seem to be less important than in the case of mimosa tannin solutions.

On the other hand, it has been observed that alkaline tannin solutions at room conditions increase viscosity through the time. In order to elucidate if this behaviour is due to the autocondensation reactions DSC scans of mimosa-hexamine tannin solutions at pH 4 and 12 have been performed at several times. Then, two samples for each solution have been simultaneously prepared. For each pH, one of the samples has been analysed after solution preparation (t_1) and the other one 24 h (t_2) after the preparation. The second one has been maintained under room conditions (25°C). From the obtained curves (Fig. 3) it can be seen that at pH 4 there are not differences between both times on the scans. On the contrary, at pH 12 and in the t_2 curves, it can be seen that only a small exothermic peak is present around 130°C. In addition, the one obtained between 50 and 130°C, which is present in curve obtained at t_1, disappears. Then, it can be deduced that the autocondensation reactions occur during storage at room temperature. This result must be taken into account in liquid adhesives manufacturing because some of the more significant parameters for the application as pot-life and viscosity could be seriously affected.

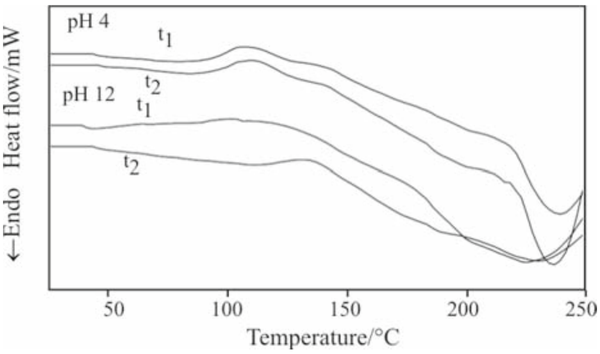


Fig. 3 DSC curves obtained from mimosa–hexamine water solutions at pH 4 and 12 at several times from solution preparation (t_1=0 and t_2=24 h)

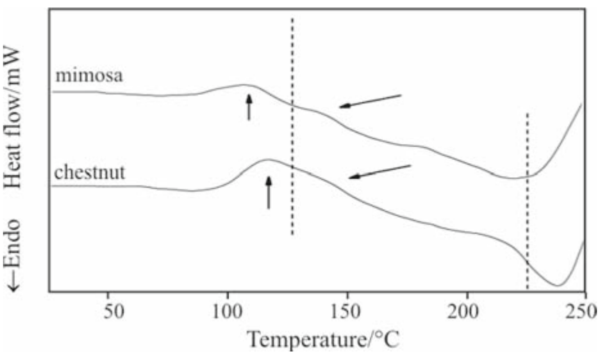


Fig. 4 DSC curves of systems of tannin–hexamine at pH 4

Analysis of reactions which result in insoluble products has also been performed. Therefore, solutions of tannin and hexamine at acid and not strongly alkaline pH have been analysed by DSC. As shown in Fig. 4, curves obtained present not only exothermic peaks at temperatures in the ranges 80–125 and 125–160°C, which are analysed below, but also deviation of baseline and another exothermic peak starting at 225°C are worth to be noted.

For the analysis of the deviation of the baseline and the high temperature exothermic peak, two factors must be considered: degradation reactions of tannins and water content of the samples. In order to check degradation reactions, thermogravimetric analysis of employed tannins has been performed (Fig. 5). As can be seen, two stages can be differentiated: at 80°C, due to the elimination of the humidity of samples and the other at 200°C, due to degradation of hydroxyl, ether, ester and other groups. This result implies that the exothermic peak present in DSC curves at temperatures around 225°C can be attributed to degradation reactions of tannins.

On the other hand, the influence of water present in samples on thermal behaviour has been analysed for tannin solution, water and hexamine solution. As can be seen in Fig. 6, water presence results in a deviation of baseline which is similar than the ones for both tannin and hexamine solutions. In addition, in the tannin solution exothermic behaviour also occurs at high temperatures. Then, it can be concluded that curves obtained for curing reactions between tannin and hexamine are influenced not only by crosslinking reactions, but also by water presence and degradation of tannins.

In order to elucidate chemical reactions for each of the exothermic peaks of tannin–hexamine mixture, FTIR analysis has been performed. For this purpose, samples obtained by DSC analysis have been analysed after scans from 25–120 and 25–160°C. Reactions have been stopped in both cases by cooling in water/ice bath.

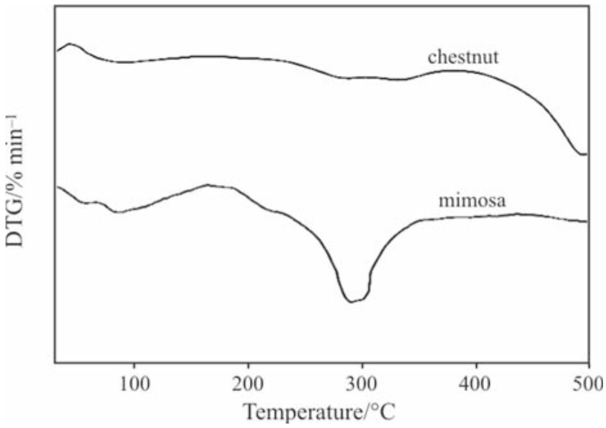


Fig. 5 TG curves of mimosa and chestnut tannin extracts

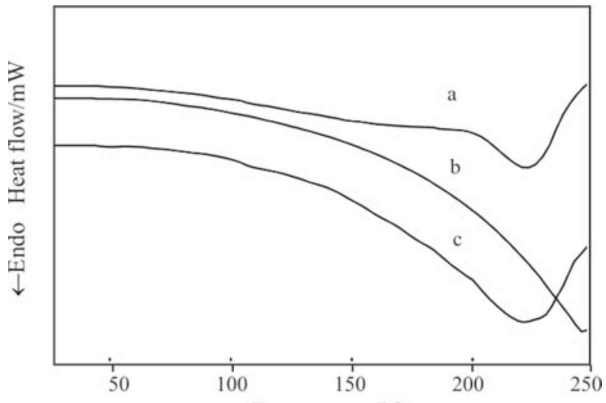


Fig. 6 DSC curves of systems: a – water solution of mimosa (40 mass/mass%); b – water; c – water solution of hexamine (10 mass/mass%)

From the analysis of the spectra after the first exothermic peak (25–120°C) (Fig. 7), it is clear the absence of C=C bands at 1500 and 1450 cm^{-1}. This result is similar than the one obtained by Aranguren *et al.* [17] with novolac resins cured with hexamine. As they have explained, the increasing of the ring substituent results in a reduction of these bands and implies cross-linking reactions between components. Likewise, bands at 1150 and 960 cm^{-1}, due to the C–O and O–H groups of resorcinol molecule of mimosa tannin [18, 19], disappear after reaction. This result also implies that reactions resulting in a modification of chemical structure occur at all pH. On the other hand, bands which can be due to ether and amine groups have been also detected for all pH. Thus, 1235 cm^{-1} band at acid pH and 1260 cm^{-1} band at pH 8 can be attributed to the antisymmetric deformation of C–O–C in ether groups. Other bands at 1110, 1030 (at pH 8) and 1007 cm^{-1} (at pH 2–6), can be attributed to presence of C–N groups [19]. Differences in the wavenumber at which ether and amine groups appear at each pH indicating that reaction mechanism is different. Analysis of the relative intensity of bands at 1007 and 1235 cm^{-1} present in spectra obtained at acid pH has also been performed using as reference band the 1600 cm^{-1}, due to the stretching of C=C in aromatic ring. In Fig. 8, the intensity of these bands increases when pH higher is. This result suggests that different chemical structures are obtained at each pH and that the most important changes occur when acid and basic pH are compared.

Finally, spectra obtained after the second exothermic peak has been analysed (Fig. 9). Differences between acid and basic conditions are clearer in this case. Analysis of the spectra at acid pH (Fig. 9a) indicates that bands at 1007 and 1235 cm^{-1} disappear and

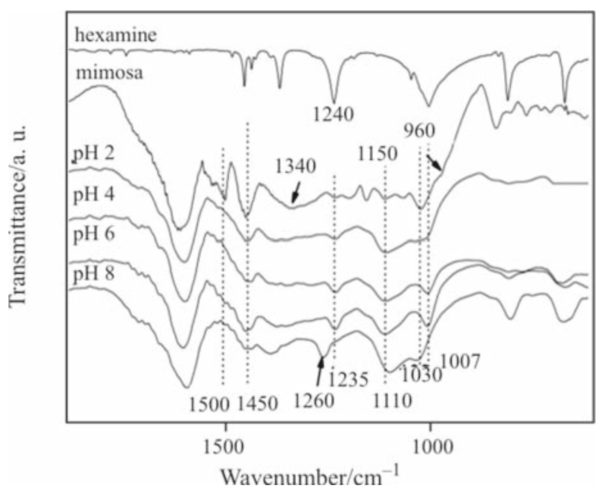


Fig. 7 FTIR spectra of hexamine, mimosa tannin and samples obtained from dynamic curing (25–250°C, 10°C min^{-1}) by DSC for mimosa tannin-hexamine systems at several pH

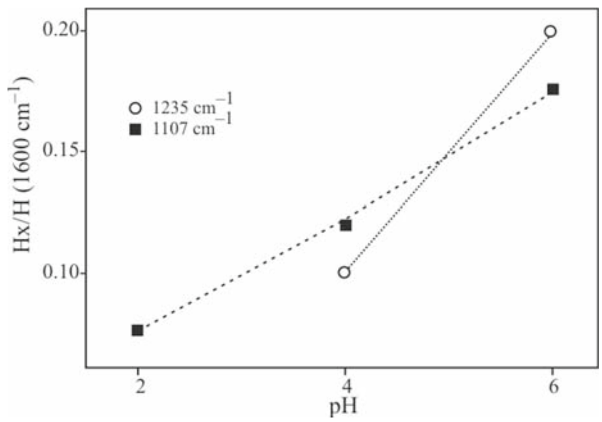


Fig. 8 Relative intensity of 1235 and 1007 cm^{-1} bands of systems based on mimosa tannin and hexamine at acid pH after dynamic curing from 25 to 120°C

the one at 1110 cm^{-1} increases. The 1007 and 1235 cm^{-1} bands are similar to the ones for the hexamine spectra. But the absence of the band at 1370 cm^{-1}, which is also present in hexamine spectra, indicates that the intensity variations of bands at 1007 and 1235 cm^{-1} must be due to the reactions of amine and ether groups of tannin and not to free hexamine in the samples. There are not more differences in spectra obtained after first and second stages defined by DSC analysis. Therefore, the reactions occurring at temperatures higher than 120°C during DSC scans at acid pH could be due to the transformation of the ether and primary and secondary amine groups of tannin into others with more substituents. On the contrary, at pH 8 more significant differences can be observed (Fig. 9b). Not only the bands of amine groups present at 1030 and 1110 cm^{-1} increase, but also the one at 1465 cm^{-1} due to methylene groups formation. These changes could indicate increases of the substituents of the amine groups. There are two new bands at 1645 and 1740 cm^{-1} probably due to the formation of azomethine groups –CH=N– [17] and to ester groups formation, respectively. Thus, from the analysis performed by FTIR, it can be concluded that ether and amine groups are the ones obtained from curing reactions between mimosa and hexamine as Pichelin *et al.* [8] and Pizzi and Tekely [7, 13] have proved by NMR analysis. Stanbury and Pizzi [21] and Pichelin and Pizzi [22] have proposed two different mechanisms for reactions between tannins and hexamine based systems. The resulting chemical structures proposed are similar in both mechanisms and there are in good agreement with the ones obtained in this work.

On the other hand, curing reactions analysis has also been performed for chestnut and hexamine systems. Comparing both Figs 1 and 2 the exothermic peaks obtained in mimosa-hexamine curves are more evident than the ones for chestnut-hexamine systems.

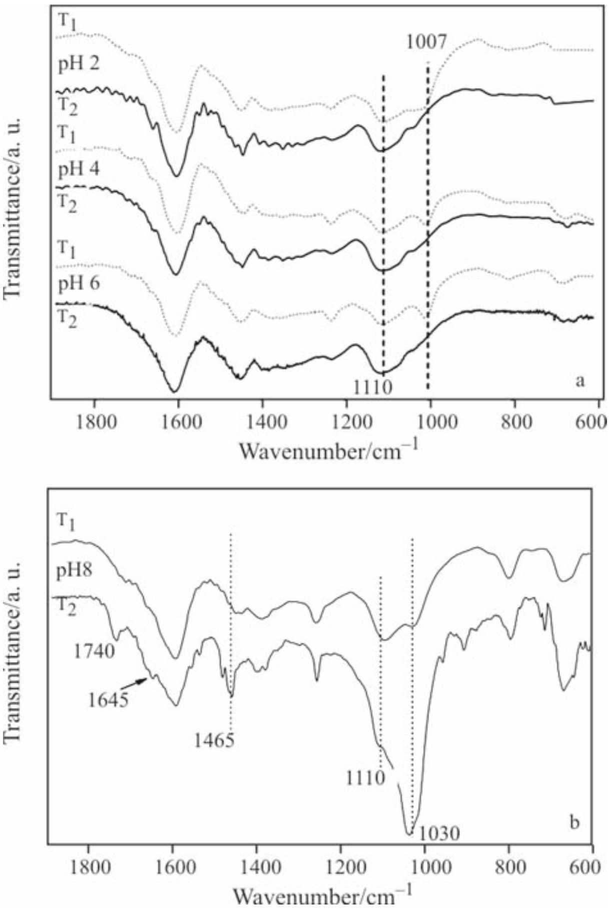
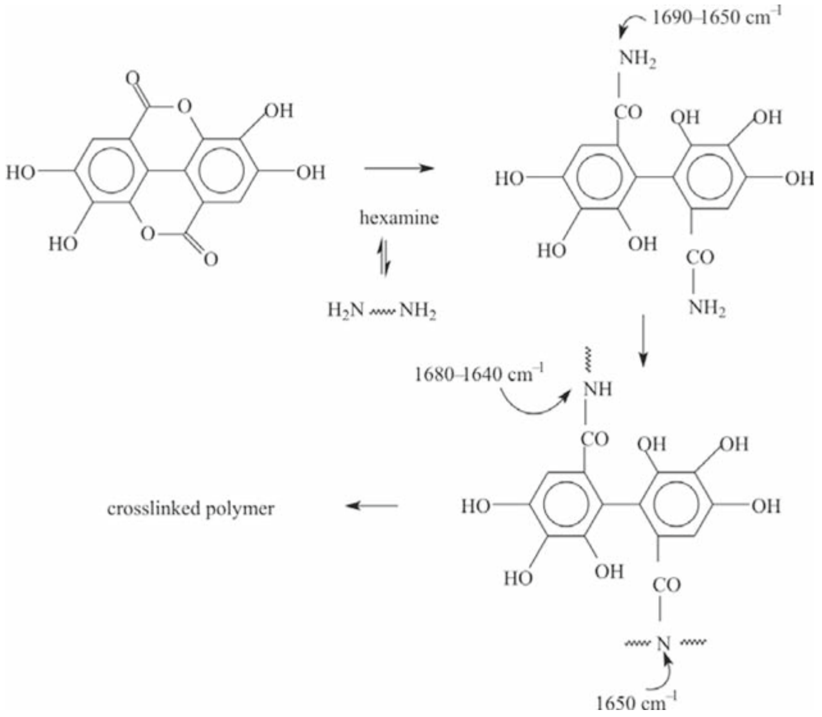


Fig. 9 FTIR spectra for samples from DSC analysis before the first and second exothermic peaks (T_1 and T_2, respectively) of mimosa tannin solutions with hexamine (10 mass/mass%) at several pH (a – pH 2 and 4; b – pH 8)

Then, the analysis of the chemical structures obtained after each exothermic peak it is not possible. For this reason, in the analysis of the resultant chemical structures from the curing reactions of chestnut tannin-hexamine solutions the used samples have been obtained in a bath at isothermal conditions. This analysis allows comparing the chemical structures obtained at each reaction time. In Fig. 10 the obtained spectra for curing reactions at 100°C of chestnut tannin solutions (40 mass/mass%) at pH 4 with hexamine (10 mass/mass%) are presented for several times t_0, t_1 and t_2 (0, 60 and 120 min, respectively). Bands at 1240 and 1007 cm^{-1} of hexamine and the one at 1730 cm^{-1} due to the ester groups of tannin decrease through curing reactions, whereas, the one obtained at 1650 cm^{-1} increases. This band could be attributed to stretching of C=O of the primary (1690–1650 cm^{-1}), secondary (1680–1640 cm^{-1}) or tertiary (1650 cm^{-1}) amide. It can also be observed that after curing reaction (t_2) another band appears at 1410 cm^{-1}, which can be also due to the C–N of primary amide group. In conclusion, it can be proposed that the chemical



Scheme 2 Chemical structures proposed for chestnut–hexamine cured system

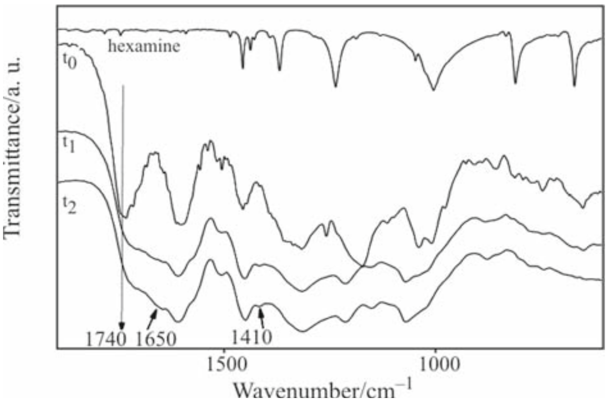


Fig. 10 FTIR spectra of chestnut tannin-hexamine solutions at pH 4 and 100°C at several times. t_0, t_1 and t_2 are the curing reaction times (0, 60 and 120 min, respectively)

structure of products obtained from chestnut–hexamine systems are mainly composed by amide groups with more or less substitution grades, as can be seen in Scheme 2.

Conclusions

In this work, it has been proved that autocondensation reactions occur in mimosa tannin solutions at alkaline pH. Autocondensation reactions can occur at room temperature resulting in an increasing of viscosity. This fact must be considered in adhesive formulation because an important parameter as the pot-life could be seriously modified.

On the other hand, DSC curves of tannin–hexamine systems are influenced not only by curing reactions but also by water presence and degradation reactions. Curing reactions between tannins and hexamine occur almost in two stages. Obtained chemical structures are influenced by both chemical structure of tannin and pH of solution. Currently, work is in progress to analyse the influence of the pH in kinetic parameters of curing reactions between tannin and hexamine.

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