# Synthesis and Characterization of Phenolic Novolacs Modified by Chestnut and Mimosa Tannin Extracts

C. Peña,[1] M. Larrañaga,[1] N. Gabilondo,[1] A. Tejado,[1] J. M. Echeverria,[2] I. Mondragon[1]

[1]Materials and Technologies Group, Escuela Universitaria Politécnica, Departamento Ingeniería Química y Medio Ambiente, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa, 1, 20018 Donostia/San Sebastián, Spain
[2]Bakelite Ibérica S.A., Ctra. Navarra, Epele 39, 20120 Hernani Gipuzkoa, Spain

**ABSTRACT:** The possibility of reacting chestnut and mimosa tannins with the intermediates of the synthesis reaction for phenolic novolacs under acid conditions has been proved using differential scanning calorimetry (DSC). The amount of intermediate compounds and the percentage of free phenol and formaldehyde in the reaction mixture is decisive for the determination of the stage in which the addition of tannin is suitable. Synthesis of novolac resins modified with 14 wt % mimosa tannin extract or with several percentages (until 40 wt %) of chestnut tannin have been performed. The reaction pathways have been investigated by DSC, fourier transformed infrared spectroscopy and gel permeation chromatography. Ester groups of chestnut tannin result in a reaction pathway different from the one for mimosa-modified resins and nonmodified resins. Preliminary studies of curing reactions of synthesized resins with hexamethylenetetramine indicate that the cure of modified-resins is even more favorable than the one for nonmodified resins. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4412–4419, 2006

**Key words:** tannins; differential scanning calorimetry; phenol; formaldehyde; model compounds

## INTRODUCTION

Phenolic resins are the condensation products of phenol and aldehydes, specifically formaldehyde, which are converted to high molecular mass polymers in a secondary curing reaction. These resins exhibit a very wide range of uses.[1] Two classes of phenol–formaldehyde (PF) resins are obtained from the reaction of phenol (P) and formaldehyde (F) under either acidic or alkaline conditions, producing novolac or resol resins respectively.

The phenol and formaldehyde toxicity and the new requirements for increasing recycling and reuse of wastes promoted the use of renewable resources such as wood.[1] Among the possible alternatives, tannin is an excellent renewable resource, which can be used for replacing petroleum-derived phenolic compounds.[2–4]

Tannins have been classified into two different types according to their chemical constituents of mainly phenolic nature: condensed and hydrolysable tannins. Condensed tannins are mainly mixtures of flavonoid and nontannins such as carbohydrates, hydrocolloid gums, and small amino and imino acid fractions. They include wattle or mimosa bark extract (*Acacia mearnsii*), quebracho wood extract (*Shinopsis balansae*), and sumach leaves extract (*Rhus semialata*). Hydrolyzable tannins are mixtures of simple phenols such as pyrogallol and ellagic acid and esters of a sugar, mainly glucose, with gallic and digallic acids. These include chestnut (*Castanea sativa*) and myrabolans (*Terminalia chebula*) extracts. Tang et al.[5] have isolated by chromatography six main fractions of chestnut tannin. In their studies, they showed that major components of chestnut extract are the isomers castalagin, vescalagin, and an unknown fraction. Hydrolyzable tannins from chestnut bark have been successfully used as partial substitutes (up to 50%) of phenol in the manufacture of phenol–formaldehyde resol resins.[6,7]

Sekaran et al.[8] have reported the preparation of novolac phenol–formaldehyde–tannin resins with addition of less than 1 wt % of tannin powder, recovered from waste water, versus phenol, showing potential applications in the paint industry as a good anticorrosive paint, due to its resistance to strong acids, alkalis, and organic solvents.

In this work, we have investigated the possibility of synthesis of novolac resins with tannins by analysis of reactivity with phenol, formaldehyde, and intermediates of the reaction. The influence on synthesis of F/P

molar ratio has also been analyzed. Chestnut and mimosa tannin extracts have been employed for novolac resin modification. Resins obtained have been characterized by several techniques.

## EXPERIMENTAL

### Materials

Commercial powders of mimosa (*Acacia mearnsii*) bark extract and chestnut (*Castanea sativa*) wood extracts were used without purification.

2-Hydroxymethylphenol (2-HMP) (99%), 4-hydroxymethylphenol (4-HMP) (98%), and 4,4′-dihydroxydiphenylmethane (4,4′-DHMP) (97%), commercial products from Sigma, have been used as model compounds to simulate intermediates of synthesis reaction. Phenol (99%), formaldehyde 50% (w/w), and oxalic acid (99%) were provided by Bakelite Ibérica (Spain).

### Resins synthesis

The novolac resins were prepared by polycondensation of phenol with formaldehyde in a F/P mol ratio of 0.45, 0.65, and 0.85 under catalysis by oxalic acid. The reaction mixture was stirred and refluxed for 90 min in the case of phenol–formaldehyde (PF) resins and 60 min in the case of phenol–formaldehyde–tannin (PFT). Water and phenol were stripped off by distillation under vacuum at the end of the synthesis.

For PFT resins, a tannin extract water solution of several concentrations (4, 14, 21, and 40 wt %, and 14 wt % for chestnut and mimosa tannins, respectively), was added when formaldehyde addition was finished. Then, residual water and phenol were removed by distillation as in the previous case.

### Analysis of resins

#### Viscosity

Viscosities of all resins were measured at 150°C according to ISO 3219, with a ICI cone and plate viscosimeter.

#### Free formaldehyde determination

Percentage of free formaldehyde in the resins was determined by the hydroxylamine hydrochloride method (ISO 9397). Approximately 10 g of resin were diluted in methanol, and the pH was adjusted to 3.5 using 1*M* NaOH. 10 ml of hydroxylamine hydrochloride solution were added and the solution was stored for 20 min.

#### Residual phenol

Samples were dissolved in acetone and the level of phenol was determined by gas chromatography using *p*-cresol as an internal standard. Capillary column was 50 m with an interior diameter of 0.2 mm. Helium was used as a carrier gas in the chromatograph.

#### Flow distance

One gram of resin-HMTA (10 wt %) was pressed into a pellet. The flow distance was determined in a metal plate that was preheated to the required temperature (175°C). The pellet was placed on the horizontal metal plate, which was slanted after 1 min to form an angle of 60° with the base plate of the device. The whole device was left in the oven in this position for 20 min. The length of the flow in mm is a measurement for melt viscosity and curing rate.

#### Fourier transformed infrared spectroscopy

The FT-IR spectra of the resins were obtained with a Nicolet spectrometer. The adquisition conditions were 400–4000 cm$^{-1}$ spectral range, 10 scans, and a resolution of 4 cm$^{-1}$. The resin samples were analyzed on KBr pellets.

#### Gel permeation chromatography

Molecular weight distribution of resins was performed using a Perkin–Elmer *S*-250 GPC, equipped with a Perkin–Elmer LC-235 UV detector set at 245 nm and a refractive index detector LC-30 RI. A set of three styrene-divinylbenzene copolymer gel columns of Waters styragel columns, HR 2, HR 4, and HR 5, whose molecular weight range detection is 500–20,000, 5000–50,0000 and 2000–4,000,000, respectively, was employed at 35°C. The mobile phase was tetrahydrofurane (THF, HPLC grade) at a flow rate of 1 mL min$^{-1}$. The calibration was performed with narrow molecular weight monodisperse polystyrene standards. Therefore, molecular weight should only be considered as a relative value. For analysis, samples were dissolved in THF at a concentration of 0.1 mg mL$^{-1}$.

#### Thermal analysis

Thermal analysis was carried out with a Mettler DSC20 differential scanning calorimeter (DSC) linked to a TC 15 TA Processor. A 2–6-mg sample was sealed in a medium pressure capsule pan that could withstand up to 20 bars. The capsule containing the sample and the reference capsule were transferred to the DSC sample holder assembly that had been set at 25°C. A scanning temperature range from 25 to 280°C was

employed for thermal characterization. The sample crucibles were heated at 10°C min$^{-1}$.

### Gelation time

The gel time of resins was determined using a Coesfeld material test. Each resin (1.5 g) was placed into the grooves at 150°C and the time for the formation of gel was determined.

### RESULTS

**Analysis of reactivity of tannin-modified novolacs**

Phenol, formaldehyde and intermediates of reaction are present during the synthesis of phenolic resins. Hence, before synthesis of novolac resins, an analysis of reactivity of chestnut and mimosa extract tannins with several compounds present in synthesis of phenolic resins has been performed. Reactivity of polyphenols with formaldehyde has been evaluated many years ago by Hillis and Urbach.[9] More recently, several authors have also proved that tannin reacts with formaldehyde.[10–14] On the other hand, Pethrick and Thomson[15] have confirmed by ^{13}C NMR that monomers (2-HMP and 4-HMP) and dimer (4,4'-DHMP) are present during phenolic resins synthesis. Thereby, differential scanning calorimetry has been used to evaluate the reactivity of monomer, dimer (2-HMP, 4,4'-DHMP, respectively), and phenol with chestnut and mimosa extract tannins.

Thermograms obtained for the 2-HMP model compound mixed with tannins are shown in Figure 1(a). Endothermic peak at 87°C corresponds to the melting of the model compound. For reproduction of the conditions present in the synthesis of PFT resins, all samples were prepared by adding to the model compound a 30 wt % solution in water of tannin extracts (40 wt %) and oxalic acid (1 wt %). Thermograms obtained when tannins were added to 2-HMP present an exothermic peak at 110°C, which is not present when the model compound was dissolved in water. Hence it is evident from calorimetric analysis that tannins can react with 2-HMP. Moreover, tannins present more nucleofility in A-ring forward electrophilic compounds than in phenol because of the ring substituents. This fact has been proved by adding phenol to 2-HMP in the same conditions as that for the tannin extracts [Fig. 1(a)]. The peak in phenol-2-HMP system is present at a higher temperature than that of chestnut and mimosa tannin extracts with the model compound (135 versus 110°C, respectively). Then, reactivity of tannins with the model compounds used for intermediates simulation seems to be higher than that of phenol.

A similar analysis has been performed for mimosa and chestnut tannins with phenol [Fig. 3(b)]. Thermograms reveal exothermic peaks that occur at lower
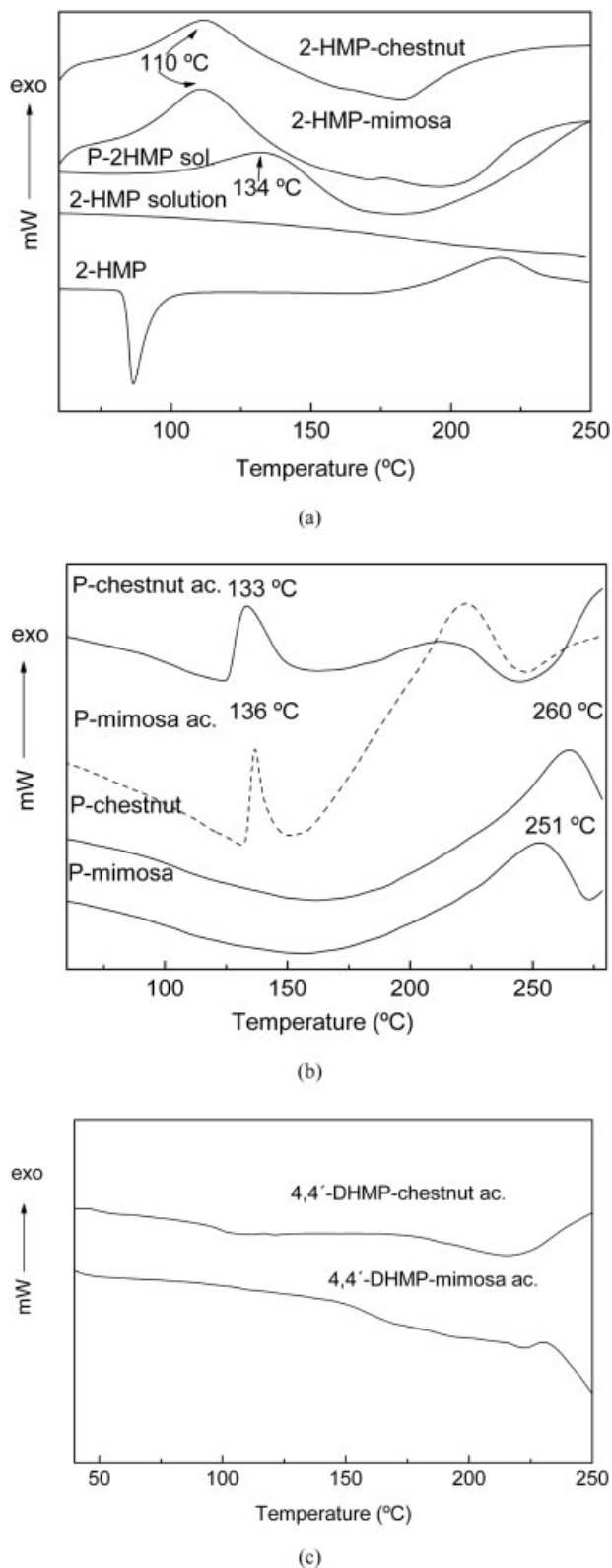


**Figure 1** DSC thermograms of systems based on several model compounds with chestnut and mimosa tannin extracts. (a) 2-HMP, (b) P, and (c) 4,4'-DHMP.

temperatures when oxalic acid is present (around 133 and 225°C as opposed to 250°C without oxalic acid). These results could indicate that acidic conditions pro-

mote reactions between tannins and phenol. Some authors have employed phenolation reaction for improving the properties of tannin-based adhesives. As suggested by Santana et al.,[16] it is possible that tannin phenolation is the result of acid catalyzed cleavage of the interflavonoid bond. This can lead to the opening of the ring containing oxygen with the formation of a carbocation, which can be captured by a nucleophilic compound such as phenol. Thus, the acid catalysis of this reaction has been confirmed in this work.

The possibility of reactions between 4,4′-DHMP and mimosa and chestnut tannin have also been analyzed by DSC. Thermograms obtained for mimosa and chestnut are shown in Figure 3(c). It is clear that tannin presence does not promote any significant reaction with the dimer. Thus, we can conclude that dimer does not react with mimosa or chestnut probably due to the absence of reactive groups in DHMP as they exist in monomer (HMP) case.

As a consequence, tannin could react with free phenol and formaldehyde but also with the first monomeric intermediates in the synthesis of PFT resins. If these reactions occur before condensation is finished, tannin will be into the novolac chain. For the analysis of the best step for tannin addition, some resins with 0.65 F/P ratio were synthesized by adding at 100°C the tannin solutions at different stages of reaction: a (before formaldehyde addition), b (after formaldehyde addition) or c (after condensation). For both tannins, in the a stage, the reaction mixture composition was formed by free phenol and formaldehyde, and a small amount of intermediates (2-HMP, 4-HMP). When tannin was added at this stage, an insoluble product was formed in the reaction mixture. This fact could be due to the high reactivity of tannin with phenol and formaldehyde at the reaction conditions (pH 2.2–2.5, 100°C). In the same stage, even without formaldehyde addition, tannin reacted for the formation of an insoluble material. Thus, the reaction conditions do not permit the addition of tannin after phenol and formaldehyde mixing. Reduction of temperature to 60°C or addition of tannin drop wise does not prevent the solid formation.

The addition of tannin in c step resulted in the formation of a solid in the reactor in the distillation stage. At this moment, the intermediates of reaction had disappeared and the mixture of reaction was composed by free phenol (6%), free formaldehyde (0.75%), dimers, trimers, etc. Solubility analysis allowed to conclude that the solid formed is soluble in water. This fact could be attributed to the lower presence of reactivity species (P, F, monomers) and the impossibility of reaction between tannin and novolac chain. The solid formed could be due to almost two factors. First, the reduction of water in synthesis by distillation and the consequent precipitation of tannin, and the second one, the reaction of acid autocondensation that has

### TABLE I
### Free Phenol and Formaldehyde Obtained at Different Times before Formaldehyde Addition for Nonmodified Resins with 0.45, 0.65, and 0.85 F/P Ratios

| F/P molar ratio | t (min) | % P | % F |
|---|---|---|---|
| 0.40 | 5 | 31.8 | 0.95 |
|  | 20 | 31.9 | 0.11 |
|  | 45 | 31.2 | 0.09 |
|  | 70 | 31.3 | 0.03 |
| 0.65 | 20 | 15.7 | 2.0 |
|  | 30 | 14.9 | 1.6 |
|  | 50 | 13.8 | 1.0 |
|  | 60 | 12.5 | 0.3 |
| 0.85 | 10 | 10.0 | 3.7 |
|  | 40 | 8.4 | 2.9 |
|  | 55 | 8.2 | 2.6 |
|  | 70 | 7.4 | 1.1 |

been described in the literature survey.[11–17] After all, the addition of tannin in stage c does not result in a novolac modified resin because of the lower presence of reactive species (monomer, P, F).

The addition of tannin in b stage did not form insoluble products. Reaction mixture at this moment was composed by free phenol (100%), free formaldehyde (3.7%), water and intermediates (2-HMP, 4-HMP, etc.). The reaction mixture presents optimal conditions for addition because tannin can react with intermediates and formaldehyde giving to the formation of methylene bridges discussed earlier. Although reaction with phenol is also possible, this probably was not the main reaction because the tannin reactivity toward formaldehyde and intermediates is higher due to their electrophility and to the strong nucleophility of the ring of flavonoid.

To elucidate the limits of F/P ratio for synthesis of novolac resins modified with tannin, analysis of free P (by gas chromatography) and F (by the hydroxylamine hydrochloride method) at different times before the second formaldehyde addition (stage b) has been performed for three nonmodified resins with 0.45, 0.65, and 0.85 F/P ratio (Table I). As can be seen, when F/P ratio increases free phenol decreases and formaldehyde increases in good accord with the expected results. Next, resins with the same F/P ratios and with addition of chestnut and mimosa tannin extract solutions have been prepared. When 0.45 F/P ratio was employed, the products of reaction were insoluble in the synthesis mixture. Then, we can conclude that when the amount of free phenol is high phenolation reactions hinder reactions with intermediate species or, in other words, when the proportion of formaldehyde is low, tannin addition to ring reactions doesn't seem to be possible.

## Synthesis and characterization of resins

Resins with different F/P molar ratios containing commercial mimosa or chestnut tannins added in stage *b* have been synthesized using oxalic acid catalyst. Reference or nonmodified resins have also been synthesized. For all novolacs the free phenol levels were reduced by distillation in vacuum to below 0.2%. Technical specifications for resins with 0.65 F/P molar ratio are given in Table II. GPC analysis is also usually performed for the characterization of novolac resins. Figure 2 shows the chromatograms obtained for nonmodified and chestnut- and mimosa-modified resins. As can be seen, chromatograms obtained for resins modified with mimosa and chestnut tannin are similar not only to the ones obtained for synthesized reference resins but also to those obtained by Solomon and coworkers.[18]
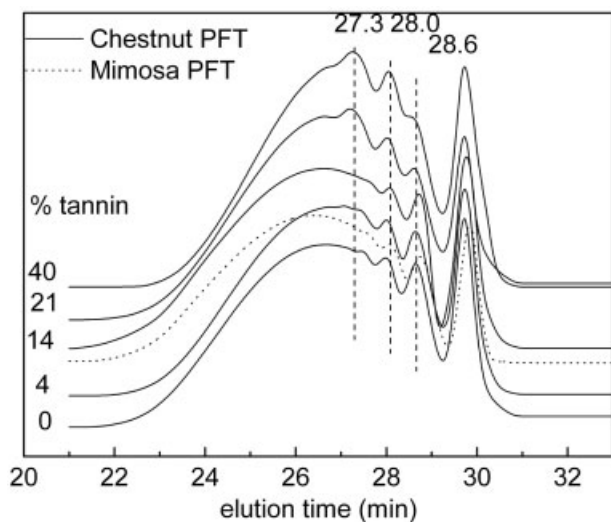


**Figure 2** GPC chromatograms of nonmodified and chestnut and mimosa modified resins.

### TABLE III
### Elution Times Obtained from GPC Chromatograms for Model Compounds

| Compound | Elution time (min) |
|---|---|
| P | 31.9 |
| 2-HMP | 31.1 |
| 4-HMP | 30.6 |
| 4.4-DMP | 29.6 |

Table III shows the times of peaks present in chromatograms of P, monomers 2-HMP, 4-HMP and dimer 4,4'-DHMP. From Figure 2 and Table III we can conclude that the smaller molecule present in resins is dimer (29.6 min) as Podzimek and Hrock[19] have previously shown. Other peaks present in chromatograms of resins at 28.6, 28, and 27.3 min must be attributed to trimer and other molecules with higher molecular mass. It is also clear that peaks which must be attributed to molecules with higher molecular weights increase when tannin content increases and the peak at 28.6 min decreases. In Table IV the average (number $\bar{M}_n$, weight $\bar{M}_w$, and viscosity $\bar{M}_z$) molecular mass of resins are shown toward tannin extract content calculated with polystyrene standards. Resin modified with 14 wt % mimosa tannin extract presents a molecular weight slightly higher than the one obtained for the resin modified with the same content of chestnut tannin. As can be seen, the average molecular weight slightly increases until 14 wt % of chestnut tannin content in resins and decreases over this content. This result could be explained because resins have been synthesized with the same F/P molar ratio but the presence of other phenolic molecules (polyphenolic molecules of tannin extract) reduces the F/P molar ratio. It is known that when F/P molar ratio decreases, molecular weight of novolac resins decreases.[1] Thereby, when tannin content is higher than 14%, variations in F/P molar ratio must also be considered.

### TABLE IV
### $M_n$, $M_w$, and $M_z$ of Nonmodified and Modified Resins with 4, 14, 21, and 40 wt % of Chestnut Tannin and 14 wt % of Mimosa Tannin Extracts

| % Tannin extract | $M_n$ | $M_z$ | $\bar{M}_w$ |
|---|---|---|---|
| 0 | 817 | 1498 | 2595 |
| Chestnut |  |  |  |
| 4 | 820 | 1500 | 2600 |
| 14 | 866 | 1613 | 2828 |
| 21 | 827 | 1427 | 2359 |
| 40 | 749 | 1229 | 1933 |
| Mimosa |  |  |  |
| 14 | 1012 | 1832 | 3116 |
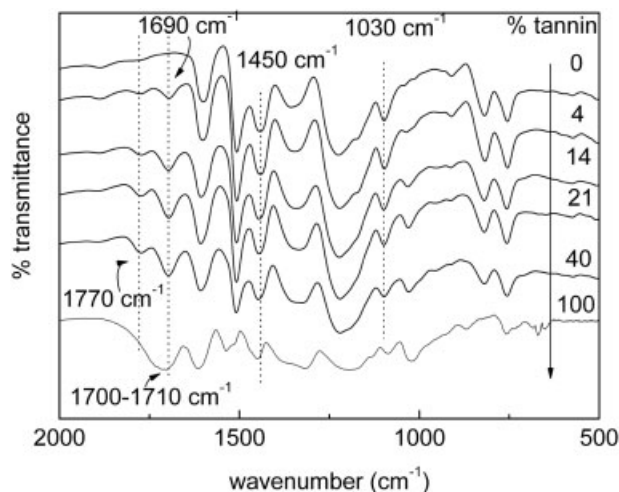
**Figure 3** FT-IR spectra of nonmodified resins (0%), chestnut modified resins (4, 14, 21, and 40 wt·%) and chestnut tannin extract (100%).



**Figure 4** Reaction mechanism proposed for synthesis of novolac resins modified with chestnut tannin.

To check the presence of reacted tannin in resins, solubility analysis and infrared spectra (FT-IR) have been performed. For solubility analysis, water was chosen because it is the best solvent for tannins. When water was added to the final resins, not one fraction of tannin was dissolved. This confirms that chestnut and mimosa reacted. Spectra of nonmodified (0%), and also of chestnut tannin modified resins with 4, 14, 21, and 40 wt % with respect to phenol at F/P 0.65 and chestnut tannin extract (100%) are shown in Figure 3. Chestnut presence is confirmed by the appearance of new bands at 1770, 1690, and 1030 cm$^{-1}$, associated to carbonyl stretching vibration of ester groups linked to bisphenol A units, carbonyl stretching vibration of acid groups linked to aromatic compounds and to the in-plane deformation vibrations of the ring hydrogen atoms of phenolic resins, respectively. These bands must be attributed to the reacted chestnut presence in resins because they are not present in reference resin spectra (0%). Moreover, these bands are not exactly the same as the ones for chestnut tannin extract. Differences are evident in Figure 3, in which chestnut tannin extract is shown. It is noteworthy that chestnut tannin presents a band associated to the carbonyl stretching vibration of ester groups linked to methylene at 1710 cm$^{-1}$ (Fig. 4) and other one for the modified resin ester group must be linked to an aromatic ring appearing at 1770 cm$^{-1}$. In the modified resin, it is also clear that the presence of a band at 1690 cm$^{-1}$ can be due to the presence of acid groups in the resin (Fig. 4). Thus, the formation of acid groups in synthesis must be considered. These groups could be attributed to the hydrolysis of ester groups by heat and acidic conditions of the reaction.[5]
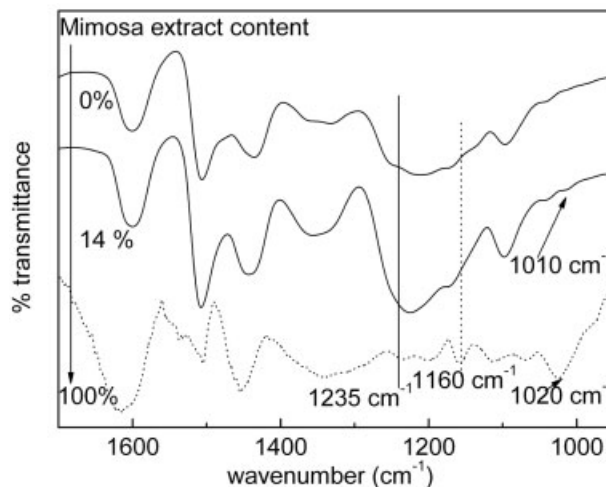
In Figure 5, the IR spectra of the mimosa tannin extract (100%), mimosa-modified novolac (14 wt %),
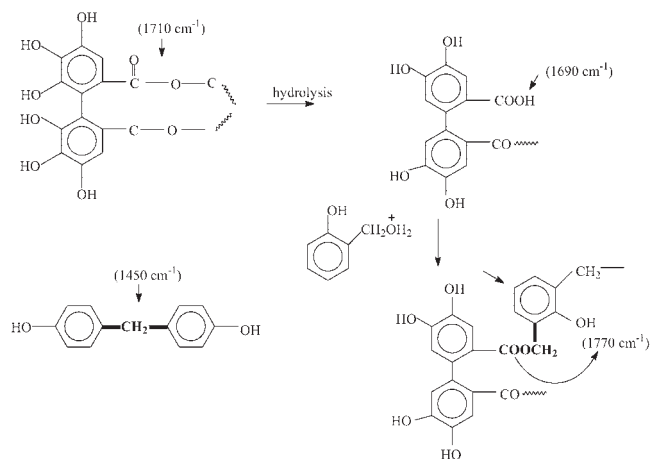
and of the nonmodified novolac are shown. In mimosa tannin spectra, the presence of bands at 1235 and 1160 cm$^{-1}$ produced by aromatic C—O bond stretching and other at 1020 cm$^{-1}$ for aliphatic C—O band stretching appear to be clear. The band at 1235 cm$^{-1}$ is characteristic of the cyclic nature of ether. From mimosa-modified resin, the presence of a small band at 1010 cm$^{-1}$ which is not present in the nonmodified novolac spectra could indicate that some ether bonds different from the one in mimosa tannin extract could be present in the modified resin. This new band could be explained because during synthesis, some opening of the cyclic ether structures could occur with the consequent formation of a carbocation which could react with formaldehyde forming a new ether bond (Fig. 6).

Table II shows glass transition temperatures ($T_g$) measured by DSC for all the synthesized resins. For



**Figure 5** FT-IR spectra of reference novolac, mimosa modified resin (14 wt %), and mimosa tannin extract.

the determination several heat treatments have been performed. First, a dynamic scan between 25 and 120°C range at 10°C min$^{-1}$ and an isothermal treatment during 10 min at 125°C were performed to remove the thermal history of the materials. Next, a second dynamic scan from 30 to 100°C has been carried out. From this scan $T_g$ was obtained. From the results it is clear that when tannin amount increases, $T_g$ values increased. The same behavior is observed for viscosity and softening temperature. These results can be explained by looking into the resins modified with chestnut as a chain of aromatic rings which increases rigidity and polarity because of the ring–ring bridges (reference resins only contain methylene bridges) and acid groups, respectively. On the other hand, the presence of ester bridges and their flexibility in chestnut-modified resins is another factor which could be responsible of the small reduction of $T_g$ of the modified resins with 4 and 14% of tannin extract with respect to the nonmodified resin.

Thermal behavior of PFT resins cured with hexamine has also been investigated. Figure 7 shows the thermograms obtained for chestnut-modified novolacs with different amounts of chestnut tannin. As tannin amount increases in resins, cure reactions occur at lower temperatures than the ones obtained for nonmodified novolacs. On the other hand, gelation time and flow distance values (Table II) decrease with increasing chestnut content in resins. These results could verify that resins modified with chestnut tannin react with hexamine more easily than conventional PF novolacs. This conclusion is in good agreement with results obtained for resols by Kulvik,[6,7] who observed that the gelation times of alkaline phenol–formaldehyde resins decreased with increasing chestnut wood tannin extract replacement. Currently, work is in progress to determine the final properties of the cured resins modified with tannins.
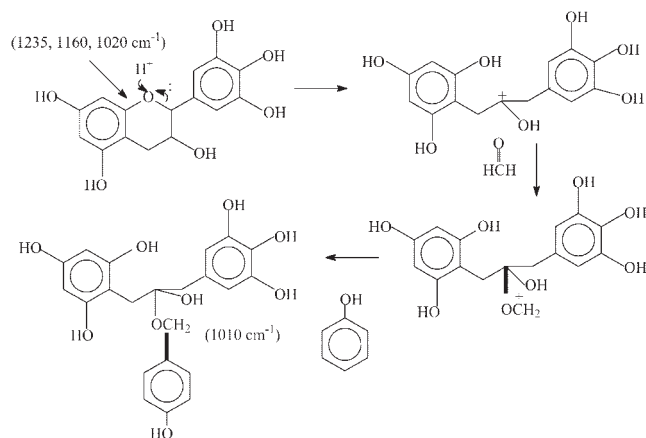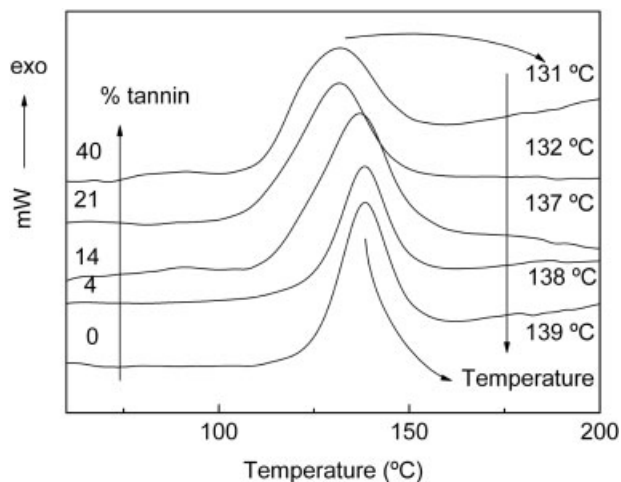
**Figure 7** DSC thermograms for synthesized resins (modified with several amounts of chestnut tannin and nonmodified) with 10 wt % hexamine.

## CONCLUSIONS

The possibility of synthesis of novolac resins modified with chestnut and mimosa tannins extracts has been analyzed. Reactions between mimosa or chestnut tannins with monomer (HMP), P, and F have been proved. A more suitable stage for adding tannin is immediately after addition of formaldehyde because the presence of intermediates of reaction appears to be the optimal. Novolac resins modified with these tannin extracts have been obtained using a similar process to the one used for traditional novolacs.

Modification of resins with high amount of chestnut tannin (until 40 wt % respect to P) results in new resins, with relatively similar specifications to those for original novolacs, which react with hexamine at lower temperature than novolac resins. Mimosa tannin resins obtained presented a high viscosity, when a low amount of extract was added. The presence of ester groups in chestnut tannin results in a reaction mechanism different from the one for mimosa modified resin and nonmodified resins.

Currently, more work is being carried out to determine the final properties of these novolacs modified with tannins cured with hexamine.

## References

1. Gardziella, A.; Pilato, L. A.; Knop, A. Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology; Springer-Verlag: Berlin, 1999.
2. Kims, S.; Lee, Y.; Kim, H. J Adhes Sci Technol 2003, 17, 1863.
3. Pizzi, A.; Scharfetter, H. O. J Appl Polym Sci 1978, 22, 1745.
4. Pizzi, A. Wood Adhesives. Chemistry and Technology; Marcel Dekker: New York, 1983.
5. Tang, H. R.; Hancock, R. A.; Covington, A. D. In Plant Polyphenols; Hemingway, R. W., Laks, P. E., Eds.; Plenum: New York, 1992.

**Figure 6** Synthesis scheme of modified resin with mimosa.

6. Kulvik, E. Adhes Age 1976, 19, 19.
7. Kulvik, E. Adhes Age 1977, 20, 33.
8. Sekaran, G.; Thamizharasi, S.; Ramasami, T. J Appl Polym Sci 2001, 81, 1567.
9. Hillis, W. E.; Urbach, G. J Appl Chem 1959, 9, 665.
10. Mitsunaga, T.; Conner, A. H.; Hill, C. G. J Appl Polym Sci 2002, 86, 135.
11. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1994, 51, 2109.
12. Pizzi, A.; Stephanou, A. Holzforschung Holzverwertung 1993, 2, 30.
13. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1993, 50, 2105.
14. Fechtal, M.; Rield, B.; Calve, L. Holzforschung 1993, 47, 419.
15. Pethrick, R. A.; Thomson, B. Br Polym J 1986, 18, 380.
16. Santana, M. A. A.; Marcos, A. E.; Baumann, M. G. D.; Conner, A. H. J Wood Chem Technol 1996, 16, 1.
17. Masson, E.; Merlin, A.; Pizzi, A. J Appl Polym Sci 1996, 60, 263.
18. Dargaville, R.; Guerzoni, F. N.; Looney, M. G.; Solomon, D. H.; Zhang, X. J Polym Sci Part A: Polym Chem 1997, 35, 1399.
19. Podzimek, S.; Hrock, L. J Appl Polym Sci 1993, 47, 2005.