

Comparison Study of Thermal Decomposition Characteristics of Wattle & Pine Tannin-based Adhesives*¹

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ABSTRACT

This study investigated the thermogravimetric analysis of two types of cured tannin-based adhesives from wattle and pine, with three hardeners of paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan), at a temperature of 170°C and a heating rate of 5, 10, 20 and 40°C/min for 10 minutes. The 5 minutes cured wattle tannin-based adhesive with each hardener at 170°C was also tested to compare the degree of curing. It was found that thermogravimetric analysis could be used to measure the degree of curing of a thermosetting adhesive. The TG-DTG curves of all the adhesive systems were similar and showed three steps in a similar way to a phenolic resin. This means that each adhesive system is well cross-linked. However, a high thermal decomposition rate was shown at 150 to 400°C in the case of the pine tannin sample with TN (tris(hydroxyl)nitromethan). The Flynn & Wall expression was used to evaluate the activation energy for thermal decomposition. As the level of conversion (α) increased, the activation energy of each system increased. The activation energy of the wattle tannin-based adhesive with paraformaldehyde was higher than the others.

Keywords: wattle tannin, pine tannin, hardener, TGA, TG-DTG, thermal decomposition, activation energy, the Flynn & Wall expression

1. INTRODUCTION

After 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. Rising the oil price and decreasing fuel energy

lead to the development of substitutes for petroleum-derived phenolic compounds from natural resources in wood adhesive industries (Alma & Kelley, 2000).

Tannin is an excellent renewable resource for replacing petroleum-derived phenolic compounds.

The major species where it can be obtained are mimosa, quebracho and radiata pine, etc. It

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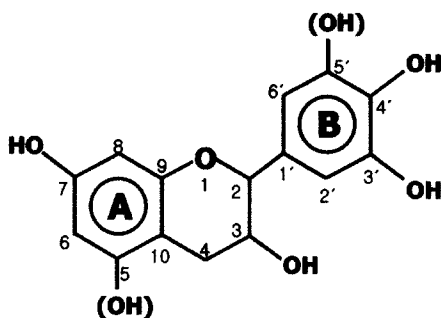


Fig. 1. Basic structure of tannin.

is mainly concentrated in the inner layer of bark and has been applied to the adhesive industry in Africa, South America and Oceania (Pizzi, 1994; Roffael *et al.*, 2000).

Tannin (Fig. 1) is present predominantly as phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings (Pizzi, 1983). The free C6 and C8 sites on the A-ring can react with formaldehyde to form the adhesive due to their strong nucleophilicity. The phenolic nuclei in tannins react with formaldehyde. This high reactivity of tannins towards formaldehyde is the result of their A-ring phloroglucinolic or resorcinolic nuclei, which have a 10 to 50 times higher rate of reaction than a reaction of phenol with formaldehyde. Because of these characteristics, there is less free formaldehyde emission than other wood adhesive such as phenol-formaldehyde, urea-formaldehyde, etc (Pizzi & Tekely, 1995).

Thermogravimetric analysis (TGA) can be used to study the thermal behavior of polymers. The rate of weight loss as a function of temperature and time is measured to predict the thermal behavior of the materials (Kim & Eom, 2001). It is a widely used technique because of its simplicity. It also provides a means to estimate the kinetic parameters in a thermal decomposition reaction. Knowledge of the thermal decomposition kinetics is an important tool for predicting the behavior of polymers under

various environmental conditions, and is also helpful for determining the strength of various bonds in the polymer backbone chain and hence the mechanism of the decomposition reaction because of the excellent physico-chemical properties of cured resins which are important in the adhesive field (Kagathara & Parsania, 2002).

In this study, two tannins (wattle and pine) and three hardeners (paraformaldehyde, hexamine and tris(hydroxyl)nitromethane) were formulated to manufacture the wood adhesive system for thermogravimetric analysis and thermal decomposition trends of each adhesive system were compared. The Flynn & Wall (Lee *et al.*, 2000; Popescu, 1996) expression was used to estimate activation energy of thermal decomposition. The curing behavior of the tannin-based adhesive and thermal decomposition of the chemical bond between tannin and formaldehyde were investigated by thermal analysis.

2. MATERIALS and METHOD

2.1. Materials

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 were a dark brown fine powder type with moisture content of 4%.

2.1.2. Hardeners

The three hardeners of paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethane) were purchased from the Aldrich Chemical Company, Inc. Their chemical structures are shown in Fig. 2.

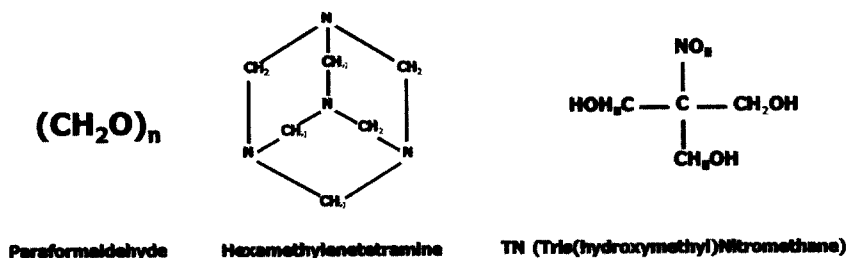


Fig. 2. Chemical structures of the three hardeners.

2.2. Methods

2.2.1. Tannin-based Adhesives

Aqueous tannin extracts with a 40% concentration were prepared by dissolving a spray-dried powder of each tannin extracts in water. To these solutions, each hardener on weight of dry tannin extract were added in a proportion of 6.5, 8 or 10% (Table 1), based on several results (Trosa & Pizzi, 2001; Pichelin *et al.*, 1999; Pizzi *et al.*, 1994). The pH ranged from 5.5 to 6. Table 1 shows the concentration of each additive. While paraformaldehyde and TN (tris-(hydroxyl)nitromethane) were used in the pure solid state, hexamethylenetetramine was used as a 35% hexamine solution (Pichelin *et al.*, 1999).

2.2.2. Thermogravimetric Analysis

The samples were cured in an oven at 170°C for 10 min and analyzed thermogravimetrically in N₂ at four heating rates: 5, 10, 20 and 40°C/min. The cure temperature, 170°C, was based on the report by Pizzi (1996) to give a higher bonding strength and a lower free formaldehyde. 10 mg of the each cured samples were placed on a balance located in the furnace and heat was applied in the temperature range from room temperature to 800°C using a Thermogravimetric Analyzer (Rheometric Scientific TGA 1000, NICEM, Seoul National University). High-purity nitrogen gas consisting of 99.5% N₂

Table 1. Additive contents of the hardeners.

Hardener	Additive Contents (on Solid Tannin Powder)
Paraformaldehyde	8%
Hexamethylenetetramine	6.5%
TN(Tris(hydroxymethyl) nitromethane)	10%

and 0.5% O₂ was used as the inert purge gas to displace air in the pyrolysis zone in order to avoid unwanted oxidation of the sample. A constant flow was fed to the system at a rate of 20 mL/min from a point below the sample.

2.2.3. Kinetic of Thermal Decomposition

The Flynn & Wall expression (Lee *et al.*, 2000; Fraga & Nunez, 2001; Nunez *et al.*, 2000) was used to evaluate the activation energy of thermal decomposition. This is one of the integral methods that can determine the activation energy without knowledge of the reaction order. It is used to determine the activation energy at given conversion values.

$$E_a = \frac{-R d(\log \beta)}{0.457d(T^{-1})} \quad \text{eq. (1)}$$

E_a = activation energy of thermal decomposition

R = gas constant

β = heating rate

T = absolute temperature

The activation energy (E_a) is estimated from the slope of the best fitted line from the relationship between $\log \beta$ and $1/T$ at a selected fraction of thermal decomposition. The selected fraction ranged from 0.05 to 0.40 and the resulting activation energy values for each fraction were compared.

3. RESULTS and DISCUSSION

3.1. Thermogravimetric Analysis

Fig. 3 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of two types of tannin extracts. The TG-DTG curves show that the tannin extracts contain 4~5% moisture and the main decomposition occurs as a single step. The shapes of these two samples are similar to each other but from DTG curve, the pine extract is more stable at the main decomposition range from 250°C to 350°C. In addition, at 800°C, the residue of the pine extracts weighs 5% more than the wattle one.

The TG-DTG curves can be used to investigate the degree of curing. Fig. 4 shows the TG-DTG curve of the 5 minutes cured wattle tannin-based adhesive sample. The moisture peak can be confirmed from the DTG curve at 100 to 150°C. This means the sample still contains moisture despite 5 minutes curing in the oven. Sufficient time due to reactivity of moisture must be applied for curing at the optimum temperature because the tannin-based adhesive is cured between the tannin extracts, hardener and water (Pizzi, 1994).

The TG curves of the wattle and pine tannin-based adhesive samples, cured for 10 minutes in the oven with each hardener, are shown in Figs. 5 and 6. According to the literature, the thermal decomposition mechanism of a phenolic resin includes three steps (Wang *et al.*, 2001; Trick & Saliba, 1995). The first step is the increase

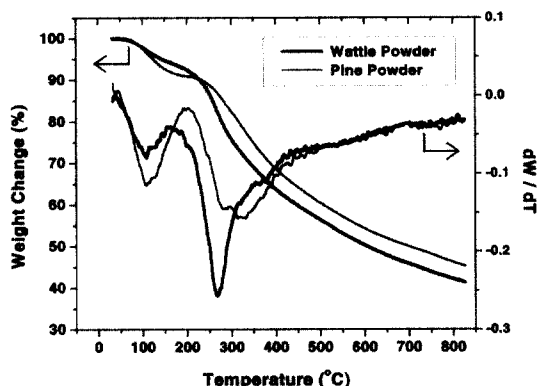


Fig. 3. Comparison of thermograms between wattle and pine tannin powders (Heating rate, 40°C/min).

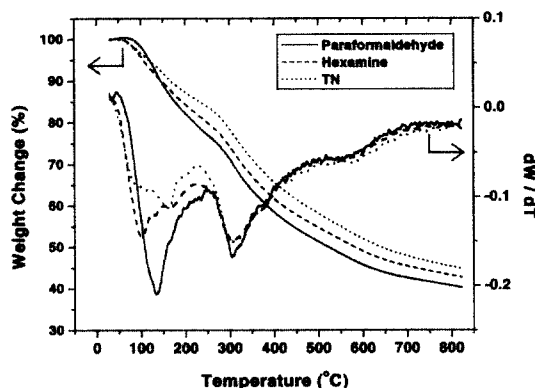


Fig. 4. Thermograms of 5 minutes cured wattle tannin-based adhesive with each hardener at 170°C (Heating rate, 40°C/min).

in the cross-linking density, which occurs from 300 to 500°C, as reported by Trick and Saliba (1995). The second step is from 400 to 800°C, which involves increasing vibrations of the molecule with temperature. At this step, the cross-linking network is broken. The third step is from 560 to 800°C. This involves the cleavage of the C-H groups in phenol and the formation of hydrogen gas. Although, from Figs. 5 and 6, tannin is similar to phenol in structure and reactivity to formaldehyde, the thermal decomposition trend of a tannin-based adhesive

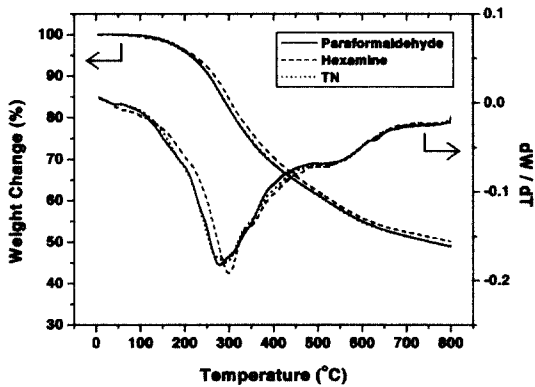


Fig. 5. Thermograms of 10 minutes cured wattle tannin-based adhesive with each hardener at 170°C (Heating rate, 40°C/min).

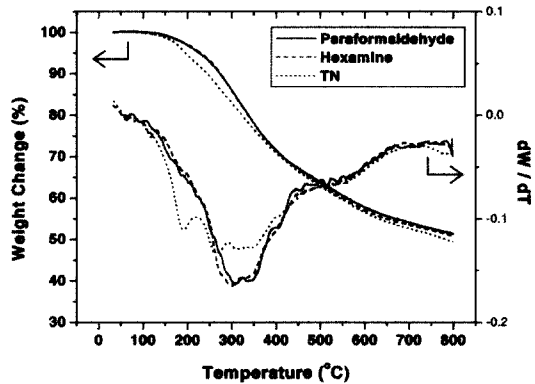


Fig. 6. Thermograms of 10 minutes cured pine tannin-based adhesive with each hardener at 170°C (Heating rate, 40°C/min).

with the noticed hardeners is shifted to a lower temperature. A comparison of the TG-DTG curves of each hardener showed there was little difference. However, in the case of the pine tannin sample with TN (tris(hydroxyl)nitromethan), a higher thermal decomposition rate was observed between 150 to 400°C. Although the thermal decomposition behavior of the pure hardeners is different as it shown in Fig. 7, the TG curves of the cured samples did not exhibit this effect. This means that hardeners are already participated in curing and thermal decompo-

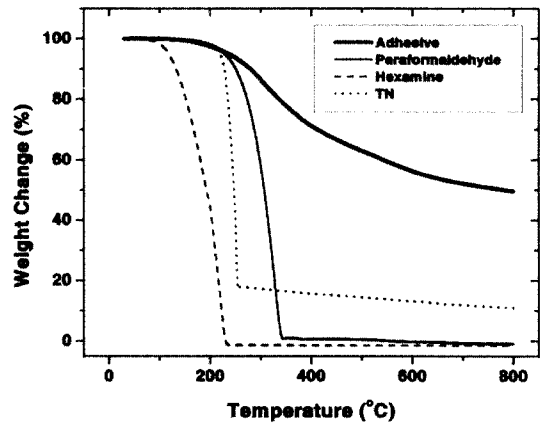


Fig. 7. Comparison of the thermograms between 10 minutes cured wattle tannin-based adhesive at 170°C and pure hardeners (Heating rate, 40°C/min).

sition is not a degradation of the material itself but a decomposition of the cross-linking.

3.2. Activation Energy of Thermal Decomposition

Figs. 8 and 9 show the thermal decomposition curves from the dynamic experiments carried out at different heating rates: 5, 10, 20 and 40°C/min. As the heating rate increased, the decomposition temperature (T_d) increased. The T_d was obtained from the point where the weight loss increased. The T_d is influenced by the heating rate of pyrolysis, as reported by other researchers (Nunez *et al.*, 2000; Wang *et al.*, 2001). As shown in these Figures, when the heating increased from 5 to 40°C/min, the retained weight decreased by more than 5% at a decomposition temperature of 100 to 300°C while 50% of the weight change occurred at a decomposition temperature of 800°C.

The thermal decomposition activation energy was determined using the Flynn & Wall expression [eq. (1)], from a linear fitting of $\log \beta$ vs. $1/T$ at different conversions. The plots lines of $\log \beta$ vs. $1/T$ are plotted in Figs. 10

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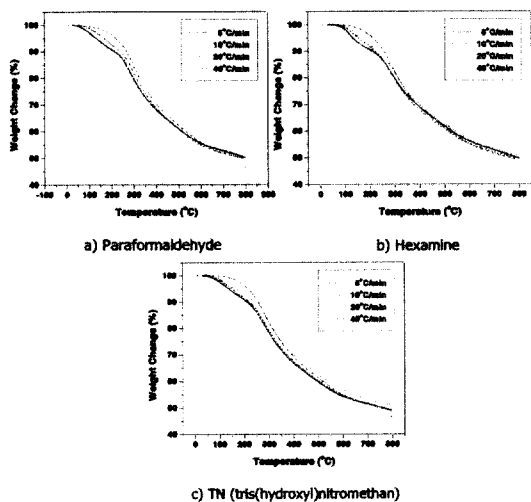


Fig. 8. Thermograms of 10 minutes cured wattle tannin-based adhesive with each hardener by the heating rate at a curing temperature of 170°C.

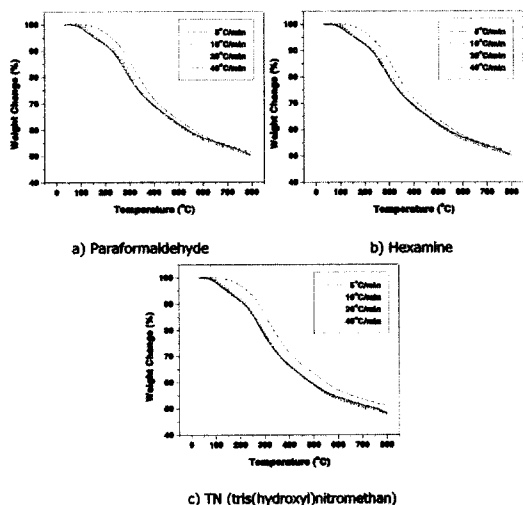


Fig. 9. Thermograms of 10 minutes cured pine tannin-based adhesive with each hardener by the heating rate at a curing temperature of 170°C.

and 11, and the activation energies for thermal decomposition were estimated from the slopes, as $0.457 E_a/R$. Similar slopes over the α range

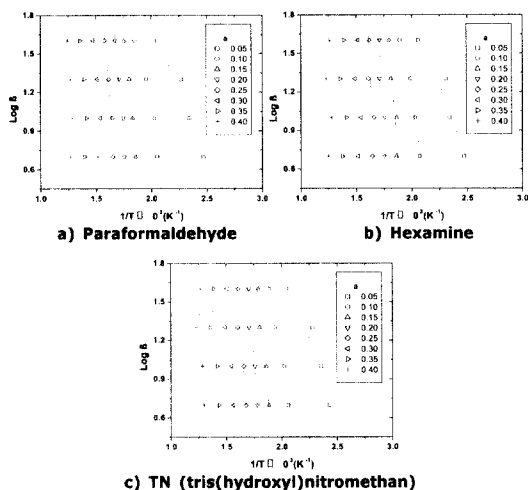


Fig. 10. Isoconversional curves of wattle tannin-based adhesives with each hardener from the Flynn & Wall expression.

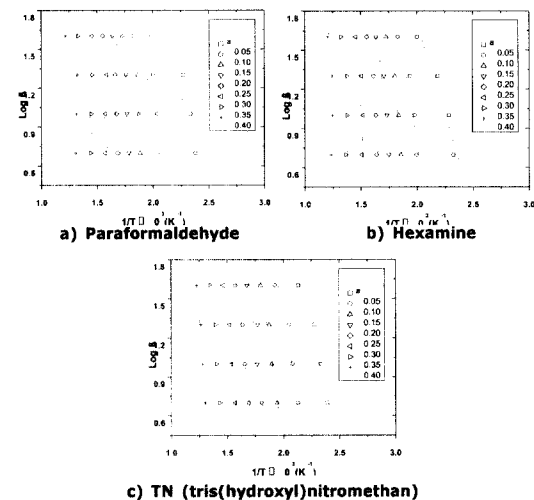


Fig. 11. Isoconversional curves of pine tannin-based adhesives with each hardener from the Flynn & Wall expression.

of 0.05~0.40 indicate that the same reaction mechanism is acting on the decomposition of the cross-linked chains with a constant activation energy (Lee *et al.*, 2001).

In Figs. 12 and 13, the thermal decomposition

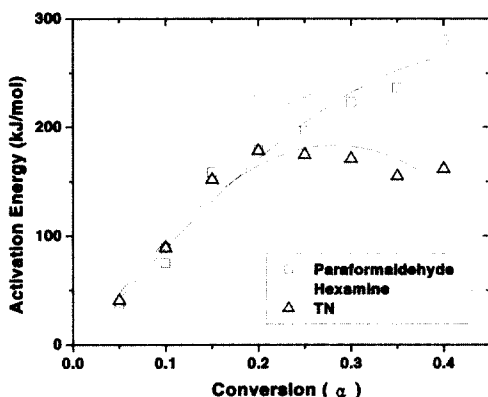


Fig. 12. Comparison of the activation energies of thermal decomposition of the wattle tannin-based adhesives according to each hardener.

activation energies for the two types of tannin-based adhesives with the three hardeners are shown. As the conversion (α) increased, the activation energy of each system generally increased. But the wattle tannin-based with hexamine and TN (tris(hydroxyl)nitromethan) decreased from a conversion of 0.25. This means that the wattle tannin-based adhesive with paraformaldehyde yields the cross-link more stable to high temperatures than the others. However, the trend was totally different from pine one. The activation energy for the decomposition of the pine tannin-based adhesive with paraformaldehyde is low at any conversion. From this performance, it is expected that the particleboard made by the wattle tannin-based adhesive with paraformaldehyde would have better mechanical and physical properties than the pine tannin-based adhesive with paraformaldehyde.

4. CONCLUSION

From this study, it is proved that thermogravimetric analysis and activation energy measurements of thermal decomposition can be used for determining the degree of curing and predicting the cross-linking degree between the

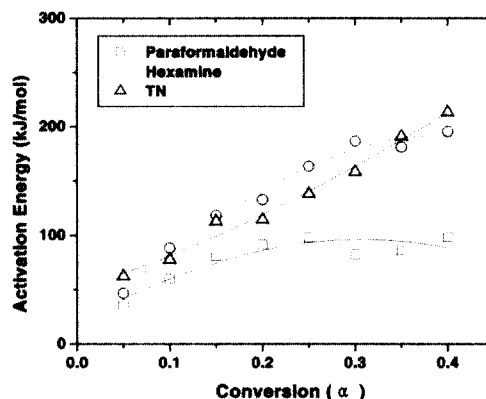


Fig. 13. Comparison of the activation energies of thermal decomposition of the pine tannin-based adhesives according to each hardener.

tannin solution and the hardeners. The TG-DTG curves of two types of tannin adhesive from wattle and pine with the three hardeners of paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan) were similar and they showed three steps as did the phenolic resin. This means that each adhesive system is well cross-linked. However, in the pine tannin sample with TN (tris(hydroxyl)nitromethan), a higher thermal decomposition rate was observed at 150 to 400°C.

A comparison of the 5 minutes and 10 minutes cured wattle tannin-based adhesives with each hardener showed that the 5 minutes cured one still contained moisture, which can be detected by the peaks in the DTG curve at 100 to 150°C.

From the results of thermal decomposition activation energy, activation energy of each system increased as the level of conversion (α) increased. The activation energy of the wattle tannin-based adhesive with paraformaldehyde was higher than the others. From this performance, it is expected that a particleboard made by the wattle tannin-based adhesive with paraformaldehyde will have superior mechanical and physical properties than the other systems.

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