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CURING OF A PHENOL–FORMALDEHYDE–TANNIN ADHESIVE IN THE PRESENCE OF WOOD

Analysis by differential scanning calorimetry

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The curing of a phenol–formaldehyde–tannin (PFT) adhesive in the presence of pine or eucalyptus wood has been studied using differential scanning calorimetry. The influence of the adhesive/wood ratio on the activation energy (E_a), the temperature of the maximum of the exothermic peak (T_p) and the enthalpy of the curing process (ΔH) was analysed. E_a, T_p and ΔH of the curing reaction decreased when wood was added in the curing system. The adhesive/wood interaction did not depend significantly on wood species.

Keywords: *activation energy, adhesive/wood interaction, curing enthalpy, DSC, phenol–formaldehyde–tannin adhesive*

Introduction

In order to evaluate the performance of thermosetting adhesives on wood bonding, several studies have been conducted which analyse the effect of wood/adhesive interaction using different techniques: Thermomechanical analysis [1]; differential scanning calorimetry, alone [2, 3] or combined with thermogravimetric analysis [4] and/or FTIR spectroscopy [4, 5]; dynamic thermomechanical analysis [6] or the rate of bond strength development [7]. The influence of wood species has been also considered [5, 8].

Phenol–formaldehyde–tannin (PFT) adhesives have been developed employing tannins extracted from *Pinus Pinaster* bark with promising results in plywood manufacture. With respect to conventional PF resins, these resins implied not only a reduction of the consumption of petrochemical phenol, which was replaced with tannins obtained from a renewable resource, but also the improvement of the application properties of the adhesive [9]. In a previous work [10], the curing kinetics of a PFT adhesive was studied by DSC using the model-free kinetics isoconversional method [11] and compared to a commercial phenol–formaldehyde (PF) resin. The kinetic calculations predicted that the PFT resin cures faster than the PF resin, which allows the use of shorter press times, implying a higher productivity. In order to have a more realistic approach of the real resin curing process in wood bonding, the influence that the presence of wood has on the curing behaviour of a PFT adhesive has been analysed in this paper.

Experimental

Adhesive formulation

A phenol–formaldehyde–tannin (PFT) adhesive was prepared by copolymerisation at room temperature of *Pinus pinaster* bark tannins with a phenol–formaldehyde (PF) resol.

Pine bark tannins were obtained by alkaline extraction under the conditions that in a previous work [12] led to the highest formaldehyde-condensable polyphenol yield: NaOH concentration 5% (based on o.d. bark), solid–liquid/ratio 1/6 (mass/mass) and temperature 363 K.

PF resols were prepared using the following molar ratios: phenol/formaldehyde, F/P=2.0 and sodium hydroxide/phenol, S/P=0.5, and a theoretical solids content of 47% (40% measured). The reaction was conducted at 363 K and the evolution was followed by measuring the viscosity at 298 K. Two fractions were separated with viscosities of 100 and 300 mPa s (R100 and R300 resols, respectively).

The resols were mixed in the ratio R300/R100, 60:40 (by mass) to give a resol with a viscosity at 298 K of 197 mPa s. Then, tannins, which represented a 10% by mass of the PFT adhesive, water and sodium hydroxide (1% by mass of the resol) were added and the mixture was allowed to react overnight at room temperature prior to thermal characterisation. In short, the PFT formulation was as follows (in % by mass of PFT): R300, 43.5%; R100, 28.9%; pine bark tannins, 10%; water, 16.9% and sodium hydroxide, 0.7%.

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The rheological behaviour of the PFT adhesive at 298 K was studied using a Brookfield DVII+ viscometer with the small sampler adapter. The Ostwald de Waele rheological parameters, the power law index (n) and the consistency index (k), were obtained at different times from adhesive preparation to thermal characterization.

Preparation of wood/adhesive samples

Wood samples (2.5×2.5×1 mm) cut from *Eucalyptus globulus* and and *Pinus pinaster* rotary peeled veneers (8–9% dry basis) were dipped in the PFT adhesive and, once wetted, some of the excess was removed to attain different adhesive/wood mass ratios. Experiments were made from 30 to 100% of the PFT adhesive (g PFT adhesive/(100 g (wood+PFT adhesive)). Samples were prepared at regular intervals so that the wetting time before the DSC scan was approximately the same for all of them (approximately 15 min).

DSC experiments

DSC data were obtained with a Mettler-Toledo DSC 821^e apparatus equipped with a sample robot and the STAR^e software. The sample was sealed under air in a 120 μL medium pressure stainless steel crucible with a Viton O-ring which can withstand pressures up to 2 MPa. The temperature was scanned from 298 to 473 K at a heating rate of 10 K min^{-1}. Temperature and enthalpy calibrations were performed with indium.

Results and discussion

The power law parameters of the TPF adhesive for different times at room temperature since its preparation are shown in Fig. 1. As it has been found previously for other adhesive systems containing tannins [9], the PFT adhesive showed a pseudoplastic behaviour (n<1) which was more pronounced with increasing time. A significant increase of the apparent viscosity (proportional to k) with time was also observed, which demonstrated that a copolymerisation reaction proceeded at room temperature prior to thermal characterization.

Figure 2 shows the DSC scans obtained at a heating rate of 10 K min^{-1} for the TPF adhesive alone and for different adhesive/wood ratios of the PFT adhesive with pine wood. All the curves presented a single exothermic peak, whose maximum is found between 415 K (PFT adhesive) and 406 K depending on the adhesive/wood ratio. The position of the maximum (T_p) was shifted towards lower temperatures when the percentage of adhesive decreased below 65% independently of the wood species, pine or eucalyptus (Fig. 3), as also found by Vick and Christiansen [2] for mixtures of southern pine with a PF adhesive.

The activation energy of the curing process (E_a) was calculated using the Borchardt and Daniels kinetic model (n-order kinetics) and its variation in function of the percentage of PFT adhesive in the mixture is shown in Fig. 4. It is observed that E_a decreased when the % of wood in the sample increased, this suggesting that wood enhances the resin curing reaction, which is also supported by the decrease of T_p. As reported before for T_p, there has not been a significant influence of the wood species, softwood or hardwood, on the variation of E_a with the PFT adhesive/wood ratio.

This behaviour can be explained, as suggested by Pizzi *et al.* [4] and Pizzi and Panamgama [3], considering that when the resin cures on a wood surface

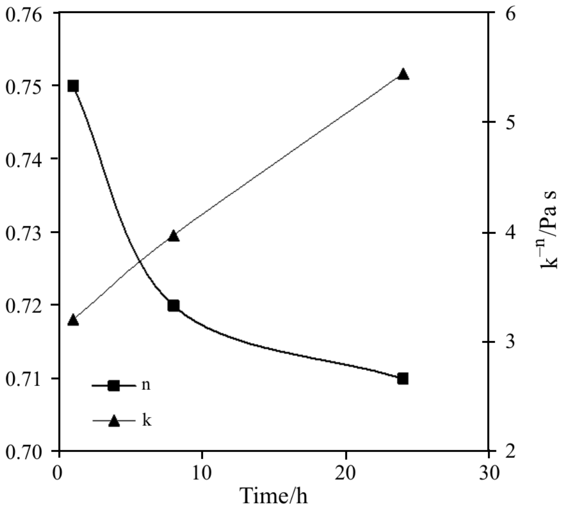

Fig. 1 Power law parameters of the PFT adhesive in function of time at room temperature

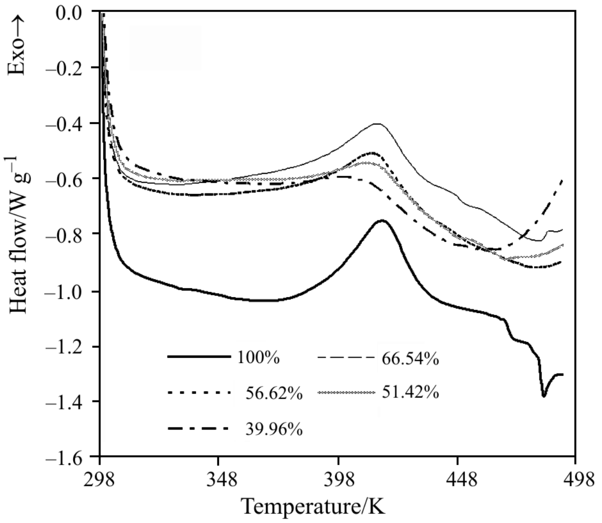

Fig. 2 DSC scans of the PFT adhesive alone and with different percentages of *Pinus pinaster* wood

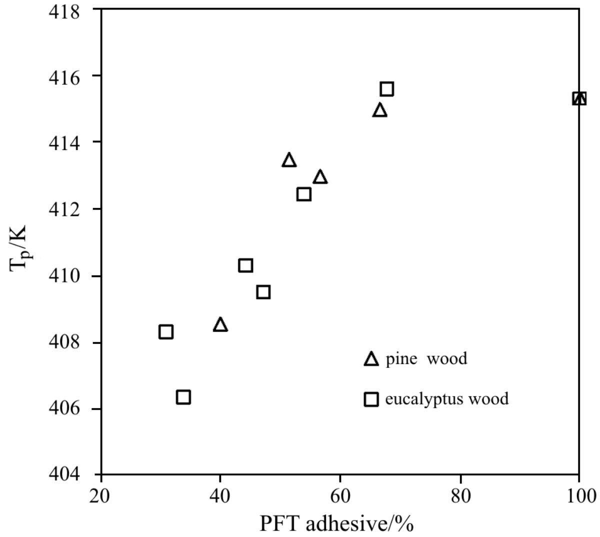

Fig. 3 Temperature of the maximum of the exothermic peak (T_p) in function of the percentage of PFT adhesive for pine and eucalyptus wood

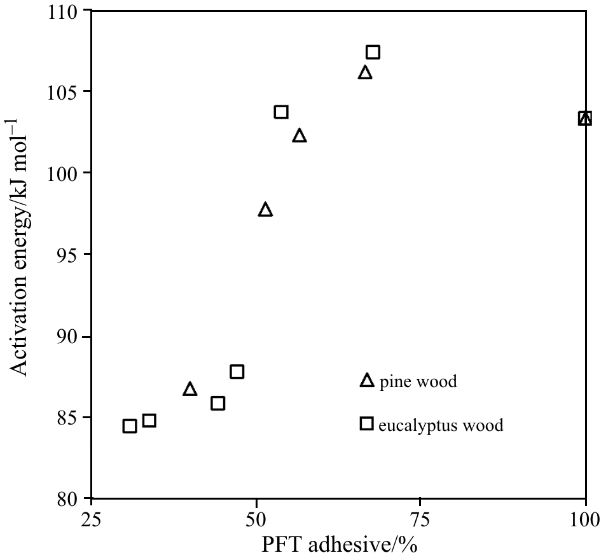

Fig. 4 Activation energy (E_a) of the curing reaction in function of the percentage of PFT adhesive for pine and eucalyptus wood

two effects are present: the catalytic activation of the resin self-condensation induced by carbohydrates and the formation of resin/substrate covalent bonding induced by lignin, the former being the most significant in the curing of thermosets. On the contrary, other authors [5, 7] found an increase of the activation energy when a PF resin cures in the presence of various wood species, or that, depending on the wood species, adhesive curing may be enhanced or inhibited, which is reflected in a decrease or an increase of the activation energy of the curing reaction, respectively [8].

Finally, Fig. 5 shows the variation of the curing enthalpy with the percentage of PFT adhesive. It is observed that for both wood species, reaction enthalpy decreases when wood is added in the curing system, as also found by He and Riedl [5] for a PF resin. Considering a proportionality between ΔH and the cross-linking created, less heat release would suggest less cross-linking due to adhesive self-condensation in the presence of wood, but the appearance of adhesive/wood bonding with a lower enthalpy, which makes more significant the greater the percentage of wood in the sample.

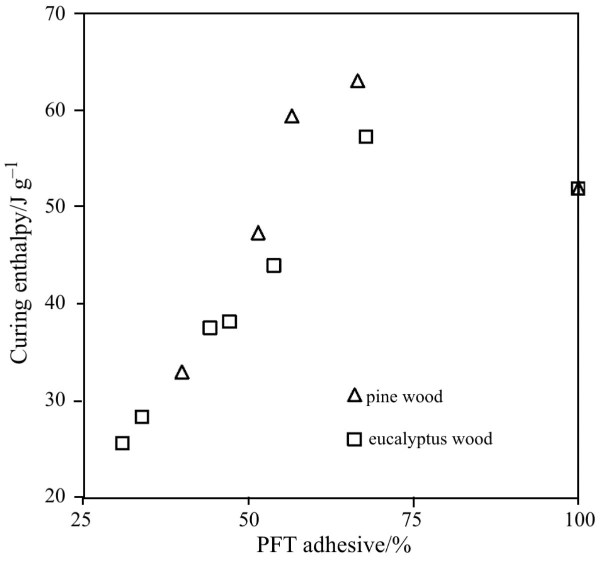

Fig. 5 Curing enthalpy (ΔH) in function of the percentage of PFT adhesive for pine and eucalyptus wood

Conclusions

The curing of a phenol–formaldehyde–tannin adhesive in the presence of wood has been studied and the main conclusions are as follows:

- Wood enhances the curing process of the PFT adhesive, which is supported by the decrease of the activation energy of the curing reaction, the temperature of the maximum of the exothermic peak and the curing enthalpy.
- The interaction between wood and the PFT adhesive did not depend on wood species, pine or eucalyptus.

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References

1 A. Pizzi, X. Lu and R. García, J. Appl. Polym. Sci., 71 (1999) 915.
2 Ch. B. Vick and A. W. Christiansen, Wood Fiber Sci., 25 (1993) 77.
3 A. Pizzi and L.A. Panamgama, J. Appl. Polym. Sci., 58 (1995) 109.
4 A. Pizzi, B. Mtsweni and W. Parsons, J. Appl. Polym. Sci., 52 (1994) 1847.
5 G. He and B. Riedl, Wood Sci. Technol., 38 (2004) 69.
6 L. Onic, V. Bucur, M.P. Ansell, A. Pizzi, X. Deglise and A. Merlin, Int. J. Adhes., 18 (1998) 89.
7 X.-M. Wang, B. Riedl, A. W. Christiansen and R. L. Geimer, Wood Sci. Technol., 29 (1995) 253.
8 H. Mizumachi and H. Morita, Wood Sci., 7 (1975) 256.
9 G. Vázquez, J. González-Álvarez and G. Antorrena, Recent Research Developments in Chemical Engineering, Transworld Research Network, Trivandrum 2000, p. 313.
10 G. Vázquez, J. González-Alvarez, S. Freire, F. López-Suevos and G. Antorrena, J. Therm. Anal. Cal., 70 (2002) 19.
11 P. Šimon, J. Therm. Anal. Cal., 76 (2004) 123.
12 G. Vázquez, J. González-Alvarez, S. Freire, F. López-Suevos and G. Antorrena, Holz Roh Werkst., 59 (2001) 451.

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