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Sumin Kim & Hyun-Joong Kim

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Curing behavior and viscoelastic properties of pine and wattle tannin-based adhesives studied by dynamic mechanical thermal analysis and FT-IR-ATR spectroscopy

SUMIN KIM and HYUN-JOONG KIM *

*Laboratory of Adhesion and Bio-Composites, Department of Forest Products,
Seoul National University, Suwon 441-744, South Korea*

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Abstract—This study investigated the curing behavior and viscoelastic properties of two types of tannin-based adhesives, wattle and pine, with three hardeners: paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxymethyl)nitromethane), by FT-IR-ATR spectroscopy and dynamic mechanical thermal analysis (DMTA). Using FT-IR-ATR spectroscopy, the chemical structures of tannin-based adhesives were determined and the degrees of curing as a function of temperature and time were compared with the conversion degrees of the hydroxyl groups. Paraformaldehyde was shown to be more reactive with wattle tannin than the other hardeners, while hexamethylenetetramine was the most reactive with the pine tannin. As the quantity of hardener was increased, the conversion degree also increased. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of each adhesive system were obtained by DMTA. With increasing temperature, as the tannin-based adhesives hardened, the storage modulus (E') increased in all adhesive systems. The curing behavior results obtained by DMTA showed a similar tendency as seen from the FT-IR-ATR spectroscopy results. The curing behavior of the tannin-based adhesives was successfully determined using FT-IR-ATR spectroscopy in combination with DMTA.

Keywords: Wattle tannin; pine tannin; hardener; FT-IR-ATR spectroscopy; dynamic mechanical thermal analysis; curing behavior; viscoelastic properties.

1. INTRODUCTION

Following the oil crisis in the early 1970s, increasing oil prices and the high energy requirements for the production of synthetic polymers prompted the use of renewable resources, such as wood, tree bark, nut shells, etc., in material applications rather than in energy production. A rise in the price of oil and

*To whom correspondence should be addressed. Phone: (82-31) 290-2601. Fax: (82-31) 293-9376.
E-mail: hjokim@snu.ac.kr

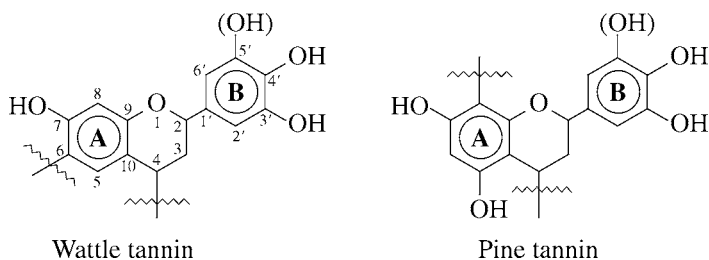


Figure 1. Chemical structures of wattle and pine tannins.

decreasing fuel energy led to the development of replacement materials from natural resources for petroleum-derived phenolic compounds in the wood-adhesive industries [1].

Tannin is an excellent renewable resource for replacing petroleum-derived phenolic compounds. The major wood species from which it can be obtained are mimosa, quebracho and radiata pine. It is mainly concentrated in the inner layer of the bark and has been utilized in the adhesives industry in Africa, South America and Oceania [2, 3]. In particular, tannin-based wood adhesives have been used industrially for quite a long time in several countries for the manufacture of exterior wood panels [4]. There are two different types of tannin: wattle tannin composed of resorcinol A-rings and pine tannin composed of phloroglucinol A-rings with catechol or pyrogallol B-rings, as shown in Fig. 1 [5]. The free C6 or C8 sites on the A-ring react with formaldehyde, due to their strong nucleophilicity, to form the adhesive. The phenolic nuclei in tannins also react with formaldehyde. This high reactivity of tannins towards formaldehyde is the result of their A-ring phloroglucinolic or resorcinolic nuclei, which have 10- to 50-times higher rate of reaction than the reaction of phenol with formaldehyde. Because of this characteristic, less free formaldehyde emission occurs than from other wood adhesives such as phenol-formaldehyde, urea-formaldehyde, etc. [6].

Several studies have been done on the hardening, mechanisms of tannins with hardeners, such as paraformaldehyde, hexamethylenetetramine and MDI (methylene diphenyl diisocyanate), based on ^{13}C -NMR [2, 6–10] analysis and on their mechanical properties [10–15] when used as a wood adhesive. These results mainly involved analysis made after the adhesive had been cured.

FT-IR spectroscopy is a powerful analytical method for monitoring the curing process. It offers a unique capability in terms of its rapid and quantitative measurement of the conversion of a specific functional group [16]. Valuable qualitative and semi-quantitative information, for example, on the type of reaction, can be obtained from IR studies. In particular, the appearance of the hydroxyl group, methylol group and dimethylene ether bridges can be easily monitored [17].

The dynamic mechanical technique involving application of a sinusoidally oscillating stress to a material and the analysis of the resultant strain is now widely practiced as a polymer characterization technique. It has far greater sensitivity to both macroscopic and molecular relaxation processes than thermal analysis techniques

based on a temperature probe alone. It is the viscous or time-dependent behavior of polymers that makes dynamic mechanical testing such a useful characterization technique. One of the most common uses of dynamic mechanical testing is the determination of the glass transition temperature (T_g) of a sample. Another important application area for dynamic mechanical thermal analysis (DMTA) is in monitoring the curing of resins. DMTA is very sensitive to the curing process and isothermal experiments enable the development of an ideal curing schedule [18].

This study focused on two main areas. Firstly, the curing behavior of tannin-based adhesives, wattle and pine, with three hardeners (paraformaldehyde, hexamethylenetetramine and tris(hydroxymethyl)nitromethane) during the curing process was investigated. A method was devised to study the curing of tannin-based adhesives using FT-IR-ATR spectroscopy in combination with dynamic mechanical thermal analysis. Secondly, the viscoelastic properties of the tannin-based adhesives, used as a thermosetting adhesive, were measured by DMTA.

2. EXPERIMENTAL

2.1. Materials and sample preparation

2.1.1. Tannin extracts. Two types of commercial tannin extracts, wattle and pine, were prepared. The wattle (*Acacia mearnsii*, mimosa) was supplied by Bondtite Co. Ltd. in Australia and the pine (*Pinus radiata*, radiata pine) was supplied by DITECO Ltd. in Chile. These tannins consisted of a fine dark brown powder with a moisture content of 4%.

2.1.2. Hardeners. The three hardeners, paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxymethyl)nitromethane), were purchased from Aldrich Chemical Company.

2.1.3. Tannin-based adhesives. Aqueous tannin extracts with 40% concentration were prepared by dissolving the spray-dried powder of each tannin extract in water. To these solutions, 6.5, 8 or 10 wt% of each hardener based on dry tannin extract were added. Each additive concentration was based on several results [4, 7, 11]. The pH ranged from 5.5 to 6. While paraformaldehyde and TN (tris(hydroxymethyl)nitromethane) were used in pure solid state, hexamethylenetetramine was used as a 35% solution [7].

For the determination and comparison of the effect of hardener content, paraformaldehyde for wattle and hexamethylenetetramine for pine were selected. 0, 4, 8 or 12 wt% of paraformaldehyde, based on dry tannin extract, were used for the wattle tannin, and 0, 3, 6.5 or 10 wt% of hexamethylenetetramine for the pine tannin. The final composition of the adhesive systems used is shown in Table 1.

Table 1.
Adhesive formulations showing amounts (by wt%) of different hardeners

	Wattle tannin	Pine tannin
Paraformaldehyde	0 (wattle only)	8
	4	
	8	
	12	
Hexamethylenetetramine	6.5	0 (pine only)
		3
		6.5
		10
TN	10	10
(Tris(hydroxymethyl)nitromethane)		

2.2. Methods

2.2.1. *FT-IR-ATR spectroscopy.* FT-IR spectroscopy analysis was carried out on a Bio-Rad FTS-60 FT-IR spectrophotometer at a resolution of 4 cm⁻¹, in the mid-infrared range from 4000 to 600 cm⁻¹ in the absorbance mode for resin characterization during the curing process. To obtain samples for FT-IR spectroscopy analysis, each adhesive system was cured in an oven at 160, 170, 180 or 190°C for 1, 2, 3, 5, 7, 10 or 20 min. As the samples were still in the liquid phase after 1 or 2 min, while they were already in the brittle solid state after 10 or 20 min, the FT-IR spectra were obtained for these different types of samples using a Bio-Rad UMA-250 FT-IR spectrometer equipped with a Spectra Tech ATR adapter. The ATR adapter had a penetration depth of approximately 1 μm and allowed the spectra to be acquired directly from the cured samples.

2.2.2. *Dynamic mechanical thermal analysis (DMTA).* The viscoelastic properties of each sample were determined from 40°C to 200°C at a heating rate of 5°C/min using a dynamic mechanical thermal analyzer (DMTA; Rheometric Scientific DMTA MARK IV, in NICEM of Seoul National University). As they were in the viscous liquid state, so to obtain the DMTA samples, the tannin-based adhesives were placed between two layers of beech wood veneer of 0.6-mm thickness as shown in Fig. 2, and a three-point bending mode was applied. The adhesive thickness was 0.2 mm and the total tested sample dimensions were 28 × 5 × 1.4 (mm). During the DMTA experiments, the static force was kept at 20% of the dynamic force and the frequency was maintained at 1 Hz with a strain of 0.05.

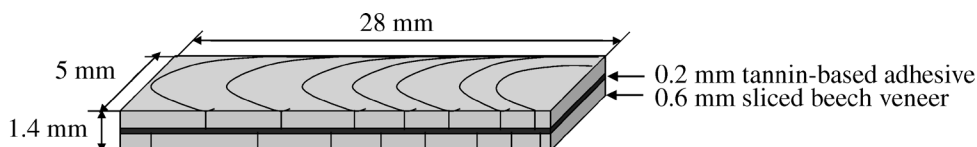


Figure 2. Sample configuration for the DMTA (three-point bending mode) test.

3. RESULTS AND DISCUSSION

3.1. FT-IR-ATR spectroscopy

3.1.1. Reactions of tannin-based adhesives with hardeners. The formation of a tannin-based adhesive is based on the reaction between the tannin and formaldehyde (hardener). Polyphenolic tannins can react with formaldehyde, even at normal temperatures, to yield condensation products with high adhesion potential. However, the reactivity of the different tannins varies considerably [3].

The curing behaviors and chemical reactions of the tannin resins with three hardeners (paraformaldehyde, hexamethylenetetramine and TN) were investigated at various curing temperatures (160, 170, 180 and 190°C) by an *in situ* method using FT-IR-ATR spectroscopy. Figure 3 shows the spectra at 170°C of a wattle tannin-based adhesive with paraformaldehyde and a pine tannin-based adhesive with hexamethylenetetramine. Since a tannin-based adhesive with paraformaldehyde hardener system is to replace phenol–formaldehyde adhesive, it tends to perform like a phenol–formaldehyde adhesive [2, 5].

The broad peak in the region 3000–3700 cm^{-1} is characteristic of the —OH stretchings of the benzene nucleus and of the methylol group of tannin. The small peaks in the region 2700–2800 cm^{-1} are associated with the —CH stretchings of the benzene nucleus, the methylene ($\text{—CH}_2\text{—}$) and dimethylene ether ($\text{—CH}_2\text{OCH}_2\text{—}$) bridges of the tannin-based adhesive, and the methylene unit ($\text{—CH}_2\text{—}$) of each hardener. It has been demonstrated that a large number of methylene ether bridges ($\text{—CH}_2\text{OCH}_2\text{—}$) occur, which rearrange themselves with relative ease to form methylene ($\text{—CH}_2\text{—}$) bridges with the release of formaldehyde [19]. The signal at 1605 cm^{-1} is characteristic of the elongation of the aromatic double bond (C=C) of the benzene nucleus. The peak at around 1200 cm^{-1} is associated with the —CO stretchings of the benzene nucleus and the dimethylene ether bridges formed by reaction with the hardeners. The deformation vibrations of the C—H bond in the benzene rings give absorption bands in the 740–910 cm^{-1} range. This group disappears during the process of polymerization; therefore, its concentration can be used as an index of the degree of polymerization. The deformation vibration of the carbon-carbon bonds in the phenolic groups absorbs in the region of 1400–1500 cm^{-1} . This group does not participate in any chemical reaction during the polymerization. However, this peak showed a gradual decrease as the process of polymerization progressed, because when the reaction takes place, the volume of the system contracts [20, 21]. Generally, wattle tannin is known to have a lower degree of polymerization and a lower number of C4–C8 interflavonoid linkages

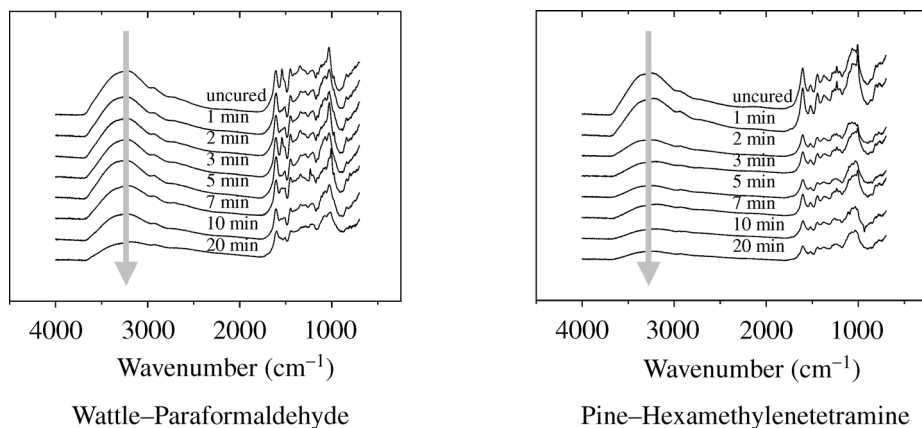


Figure 3. FT-IR ATR spectra for wattle-based tannin with paraformaldehyde and pine-based tannin with hexamethylenetetramine for various curing times at 170°C.

than pine tannin [2]. This explains why, as shown in Fig. 3, the wattle tannin-based adhesive showed a lower C—C stretching peak at 1606 cm^{-1} than the pine tannin-based adhesive.

According to the literature [7], the pine tannin-based adhesive in the presence of hexamethylenetetramine produces not only methylene bridges but also a very high proportion of benzylamine bridges during the process of cross-linking, because hexamethylenetetramine is in equilibrium (hexamethylenetetramine \leftrightarrow formaldehyde + ammonia) in the solution. This was investigated by ^{13}C -NMR analysis at a curing temperature of 100°C [7]. However, the N—H wagging peak in the 700–750 cm^{-1} range [22] could not be recognized and the N—H stretch peak in the 3280–3320 cm^{-1} range overlapped with the —OH peaks around 3000–3700 cm^{-1} . This can be explained by the curing temperature being above 160°C, at which point the benzylamine bridges are known to start to rearrange themselves to form methylene bridges [6].

3.1.2. Curing conversion. Based on above findings, the most important reaction is the condensation of hydroxyl groups (—OH) with the unreacted active positions of other phenolic rings. The —OH peaks in the region of 3000–3700 cm^{-1} , where the hydroxyl stretching vibration can be observed, decreased with increasing curing time at all test temperatures. These peaks eventually almost disappeared in the case of pine tannin with paraformaldehyde and hexamethylenetetramine after 20 min. This is attributed to the wide distribution of the hydrogen-bonded hydroxyl groups, whereas a low band is observed at low curing temperature, which corresponds to free hydroxyl groups. As the temperature increased, the relative absorption of the free hydroxyl groups increased, while that of the hydrogen-bonded hydroxyl groups decreased [23, 24]. This behavior was attributed to the hydroxyl group in tannin, because the peak of the hydroxyl group in tannin was smaller due to internal reactions which caused the tannin to link together. Molecules of the tannin

prepolymer, formed from the reaction of tannin with formaldehyde, are cross-linked with each other, with the elimination of H_2O , due to heating.

The degree of conversion (α) was determined from the ratio of the peak areas of phenolic OH after a certain curing time to that of the non-baked phenolic OH ($3000\text{--}3700\text{ cm}^{-1}$) in the spectra as:

$$A_t/A_{(0)} = 1 - \alpha, \quad (1)$$

where A_t is the peak area of phenolic OH ($3000\text{--}3700\text{ cm}^{-1}$) at a given curing time and $A_{(0)}$ is the peak area of phenolic OH in the non-baked sample [25].

A comparison of the degree of conversion behaviors for wattle tannin-based adhesive with the three hardeners, obtained from isothermal analysis at different curing temperatures, is shown in Fig. 4. Higher conversion was associated with increased curing, for all hardeners, and the degree of conversion increased with increasing temperature and curing time. The same behavior was also observed in the case of pine tannin. As shown in Fig. 4, the wattle tannin-based adhesive shows the highest degree of conversion with paraformaldehyde, as compared to other hardeners, especially at the highest curing temperature of 190°C . The conversion at 190°C for 20 min was 0.9, while the conversion at 160°C was 0.6. This shows the temperature-sensitivity of wattle-tannin adhesive with paraformaldehyde. Generally, when higher pressures and temperatures are employed, particleboards manufactured demonstrate superior mechanical properties [13]. As shown in Fig. 4, the conversions of wattle tannin-based adhesive with hexamethylenetetramine and TN were lower than those with paraformaldehyde, being only about 0.25 at 160°C and 170°C in the case of TN. In the case of hexamethylenetetramine, there was very little temperature variation. The overall degree of conversion in the case of wattle tannin was in the order paraformaldehyde > hexamethylenetetramine > TN. From these results it can be said that wattle tannin is cured best with paraformaldehyde, then hexamine and then TN.

The degree of conversion of pine tannin-based adhesives are shown in Fig. 5. In all cases, they were higher than those of the wattle tannin-based adhesives. Particularly, in the case of the pine tannin-based adhesive with hexamethylenetetramine, a high degree of conversion was indicated at an earlier curing time. It can be seen in Fig. 5 that about 70% curing took place after 5 min. According to several reports, pine tannin reacts faster with formaldehyde than wattle tannin and has a short pot life [9]. Also, hexamethylenetetramine was found to be a suitable hardener for pine tannin because of its high reactivity toward formaldehyde and low formaldehyde emission [7, 11]. The order of reactivity of the pine tannin-based adhesive system was hexamethylenetetramine > paraformaldehyde > TN, in contrast to that of wattle tannin-based adhesive.

However, the degree of conversion of tannin-based adhesives is low in comparison to that of resol resin, whose conversion was almost 1.0 at high temperature ($160\text{--}170^\circ\text{C}$) after 20 min [24, 26]. The process of cross-linking is complicated in the case of tannin, whereas resol resin produces linear and regular cross-linking.

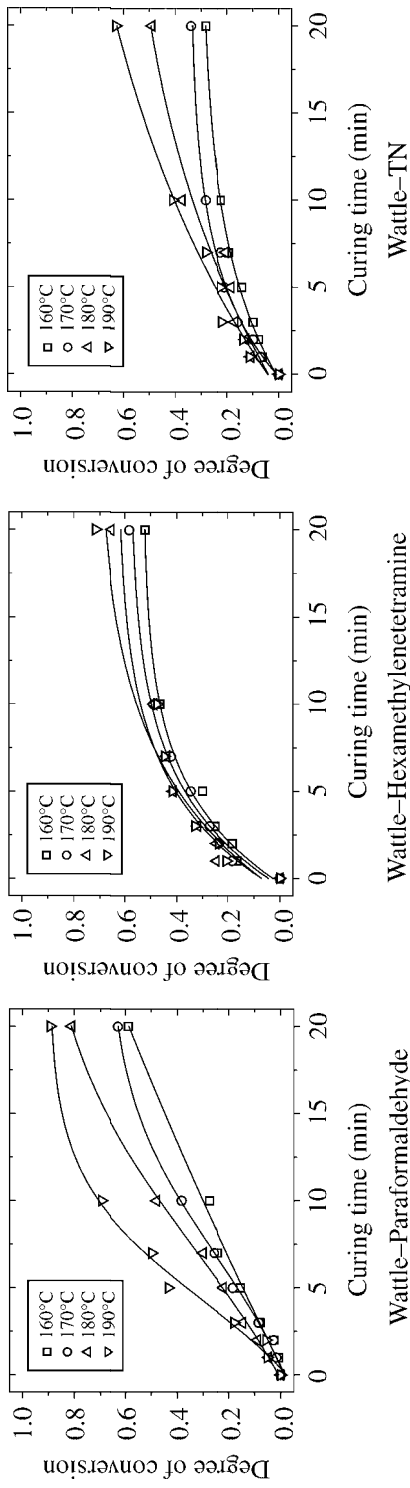


Figure 4. Degree of conversion of wattle tannin-based adhesive with three hardeners at various curing temperatures.

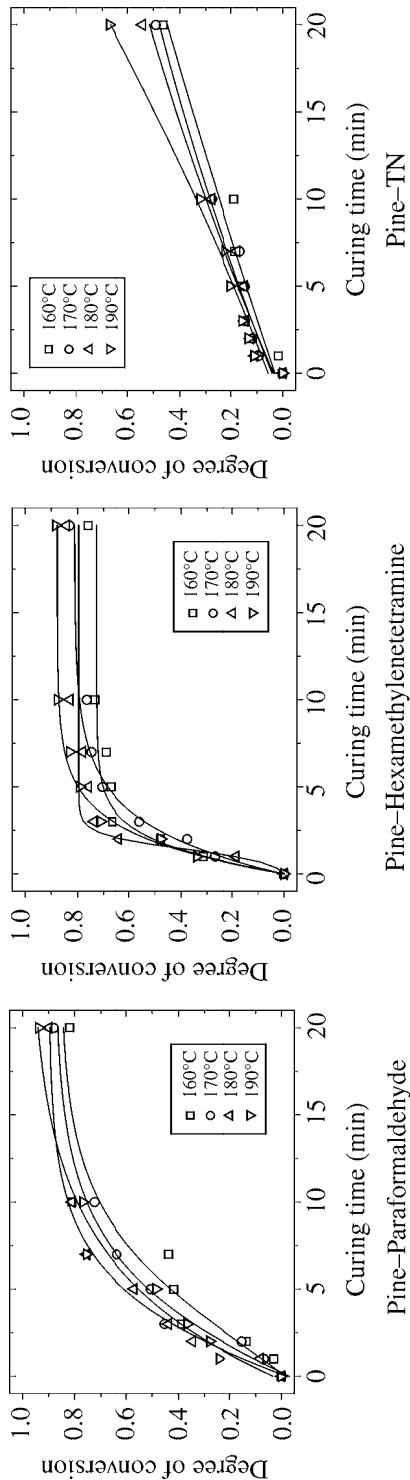


Figure 5. Degree of conversion of pine tannin-based adhesive with three hardeners at various curing temperatures.

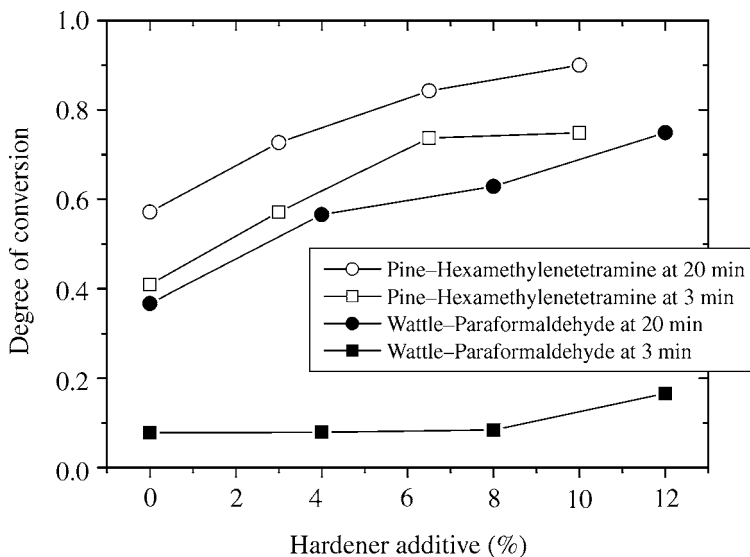


Figure 6. Comparison of conversion of wattle tannin-based adhesive with paraformaldehyde and pine tannin-based adhesive with hexamethylenetetramine as a function of the level of hardener.

This is due to the structure and high molecular weight of tannin. Furthermore, in the case of tannin, non-participating OH groups remain, because the distance between the OH groups that might react with each other is longer than in the case of resol resin for structural reasons.

In Fig. 6, the degree of conversion is shown as a function of amount of hardener. As shown above, paraformaldehyde was the best hardener for wattle tannin, and hexamethylenetetramine was the best hardener for pine tannin, so from the point of view of reactivity between the tannin and the hardener, these hardeners were chosen. With increasing amount of hardener, the degree of conversion increased. This implies that increasing the amount of hardener promotes the curing reaction of the tannin. The degree of conversion of pine tannin-based adhesives with hexamethylenetetramine after only 3 min of curing was already higher than that of the wattle tannin-based adhesives with paraformaldehyde after 20 minutes of curing. This implies that pine tannin has a very short pot life.

From these results, it can be said that the increase in the degree of cross-linking and strength obtained by increasing the amount of hardener was limited. As shown in a previous report, the degree of cross-linking and the resultant strength depend on the molar ratio of the resin and hardener [24].

3.2. Dynamic mechanical thermal analysis

It is important to understand the thermal properties of tannin-based adhesives because, as thermosetting adhesives, they are strongly affected by and indeed cured by heating. Tannin-based adhesives are in the liquid state at room temperature and become solid at high temperature after curing has taken place. The viscoelastic

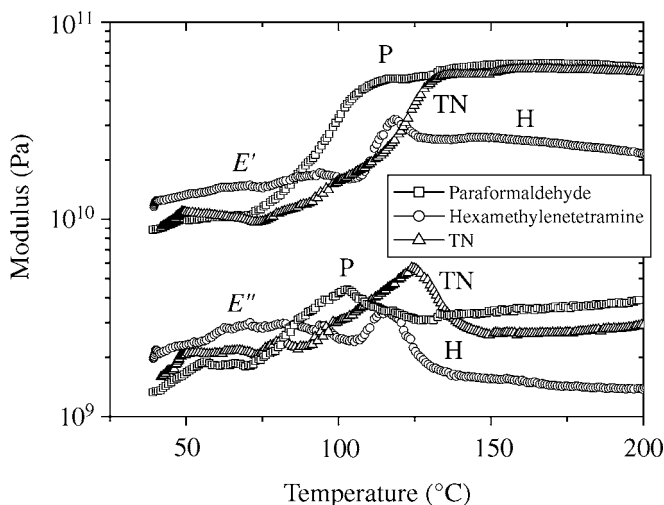


Figure 7. Storage modulus (E') and loss modulus (E'') of wattle tannin-based adhesives with three hardeners (heating rate 5°C/min). P: paraformaldehyde; H: hexamethylenetetramine.

properties of tannin-based adhesives with the three hardeners were investigated with a dynamic mechanical thermal analyzer. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of each adhesive system were obtained by DMTA.

In Fig. 7, the storage modulus (E') and loss modulus (E'') of the wattle tannin-based adhesives with each of the three hardeners are presented. As the temperature increased, the storage modulus (E') increased. It should be noted that the storage modulus increased rapidly at around 110°C. The temperature of the active curing reaction can be determined from the maximum value of the loss modulus (E'') in this temperature range. The temperatures corresponding to the maximum values of the loss modulus (E'') were 102.9°C for paraformaldehyde, 112.7°C for hexamethylenetetramine and 124.0°C for TN. From these results it can be said that wattle tannin reacts with paraformaldehyde better than with the other hardeners, because the reaction occurs at the lowest temperature. Hexamethylenetetramine and TN are next, in that order. This reaction order corresponded with the FT-IR-ATR results.

The corresponding results for the pine tannin-based adhesives are shown in Fig. 8. The increase in the storage modulus (E') as a function of increasing temperature was also observed in the case of pine tannin. On the basis of the FT-IR-ATR results and several previous reports [7, 11], it is known that pine tannin reacts faster and at a lower temperature than wattle tannin. The temperatures corresponding to the maximum values of the loss modulus (E'') were lower, but the order of reaction was different. T_{\max} in the case of pine tannin was 95.0°C for paraformaldehyde, 91.9°C for hexamethylenetetramine and 114.5°C for TN, and these results corresponded with the FT-IR-ATR results, which showed that hexamethylenetetramine was the most reactive hardener with pine

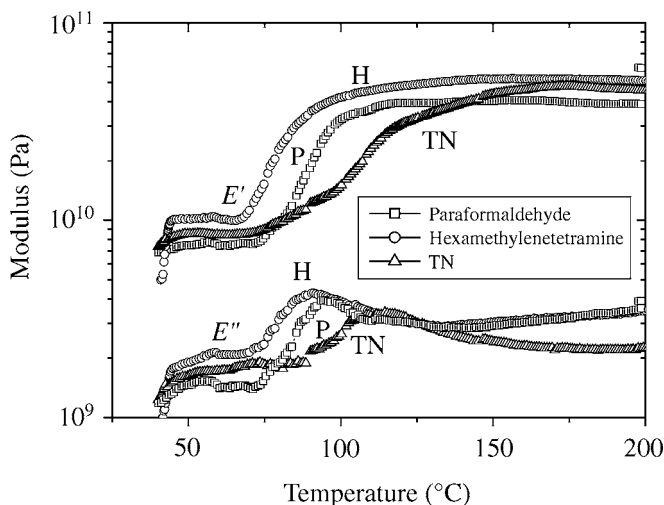


Figure 8. Storage modulus (E') and loss modulus (E'') of pine tannin-based adhesives with three hardeners (heating rate $5^{\circ}\text{C}/\text{min}$). P: paraformaldehyde; H: hexamethylenetetramine.

tannin. The temperatures at the maximum values of the loss modulus (E'') for all adhesive systems are presented in Fig. 9. However, these results differ from those reported by Garcia and Pizzi [27]. In their report, a direct comparison between paraformaldehyde and hexamethylenetetramine using thermomechanical analysis showed that the hexamethylenetetramine hardened tannin network was less cross-linked than the paraformaldehyde hardened one. Furthermore, in another report on the DMTA results on thermosetting adhesives, the observed decrease in the storage modulus (E') after E'_{max} was explained by thermal degradation [28]. As shown in Figs 7 and 8, once the storage modulus (E') is increased to 100°C , it stays practically constant with increasing temperature. The degree of thermal degradation of tannin-based adhesives was less than 3% at 200°C [29].

The viscoelastic properties of tannin-based adhesives, as a function of the amount of hardener were investigated using DMTA, as shown in Fig. 10. In the case of pine tannin with hexamethylenetetramine, the value of T_{max} for the loss modulus (E'') decreased as the amount of hexamethylenetetramine increased, while the degree of curing increased according to the storage modulus (E') data. The temperatures for maximum loss modulus (E''), T_{max} , of wattle and pine tannin-based adhesives as a function of the percentage of paraformaldehyde and hexamethylenetetramine by weight to that of tannin are compared in Fig. 11. Increasing the amount of hexamethylenetetramine tended not only to increase the degree of cross-linking, but also to lower the reaction temperature. This can be explained by the faster reactivity and shorter pot life of pine tannin, while hexamethylenetetramine acts as an accelerator. Assuming the reactivity of phenol towards formaldehyde to be 1, and that of resorcinol and phloroglucinol to be 10 and 100, respectively, the flavonoid

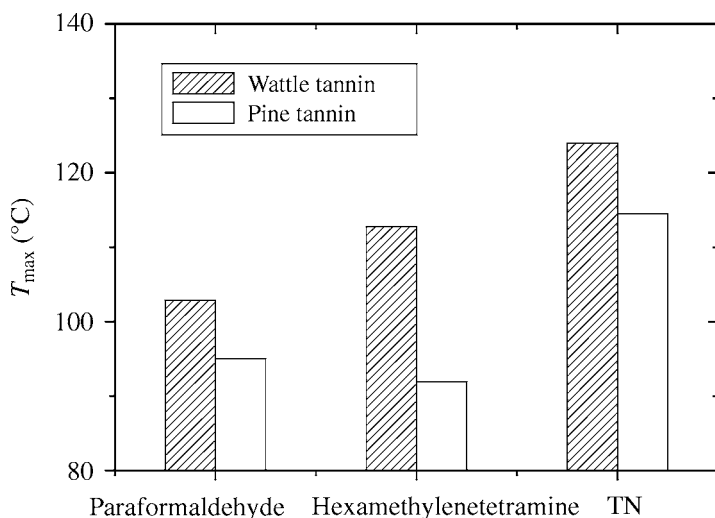


Figure 9. Temperature for maximum loss modulus (E''), T_{\max} , of wattle and pine tannin-based adhesives with three hardeners.

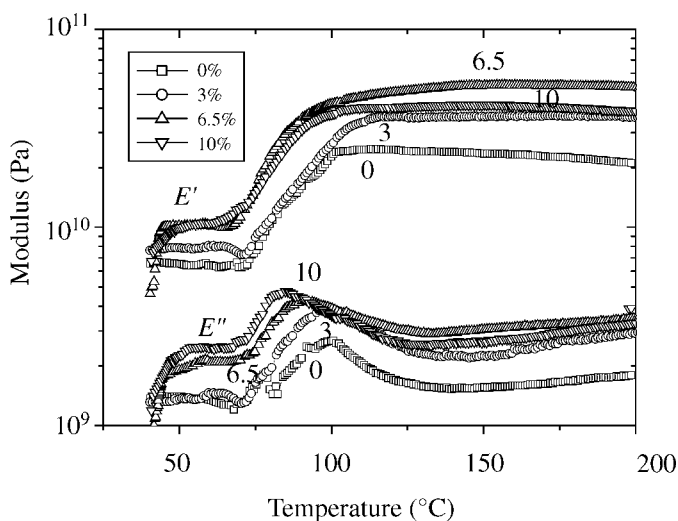


Figure 10. Storage modulus (E') and loss modulus (E'') of pine tannin-based adhesives as a function of the additive level of hexamethylenetetramine added to tannin solid by weight (heating rate 5°C/min).

resorcinolic A-rings have a reactivity of about 8–9, while the phloroglucinolic A-rings have a reactivity of well over 50 [6].

On the other hand, no major difference in the value of T_{\max} for the maximum loss modulus (E'') for wattle tannin with paraformaldehyde was determined within an error range of 2.1°C.

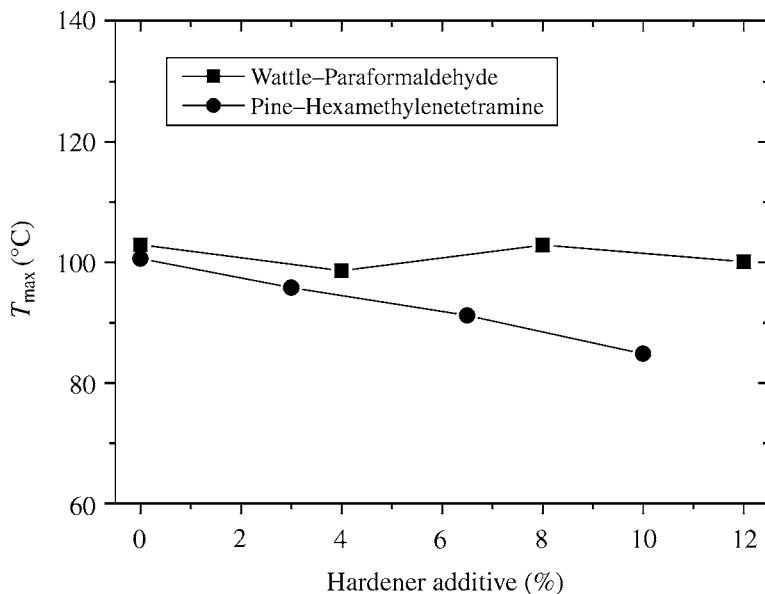


Figure 11. Temperature for maximum loss modulus (E''), T_{\max} , of wattle and pine tannin-based adhesives as a function of the level of paraformaldehyde and hexamethylenetetramine added to tannin powder by weight.

4. CONCLUSIONS

In this study, it was shown that FT-IR-ATR spectroscopy in combination with dynamic mechanical thermal analysis could be used for determining the degree of curing and for predicting the degree of cross-linking obtained between the tannin solution and hardeners paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxymethyl)nitromethane). Furthermore, the cross-linking mechanism involving the tannin-based adhesives and their hardeners, and the viscoelastic properties of tannin-based adhesives were investigated.

The tannin-based adhesives, as thermosetting adhesives, were cured by increasing the temperature, and the curing process was investigated by observing the conversion of the hydroxyl groups. The degree of conversion (α) increased with time at 160, 170, 180 and 190°C curing temperatures. Paraformaldehyde showed the fastest reaction behavior with wattle tannin, while hexamine caused the fastest reaction behavior for pine tannin.

With increasing curing temperature, the tannin-based adhesives showed viscoelastic properties. They were in the liquid state at low temperature and changed into the solid state as the temperature increased. The reactivity of the hardener toward the tannin was in the order: paraformaldehyde > hexamethylenetetramine > TN for wattle tannin, while for pine tannin the order was hexamethylenetetramine > paraformaldehyde > TN. These results were obtained from the storage modulus (E') and loss modulus (E'') data.

In conclusion, it was established in this study that the curing behavior of thermosetting adhesives, such as tannin-based adhesives, could be investigated by FT-IR-ATR spectroscopy in combination with dynamic mechanical thermal analysis.

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