

**VISCOELASTIC PROPERTIES OF *PINUS RADIATA*
ACETYLATED WOOD**

JUSTO LISPERGUER, CYNTHIA DROGUETT, BEATRIZ RUF
BÍO-BÍO UNIVERSITY, FACULTY OF SCIENCES, CONCEPCIÓN, CHILE

ABSTRACT

The viscoelastic properties of wood have been studied extensively using different analysis techniques.

As wood is a complex composite material, it is not surprising that the literature includes different interpretations of the relaxation behaviour of wood and wood based materials.

In this research, dynamic mechanical analysis and differential scanning calorimeter were used to study the thermal behaviour of acetylated and non-acetylated wood.

Dry wood samples with 1-2% moisture content and samples at room temperature with 10-12% moisture content were characterized.

Dynamic mechanical analysis and differential scanning calorimeter studies are used to identify different thermal behaviour of untreated and acetylated wood. Whereas dry untreated wood shows a high glass transition temperature (150°C), acetylated dry wood exhibits thermal softening at 50°C, attributed to the esterification effect of wood acetylation.

At room temperature, the behaviour of untreated and acetylated wood is similar with a glass transition temperature of 50°C, due to the plasticization effect of water molecules in the wood.

KEY WORDS: thermal properties, acetylated wood, *Pinus radiata*

INTRODUCTION

The thermal properties of wood and its polymeric components, (cellulose, hemicellulose, lignin) have been studied extensively by means of thermal analysers such as differential scanning calorimeter (DSC) and dynamic mechanical analysis (DMA) (Scandola and Caccorulli 1985, Dias de Moraes et al. 2004, Laborie et al. 2004).

Wood is a complex composite material that consists of several phases, each of which is heterogeneous in itself (Furata et al. 1997). It is not a continuous material, as it includes a significant void volume. It is strongly, irregular, anisotropic and its hygroscopy and grain direction, relative to the sample configuration, have a large effect on the results of the studies about thermal and mechanical behaviour (Backman and Lindberg 2001, Obataya et al. 2001, Sun et al. 2007).

The strength properties of wood depend on, among other things, the glass transition of the amorphous components to an extent determined by their concentrations and structural arrangements in various local entities. Since the hemicelluloses, lignin and disordered part of the

cellulose absorb water, a softener for these polymers, the glass transition depends on the respective moisture contents (Back and Salmén 1982).

In another early study on the glass transition of lignin and hemicelluloses, Irvine (1984) used differential thermal analysis (DTA) to determine the glass transition temperature (T_g) of lignin within the 60 to 90°C interval. Back and Salmén (1982), report T_g between 200 and 250°C for semicrystalline cellulose and native lignin.

Kelley et al. (1987), found two separate T_g in solid hard (maple) and soft (spruce) woods using dynamic mechanical thermal analysis (DMTA) and DSC. The $\tan \delta$ response reveals a low transition temperature, β at -90°C followed by a broad transition, α_1 , at higher temperatures centred around 80 to 100°C and a shoulder, α_2 , between 10 and 60°C. According to these authors, the behaviour of the β transition is characteristic of a secondary dispersion involving only small-scale motion, whereas the α transitions imply large-scale segmental motions that are characteristic of a glass transition. DSC provides an additional method for studying the nature of these thermal transitions. The same authors present a series of DSC scans of milled wood with an endothermic peak around 50°C, known as enthalpy relaxation, which is clearly associated with T_g . The moisture content of the samples ranged from 5 to 30%.

Birkinshaw et al. (1986), used DMA to confirm a transition in several wood species at -50°C in the $\tan \delta$ of all species and a progressive increase in relative damping from 50°C upwards.

Hon (1989), studied, thermal and viscoelastic properties of benzylated, hydroxypropylated and hydroxybutylated woods with DSC and DMTA. This author reported four transition relaxations between -150°C and 200°C. The T_g of all modified woods decreased with esterification when the weight percent gain was increased from 20 to 100%.

Despite the many works published in the area, little research has considered the thermal behaviour of dry wood. Because of the importance of moisture for processing some composites (e.g. wood-plastic materials) that require less than 2% water, one of the goals of this study is to evaluate the viscoelastic response of *P. radiata* wood at this moisture content.

Moreover, the work reported herein was carried out from room temperature to 250°C in order to study the α transitions. According to the literature, the α transitions are the characteristic phenomenon of the T_g of wood.

In order to increase the thermoplastic properties of wood an esterification reaction with acetic anhydride was carried out and the changes of T_g of acetylated wood was also studied.

Dynamic mechanical analysis and differential scanning calorimetry, were used to determine T_g . A Fourier transform infrared (FTIR) analysis was performed to investigate the acetylation reaction of wood flour, following the method published by Sun and Sun R.C. (2002)

MATERIAL AND METHODS

Wood flour Acetylation

The acetylation reaction of wood, without a catalyst, was carried out by the method described in the literature (Sun and Sun 2002) with a 10.7% weight percent gain of wood flour for 1 hour of reaction time.

Pinus radiata wood flour (15g) was sieved with a mesh (size 100) and oven-dried at 60°C for 16 hours. Then 10 g of wood flour were placed in a 500-mL flat bottom flask. 300 mL of acetic anhydride were added to this. The flask was dipped into an oil bath set at 120°C and fitted with a reflux condenser. Once the 1 hour reaction time was completed, the flask was removed from the oil bath and the reagents were filtered off. The wood flour was then washed with ethanol to remove

any unreacted anhydride and acetic acid by-products. The acetylated wood flour was oven-dried at 60°C for 16 hours and weighed. The weight percent gain due to acetylation was calculated based on the weight of the oven-dried unreacted wood flour.

Spectroscopic and thermal characterization

The FTIR spectra of unmodified and acetylated wood were recorded on a Nicolet model Nexus spectrophotometer, using KBr pellets containing 1% finely ground samples.

A mechanical dynamic analyzer (DMA, Perkin Elmer 7 e) was used to study the thermal behaviour of the untreated and acetylated wood. The samples dimensions were 4 x 2 x 20 mm. The samples were tested for bending at three points with a 15 mm light. The test was dynamic, with a temperature range of 20° to 300°C at a heating rate of 5°C/min. A 1 Hertz load frequency was used.

A Mettler Toledo DSC 822^e equipped with a thermal analysis data STAR^e software system was used for the thermal behaviour study. Aluminium sealed capsules were filled with 5-10 mg of ground dry wood. The scans were performed at a heating rate of 10°C/min under a dry nitrogen atmosphere between 25 and 250°C.

The ground wood for the DSC analysis and all DMA specimens were dried in an air-circulated oven at 100°C for 12 hours. The moisture content of the wood was ≤ 2%.

RESULTS AND DISCUSSION

FTIR Spectra

The IR spectral characterization was performed to determine whether a chemical reaction was taking place between the wood flour and the acetic anhydride.

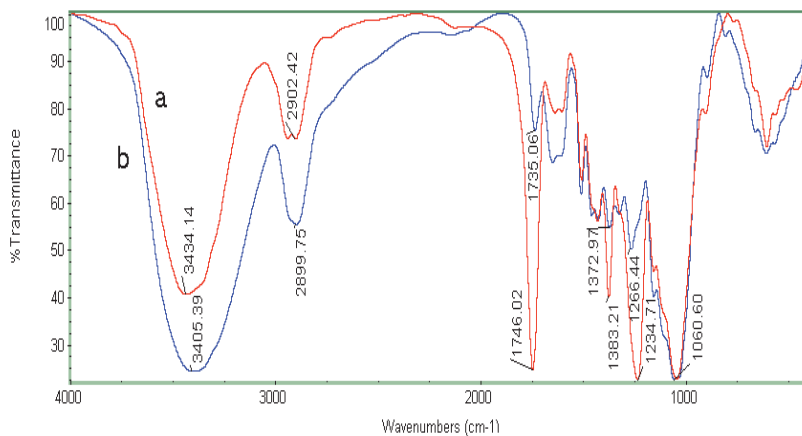


Fig. 1: FTIR spectra of untreated wood (spectrum b) and acetylated wood (spectrum a)

Fig. 1 illustrates the FTIR spectra of acetylated (a) and unmodified (b) wood prepared at 120°C for 1 hour. The most important features of the acetylated wood flour spectrum are: the increasing of three ester bands at 1746 (C=O), 1383 (-C-CH₃) and the -C-O- stretching

band at 1234 cm^{-1} . Furthermore, the peak area of the esterification reaction of the wood flour decreased at 3434 cm^{-1} due to stretching vibrations of OH, indicating partial acetylation. No significant differences were observed for acetylated and unmodified wood flour in the other bands of the spectra.

DMA and DSC analysis

The miscibility and structure of multicomponent polymer systems such as blends or block copolymers can be studied by DMA and DSC. These techniques are very useful due to their ability to differentiate between the single T_g of a homogeneous polymer and the thermal transitions of a heterogeneous material.

This differentiation defines the degree of compatibility or incompatibility of a polymer mixture.

The wood cell wall is comprised of three individual polymers: (cellulose, hemicellulose, lignin) and can be considered to be a complex mixture. Thus, it follows that these techniques used should be sensitive to the thermal transitions associated with the wood's amorphous components.

The observation of one or several T_g values and the effect of the chemical modification of wood can be related to the wood's viscoelastic response.

Dynamic mechanical properties are the properties of materials as they are deformed under periodic forces. The dynamic modulus is often considered to be the most sensitive indicator for determining all kinds of molecular motions when the solid material is heated in a give temperature range.

The storage modulus (E''), is defined as the stress in phase with the strain in a sinusoidal shear deformation divided by the strain. It is a measure of the energy stored and recovered per cycle when different systems are compared at the same strain amplitude. The loss modulus (E') is defined as the stress 90°C out of phase with the strain divided by the strain. The ratio of these two moduli gives the loss tangent, $\tan(\delta) = E' / E''$.

The dynamic mechanical spectra of dry acetylated and untreated dry *Pinus radiata* wood test specimens are shown in Fig. 2.

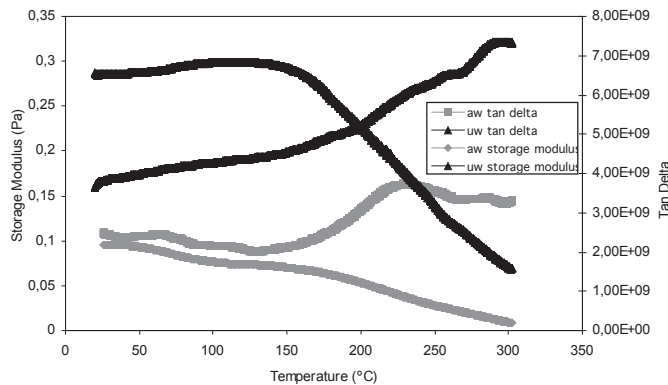


Fig. 2: Comparison of storage modulus and $\tan \delta$ of untreated dry wood (uw) and acetylated dry wood (aw)

These reveal important differences between dry acetylated and dry untreated wood. Whereas the storage modulus (E'') of dry untreated wood is constant from room temperature (30°C) to

150°C, the E'' of acetylated wood decreases in two stages. The first decrease in the modulus of acetylated wood occurs from 50°C to 100°C and the second from 150°C to the final temperature.

According to the literature, the decrease of E'' at temperatures greater than 0°C is associated with the α transition. The α transition is attributed to the initiation of micro-Brownian motion of large segments of polymeric chains in wood and corresponds to the T_g .

The thermal behaviour of E'' in acetylated wood shows a plasticizing effect due to the esterification reaction. This phenomenon produces a first decrease of the modulus at 50°C probably attributed to lignin and hemicellulose components and a second transition at higher temperatures (150°C) that is attributed to cellulose.

Dry untreated wood specimens exhibit a significant storage modulus increase over 150°C. Dry wood exhibits only very weak secondary relaxations, because, under these moisture conditions, the *in situ* T_g values for cellulose, hemicellulose and lignin occur at temperatures over 150°C. (Back and Salmén 1982).

When the test specimens of untreated and acetylated wood are tested using DMA analysis at room temperature with 10-12% moisture content, a substantial change occurs in the untreated wood.

Fig. 3 shows the effects of moisture on the storage modulus and $\tan \delta$ of untreated and acetylated wood.

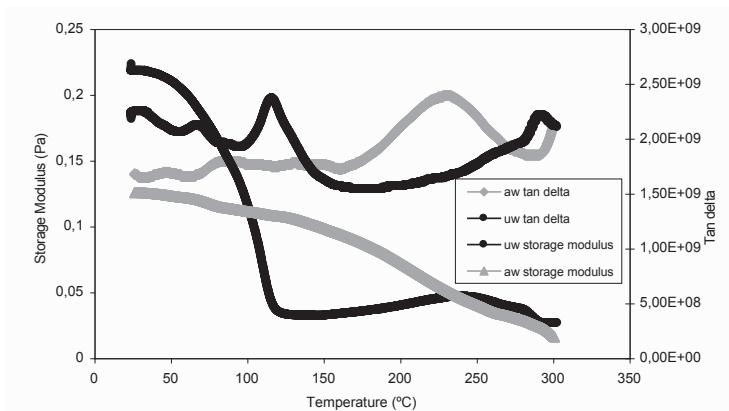


Fig. 3: Comparison of storage modulus and $\tan \delta$ of untreated wood (uw) and acetylated wood (aw) at 10% moisture content

It is possible to appreciate that although the storage modulus of acetylated wood is similar to that of dry acetylated wood (Fig. 2), the storage modulus of untreated wood decreases sharply from 50°C to 120°C. The T_g value of untreated wood with 10% moisture content clearly drops (with respect to dry wood), due to the presence of water molecules.

The presence of a low molecular weight species often serves to plasticize an amorphous polymer. Plasticization causes a reduction of the energy required to initiate chain mobility (Sun et al. 2007).

The DMA spectra of acetylated wood with 10% moisture content reveals remarkable similarities with the dry acetylated wood spectra. The DMA spectra in Figs. 2 and 3 show that the thermal behaviour of dry acetylated wood and acetylated wood with 10% moisture content do not exhibit differences in T_g values due to the plasticizing effect of the esterification process of wood.

Differential scanning calorimetry provides an additional method for studying the nature of

observed thermal transitions. Fig. 4 shows DSC scans made on milled, dry untreated and acetylated *Pinus radiata* wood with approximately 1 to 2% moisture content.

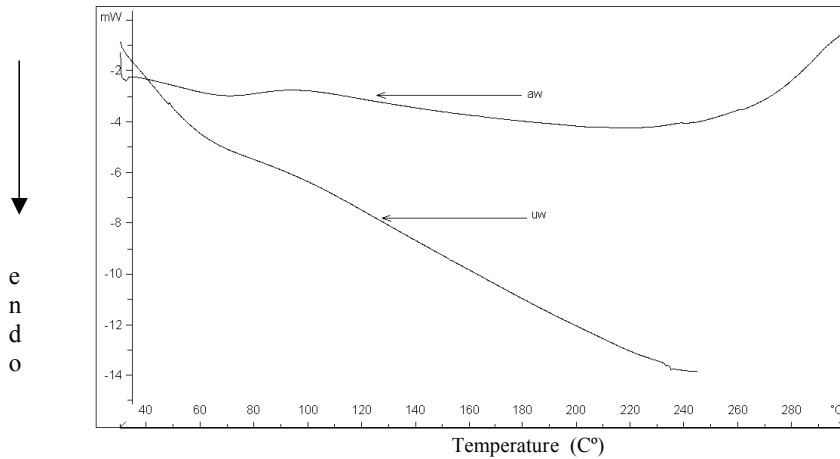


Fig. 4: DSC thermograms of dry untreated wood (uw) and acetylated dry wood (aw)

The thermograms show an endothermic peak at about 60°C for dry acetylated wood (aw). According to some researchers (Kelley et al. 1987), this phenomenon is the enthalpy relaxation attributed to the α thermal transition and corresponding to the T_g of wood, measured by DSC.

The relaxation peak at 60°C for acetylated wood agrees well with the storage modulus and $\tan \delta$ measured by DMA (Figs. 2 and 3).

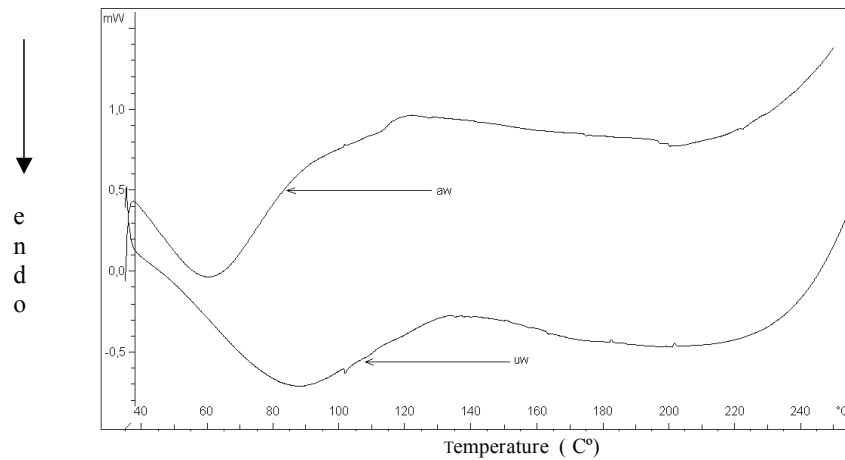


Fig. 5: DSC thermograms of untreated wood (uw) and acetylated wood (aw) with 10-12% moisture content

Untreated dry wood does not exhibit thermal transitions under 200°C detectable by DSC. This phenomenon also agrees with the thermal behaviour of dry untreated wood observed by DMA and shown in Fig. 2.

Fig. 5 shows DSC scans of acetylated (aw) and untreated wood (uw) with 10-12% moisture content.

It is evident that after the esterification reaction with acetic anhydride, the reduction of hydroxyl groups in wood resulted in a reduction of absorbed water in the cell walls. The vaporization heat of untreated wood, measured in the endothermic reaction, is 45 cal/g. This value decreases in acetylated wood to 28 cal/g.

In addition, the endothermic peak of acetylated wood is shifted to a lower temperature (60°C) than that of untreated wood, which has a broad endothermic transition, with a peak at about 90°C.

CONCLUSIONS

The experimental evidence obtained from the DMA and DSC studies, supports the identification of different behaviour for untreated and acetylated wood.

Dry wood shows a high-temperature transition at 150°C as its T_g value. This thermal transition can be attributed to cellulose, which has the highest softening temperature among the wood components.

In contrast, acetylated dry wood exhibits two thermal transitions: one from 50°C to 150°C, probably associated with the wood's amorphous components of lignin and hemicellulose, and a second one at 150°C attributed to cellulose.

At room temperature and 10-12% moisture content, the T_g of untreated wood decreases dramatically from 50°C to 120°C without any other thermal event and the thermal transition attributed to cellulose disappears at 150°C due to the plastification effect of water molecules.

At room temperature acetylated wood and dry acetylated wood exhibits similar behaviour in the DMA spectra, since the wood can be converted into thermoplastic materials by the esterification reaction with lower water absorption.

Otherwise, the DSC studies confirm that the esterification reaction decreases the water absorption in wood. The DSC studies also show the enthalpy relaxation phenomenon in acetylated dry wood attributed to the T_g of lignin and hemicellulose at 60 to 90°C. Untreated dry wood does not exhibit thermal changes detectable by DSC under 150°C.

Finally, the analysis of the relaxation processes of wood with both DMA and DSC techniques, has demonstrated that the acetylation reaction of wood decreases the T_g of dry wood. This phenomenon make it easier to use wood as thermoplastic material in other blends or composites, such as wood-plastic products.

ACKNOWLEDGEMENTS

This work was supported by grants from DIUBB 074206/3R and CIPA (Advanced Polymer Research Center).

REFERENCES

1. Back, E.L., Salmén, N.L., 1982: Glass transitions of wood components hold implications for molding and pulping processes. TAPPI 65(7): 107-110
2. Backman, A.C., Lindberg, K.A.H., 2001: Differences in wood material responses for radial and tangential directions as measured by dynamic mechanical thermal analysis. J. Mater. Sci. 36: 3777-3783
3. Birkinshaw, C., Buggy, M., Henn, G.G., 1986: Dynamic mechanical analysis of wood. J. Mater. Sci. Lett. 5: 898-900
4. Dias de Moraes, P., Rogauze, Y., Triboulot, P., 2004: Influence of temperature on the modulus of elasticity (MOE) of *Pinus sylvestris* L. Holzforschung 58: 143-147
5. Furata, Y., Aizawa, H., Yano, H., Norimoto, M., 1997: Thermal softening properties of water-swollen wood IV. The effects of chemical constituents of the cell wall on the thermal-softening properties of wood. Mokusei Gakkaishi 43: 725-730
6. Hon, D.N.S., 1989: Viscoelastic properties of thermoplasticized wood. TAPPI Proceedings, International Symposium on Wood and Pulping Chemistry. Atlanta. USA. Pp. 184-191
7. Irvine, G. M., 1984: The glass transitions of lignin and hemicellulose and their measurement by differential thermal analysis. TAPPI Journal 67: 118-121
8. Kelley, S.S., Rials, T.G., Glasser, W.G., 1987: Relaxation behavior of the amorphous components of wood. J. Mater. Sci. 22: 617-624
9. Laborie, M.P.G., Salmén, L., Frazier, C.E., 2004: Cooperativity analysis of the *in situ* lignin glass transition. Holzforschung 58: 129-133
10. Obataya, E., Norimoto, M., Tomita, B., 2001: Mechanical relaxation processes of wood in the low-temperature range. J. Appl. Polym. Sci. 81: 3338-3347
11. Scandola, M., Ceccorulli, G., 1985: Viscoelastic properties of cellulose derivatives: 2. Effect of diethylphthalate on the dynamic mechanical relaxations of cellulose acetate. Polymer 26: 1958-1967
12. Sun, N., Das, S., Frazier, C.E., 2007: Dynamic mechanical analysis of dry wood: Linear viscoelastic response region and effects of minor moisture changes. Holzforschung 61: 28-33
13. Sun, X.F., Sun, R.C., 2002: Comparative study of acetylation of rice straw fiber with or without catalysts. Wood Fiber Sci. 34(2): 306-317

JUSTO LISPERGUER
Bío-Bío UNIVERSITY
FACULTY OF SCIENCES
AVDA. COLLAO 1202
CONCEPCIÓN
CHILE
E-mail: jlisperg@ubiobio.cl

CYNTHIA DROGUETT
Bío-Bío UNIVERSITY
FACULTY OF SCIENCES
AVDA. COLLAO 1202
CONCEPCIÓN
CHILE

BEATRIZ RUF
Bío-Bío UNIVERSITY
FACULTY OF SCIENCES
AVDA. COLLAO 1202
CONCEPCIÓN
CHILE

