Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 19–28

CURING KINETICS OF TANNIN–PHENOL–FORMALDEHYDE ADHESIVES AS DETERMINED BY DSC

*G. Vázquez, J. González-Álvarez, F. López-Suevos, S. Freire and G. Antorrena**

Department of Chemical Engineering, Faculty of Chemistry, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

Abstract

Differential scanning calorimetry (DSC) was used to compare the thermal curing of two adhesives suitable for using in the manufacture of exterior-grade plywood boards: a commercial phenol–formaldehyde (PF) resin, and a tannin–phenol–formaldehyde (TPF) resin developed in our laboratory.

The experimental curves were well simulated by means of the Model Free Kinetics isoconversional method incorporated in the Mettler-Toledo STAR^e software package. The corresponding kinetic calculations predict that the TPF resin cures faster than the PF resin. This finding implies the possibility that the TPF resin may allow the achievement of higher productivity by permitting the use of shorter press times than with conventional PF resins.

Keywords: curing kinetics, DSC, phenolic resin, *Pinus pinaster* bark, tannins, tannin–phenol–formaldehyde resin

Introduction

The manufacture of plywood boards using commercial phenolic resins requires fairly strict operating conditions. The need for low moisture content in the wood – below 5% – not only implies important drying costs, but it also damages the plies, limiting their use. This is especially important in the case of eucalyptus wood due to the dimensional changes associated with moisture change. On the other hand, a rise in moisture content demands the reduction of press temperature, which implies time increase, and, consequently, a decrease in productivity. The solution to this problem would be the use of fast-curing adhesives.

Earlier work [1, 2] has proposed the use of *Pinus pinaster* bark tannins for the preparation of tannin–phenol–formaldehyde (TPF) adhesives for the manufacture of exterior grade eucalyptus plywood boards. This not only reduces petrochemical phenol consumption, replacing it with a renewable product, but also improves adhesive application properties.

* Author for correspondence: E-mail: eqgantor@usc.es

1418–2874/2002/ $ 5.00
© 2002 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Thermal analysis techniques have often been used to study and interpret the curing of thermostable adhesives and their kinetics. Curing rate is affected, apart from by formulation [3, 4], by the synthesis procedure [5] and by the presence of catalysts and other additives [6, 7]. Curing characteristics can affect resin properties such as stability, spreading and wood penetration capacity, fragility after curing, etc. thus conditioning its use in the factory. Even if dinamomechanical analysis (DMA) has been used to study curing from the point of view of its mechanical behaviour [8, 9] the difficulty in modelling the process has oriented most curing studies towards the use of differential scanning calorimetry (DSC).

The measurement of an extensive property such as the enthalpy in DSC does not allow its changes to be evaluated separately in function of the contributions of the simple reactions that take place. For this reason, DSC cannot be used to analyse the different reactions that take place during thermal transformation, especially in adhesive curing.

The most frequently used method in kinetic studies with DSC is based on the analysis of the curves obtained by a single heating rate, modelling the curing process through n order kinetics. The model, proposed by Borchardt and Daniels, is attractive due to its simplicity and, with one single experiment, gives the reaction temperature interval and the kinetic parameters: reaction order (n), activation energy (E) and preexponential factor (k_0). Even if the results obtained using a single heating rate serve to establish comparisons, the predicted conversions using the Borchardt and Daniels model are not very reliable, even for a single-step process, as one single experiment is used to define the kinetic triplet (E, k_0 and the n order kinetic equation) [10].

An approach that allows to avoid errors in E and k_0 prediction for a single-step process was suggested in the ASTM E698 standard. Accordingly several DSC experiments at different heating rates should be performed. This method allows the calculation of E without supposing a kinetic equation but the reliability of the predictions is very doubtful in the often occurring case when the process does not obey a first order reaction [10].

For complex (multi-step) reactions the form of the concentration function in the kinetic equation is complicated and generally unknown. This complexity can easily be detected from the conversion dependence of the activation energy, unattached to the reaction model, computed by the isoconversional method. A dependence of conversion on time at an arbitrary temperature, or a dependence of conversion on temperature at an arbitrary heating rate can be predicted without incorporating the kinetic model and the preexponential factor [11]. Vyazovkin and Sbirrazzuoli [12] have successfully applied the Model Free isoconversional method to study the kinetics of epoxy-anhydride cure and the results obtained were compared with those predicted by model-fitting methods.

The objective of this work is to characterise the thermal behaviour of TPF and commercial phenolic adhesives using DSC: The modelling of the curing kinetics not only allows us to establish comparisons but also to select the press operating conditions (temperature and time) for its industrial use in the manufacture of exterior-grade plywood boards.

Experimental

Extraction and concentration of tannins

Pinus pinaster bark from the debarking unit at a local sawmill was dried in the open air and ground in a hammer mill. Tannin extraction was carried out in the conditions which in a previous work [13] have given rise to the highest formaldehyde-condensable polyphenol yield, 19.8% (based on oven dried bark): NaOH concentration 5% (based on oven dried bark), solid/liquid ratio 1/6 (mass/mass), temperature 90°C and time 30 min. The extract obtained was concentrated by spray-drying.

Tannin–phenol–formaldehyde (TPF) adhesive

PF resols with a solids content of 38.4% and viscosities at 25°C of 100 (Resol 100) and 300 mPa s (Resol 300) were prepared using a formaldehyde/phenol molar ratio of 1.8 and a soda/phenol molar ratio of 0.45. These resols were blended to obtain one of intermediate viscosity ≈200 mPa s (Resol 200), made up of fractions of higher and lower molecular mass. A 37% (mass/mass) aqueous solution of the spray-dried pine bark tannins was prepared, and the resol (Resol 200) and the tannin solution were mixed at room temperature in the ratio necessary to obtain an adhesive with tannin content of 10% (by mass). The adhesive was left overnight to copolymerise at room temperature and then used for DSC measurements. Previous work [2] demonstrated that such reaction period is needed to attain a suitable viscosity level for the application of the adhesive in plywood manufacture.

Commercial resin

A commercial liquid phenol–formaldehyde resol resin (solids content, 46.7%; viscosity at 25°C, 345 mPa s) was also used for DSC analysis in order to compare its thermal behaviour with those of the synthesized resols and the TPF adhesive.

A filler should be added to this resin when used for plywood manufacture. Therefore, the influence of filler addition (22% of $CaCO_3$ and 8% of almond shell flour, based on resin) on adhesive curing has also been analysed.

Differential scanning calorimetry experiments

DSC measurements were carried out in a Mettler-Toledo DSC 821^e, equipped with a sample robot. A resin sample (10–15 mg) was sealed under air in a 120 μL medium pressure stainless-steel crucible with a Viton O-ring, which can withstand up to 2 MPa. The temperature range scanned was from 25 to 220°C with a heating rate of 5, 10 or 20°C min^{-1}. Temperature and enthalpy calibrations were performed with indium.

Data analysis was carried out with the STAR^e software furnished by Mettler-Toledo, which contains the Borchardt and Daniels kinetic model and the Model Free Kinetics isoconversional method developed by Vyazovkin [11].

Results and discussion

Figure 1 shows the DSC curves obtained at a heating rate of 10°C min^{-1} for the Resol 200, used as prepolymer for copolymerisation with the tannins, for the TPF resin and for the commercial resin, the latter also after the addition of filler.

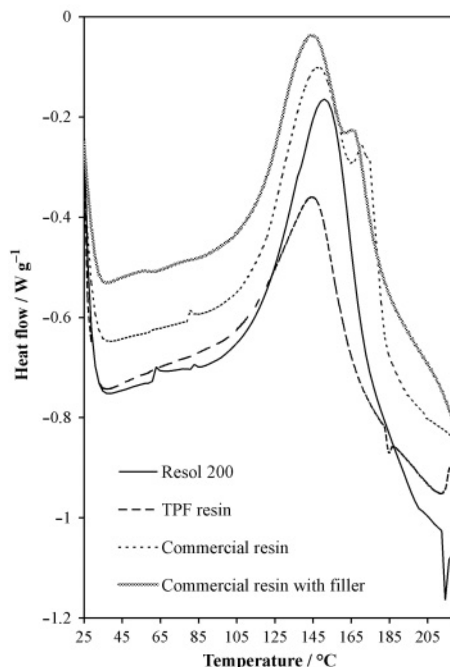

Fig. 1 DSC curves of different resin systems performed at a heating rate of 10°C min^{-1}

The curves present an exothermic peak, the maximum of which is found between 145 and 155°C, caused by the condensation of methylol groups with phenol to form methylene bridges and by the condensation of two methylol groups to form dibenzyl ether bridges [4]. The commercial resin presents a split peak with a second maximum at higher temperatures, which has been attributed to reactions such as the condensation of the dibenzyl ether bridges to methylene bridges eliminating formaldehyde, which demand higher temperatures as polymer mobility is reduced. Phillips *et al.* [8] found this split when using phenolic resins with solids contents above 45% and the separation of the peaks was more evident the higher the solids content. Holopainen *et al.* [4] found the split when increasing F/P ratio, the peaks being more separated the higher this ratio. The high concentration of methylol groups when F/P ratio increases enhances the formation of methylene and methylene ether bridges. The result is analogous to the one found when increasing solids content, mobility is reduced which makes condensation of dibenzyl ether bridges more difficult and the second peak is shifted to higher temperatures.

The position of the maximum corresponding to the first peak is shifted towards lower temperatures as resin condensation degree increases, for given solids content and formulation, or when filler is added due to increased resin viscosity as in the previous case.

Reaction enthalpy

Curing enthalpy (ΔH) resumes the process energetically with independence of the model used in interpreting it. The values obtained, based on resin solids, are shown in Table 1.

As can be seen, enthalpy increases with decreasing resin average molecular mass, or, which is the same thing, its viscosity or condensation degree for a given formulation. If we refer to an adhesive in application conditions, considering proportionality between ΔH and the crosslinking created, less heat released means less crosslinking and, as a consequence, reduced mechanical properties. In the case of the TPF adhesive, the lower ΔH values can be explained by two different reasons. Firstly, this adhesive has suffered a previous copolymerisation of a resol with the tannins, i.e. it is an advanced polymer with high viscosity, which implies fewer linking opportunities. Secondly, the tannins are oligomers that do not require excessive crosslinking to polymerise.

When the commercial resins with and without filler are compared, it is found that the higher ΔH value obtained in the first case can only be explained if the filler is not an inert additive. The resin-filler interaction is limited by diffusional processes, which are slower than resin crosslinking, with the result that the differences found between the values obtained in both series decrease with increasing heating rate and thus, for 20°C min^{-1}, they are practically identical.

For all the resin systems studied the reaction enthalpy decreased with increasing heating rate from 5 to 20°C min^{-1}. As seen previously the curing of phenolic resins is a complex process involving several competing reactions. These reactions have different activation energies and also different enthalpies. When heating rate increases the whole process shifts to higher temperatures. An increase in temperature speeds up more the reaction with the highest activation energy and, therefore, the relative contribution of this reaction to the overall reaction rate (i.e. overall heat flow measured in DSC) increases when the heating rate increases. The decrease in the overall reaction enthalpy with the heating rate indicates that the reaction with greater activation energy has smaller enthalpy.

Due to its influence on press operation, the variations in reaction enthalpy related to heating rate have to be noted. With regard to TPF resin, decreases of approx. 10% are obtained when the rate is doubled, as compared with the higher ones observed in the commercial resin in application conditions, that is, after filler addition. Consequently, for the commercial resin, and apart from of other types of limitations in use, high press temperatures lead to reduced bond strength as compared with low temperatures, and thus mechanical properties improve when operating at low temperatures using long press times. This effect is less pronounced for the TPF resin, which

Table 1 Kinetic parameters of different resin systems evaluated by Borchardt and Daniels' method

	Solid content/%	Heating rate/°C min^{-1}	ΔH/J g^{-1} resin solids	Peak temperature/°C	n	E/kJ mol^{-1}	$\ln k_0$
Resol 100	38.4	10	451.8	152.6	1.02	88.05	20.23
Resol 300	38.4	10	319.1	151.9	1.01	98.53	23.27
Resol 200	38.4	10	360.5	151.8	1.03	97.13	22.98
TPF Resin	38.0	5	237.5	135.1	0.95	74.83	16.69
		10	214.3	145.5	1.05	98.19	23.76
		20	192.0	157.6	0.99	102.57	24.79
Commercial resin*	46.7	5	359.1	134.1, 161.2	0.99	114.45	28.88
		10	292.2	145.5, 170.5	0.99	124.91	31.67
		20	268.4	157.4, 183.2	1.01	136.95	34.78
Commercial resin*+filler	59	5	430.6	129.6, 152.9	1.09	126.77	32.97
	36 resin	10	351.1	142.5, 164.9	1.07	139.03	36.15
	23 filler	20	269.4	152.5, 176.7	1.17	151.62	39.42

*n, E and $\ln k_0$ for the first peak

indicates that crosslinking and, therefore, mechanical properties are less affected by press temperature changes.

Curing kinetics

Even if the single-heating rate method gives ambiguous values of the kinetic parameters, it has been the method habitually used to analyse the curing process of phenolic resins. With a view to establishing comparisons with the results offered by other researchers, we have determined the Arrhenius parameters, E and k_0, and the reaction order using the Borchardt and Daniels method applied to the DSC curves obtained (Table 1).

The reaction orders corresponding to resols and TPF resin curing are practically equal to 1, in agreement with those obtained for the condensation stage of other PF resins and of the *o*-hydroxymethyl–phenol [6, 14].

Activation energy varies between 88 and 98 kJ mol^{-1} for the resols with different condensation degrees, which are values close to those obtained for the condensation of *o*-hydroxymethyl-phenol by Sprung and Gladstone [14] by a titration method, 77.4 kJ mol^{-1}, and by Sebenik *et al.* [6] by DSC at a heating rate of 4°C min^{-1}, 94.2 kJ mol^{-1}. Sebenik *et al.* [6] hint that the differences found between activation energy values for the condensation of *o*-hydroxymethyl-phenol, 94.2 kJ mol^{-1}, and for the condensation stage in the reaction between phenol and formaldehyde, 65.7 kJ mol^{-1}, both in the presence of 1% NaOH, are due to the existence, in the latter case, of a mixture of compounds, even if one of them is the dominating one.

For the TPF resin, values between 75 and 103 kJ mol^{-1} have been obtained, dependent on the heating rate used. The fact that activation energy changes with heating rate suggests that this is a multi-step process, i.e. that simultaneous reactions take place. When heating rate is increased, the exothermic peak moves towards higher temperature values, favouring the reaction of higher activation energy and therefore increasing the global one observed.

The split in the exothermic peak observed in the DSC curves of the commercial resin is an indication – which has not been previously detected – that curing is a multi-step process. Borchardt and Daniels' method has been applied to the first of the peaks, and n-values have been obtained that are practically equal to 1 and slightly higher after filler addition, which can be due to filler-adhesive interaction. Activation energy also varies with heating rate and values between 114 and 152 kJ mol^{-1} have been obtained.

A fact to be pointed out is the great variability in the values obtained for reaction order and activation energy for the curing reaction of phenolic resins: n=1.3 and E= 126.3 kJ mol^{-1} [15]; n=1.7 and E=121 kJ mol^{-1} [7]; n=2–2.1 and E= 110.6–124.6 kJ mol^{-1} [5]; n=2.1–2.7 and E=142.1–215.9 kJ mol^{-1} [16]. The differences in results are due to the chemical behaviour of the resin, which depends on formulation, on the preparation method or on the addition of stabilisers with a view to lengthening the pot life for industrial use. These divergences reflect and emphasise the multi-step character of the curing process, evidencing the necessity to use isoconversional methods.

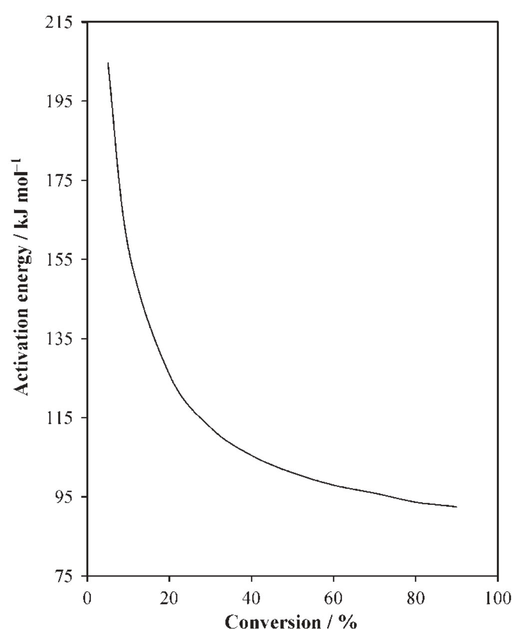

Fig. 2 Conversion dependence of the activation energy for the TPF resin calculated by means of the isoconversional method

Figure 2 shows conversion dependence of the activation energy for the curing process of the TPF resin, obtained with the Model Free Kinetics isoconversional method. The fact that activation energy does not remain constant, something that was also found for resols and commercial resin curing, shows that these are complex (multi-step) processes [10]. A decrease of the effective activation energy with the extent of cure has been earlier reported for the cure of an epoxy-novolac resin under non-isothermal conditions [17]. This dependence has been interpreted in terms of a kinetic model that accounts for viscous relaxation in the initial cure stages [18].

Figure 3 shows the curves obtained for the commercial resin at heating rates of 5, 10 and 20°C min^{-1}, and the corresponding simulated DSC curves using Model Free Kinetics. The excellent concordance observed in all cases warrants the results obtained for curing degrees in function of time, which are shown in Fig. 4 for a temperature of 130°C, habitually used in the manufacture of plywood boards with phenolic resins.

The differences observed could be explained qualitatively with the curves obtained (Fig. 1). The commercial resin presents its first maximum at lower temperature values that the laboratory resol, but the curing reaction extends to higher temperature values, which explains the necessity for longer times for complete curing. The resol and commercial resin curing rates are clearly lower than that of the TPF resin. Due to the fact that commercial resin needs the addition of filler for plywood board manufacture in order to adapt viscosity and improve spreading, comparisons between this resin and TPF adhesive show that the latter exhibits a higher curing rate for any conversion value.

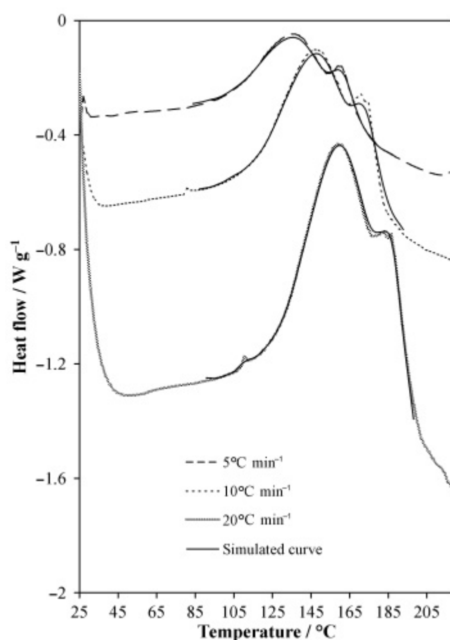

Fig. 3 Comparison between the experimental DSC curves obtained for the commercial resin at 5, 10 and 20°C min^{-1} and the simulated ones by means of the isoconversional method

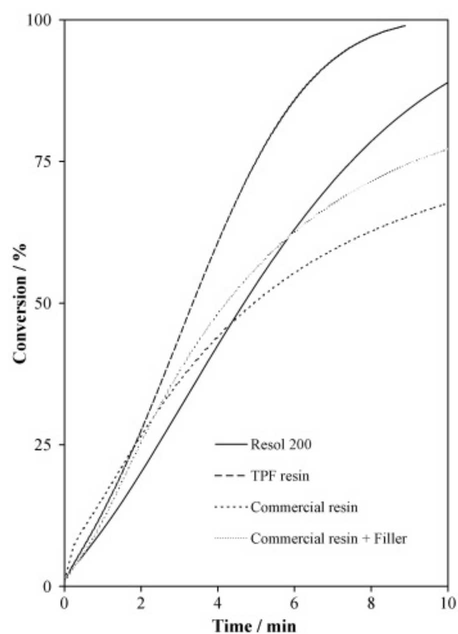

Fig. 4 Comparison of the conversion rates at 130°C for different resin systems predicted by the isoconversional method

Preliminary manufacturing tests in pilot plant have been carried out with eucalyptus plywood boards, where TPF resin was found to have higher curing rate, in accordance with the predictions made with Model Free Kinetics. This is a great advantage from the industrial point of view as it allows for shorter press times for a given temperature, and therefore increases productivity.

Conclusions

DSC data obtained for PF and TPF adhesives have been used to study the kinetics of the curing process using the Model Free isoconversional method.

The decrease of the effective activation energy with the extent of cure for the TPF adhesive has been attributed to the decrease of viscosity in the initial cure stages. This favours the rheological behaviour of the adhesive in the hot-press, which is an advantage for its application in the manufacture of wood derivatives.

The results obtained for the conversion dependence on time show that the TPF adhesive cures faster than the commercial PF adhesive, this permitting to shorten the press time and therefore to increase the productivity.

* * *

This work was supported by the CICYT (Project AGF98-0369).

References

1 G. Vázquez, G. Antorrena, J. González and J. C. Alvarez, Holz-Roh Werkstoff, 54 (1996) 93.
2 G. Vázquez, J. González and G. Antorrena, Recent Res. Dev. Chemical Eng., Vol. 4 Part I, S. G. Pandalai, Ed., Transworld Research Network, Trivandrum 2000, p. 313.
3 A. W. Christiansen and L. Gollob, J. Appl. Polym. Sci., 30 (1985) 2279.
4 T. Holopainen, L. Alvila, J. Rainio and T. T. Pakkanen, J. Appl. Polym. Sci., 66 (1997) 1183.
5 B.-D. Park, B. Riedl, E. W. Hsu and J. Shields, Holz-Roh Werkstoff, 56 (1998) 155.
6 A. Sebenik, I. Vizovisek and S. Lapanje, Eur. Polym. J., 10 (1974) 273.
7 J. M. Garro-Gálvez and B. Riedl, J. Appl. Polym. Sci., 65 (1997) 399.
8 E. K. Phillips, W. D. Detlefsen and F. E. Carlson, Proc. Wash. State Univ. Int. Particleboard/Compos. Mater. Symp. 1991, 25th, p. 231.
9 L. F. Lorenz and A. W. Christiansen, Ind. Eng. Chem. Res., 34 (1995) 4520.
10 S. Vyazovkin and W. Linert, Anal. Chim. Acta, 295 (1994) 101.
11 S. Vyazovkin, Int. J. Chem. Kinetics, 28 (1996) 95.
12 S. Vyazovkin and N. Sbirrazzuoli, Macromol. Chem. Phys., 200 (1999) 2294.
13 G. Vázquez, J. González-Alvarez, S. Freire, F. López-Suevos and G. Antorrena, Holz-Roh Werkstoff, 59 (2001) 451.
14 M. M. Sprung and M. T. Gladstone, J. Am. Chem. Soc., 71 (1949) 2907.
15 L. Calvé, G. C. J. Mwalongo, B. A. Mwingira, B. Riedl and J. A. Shields, Holzforschung, 49 (1995) 259.
16 B.-D. Park, B. Rield, H.-J. Bae and Y. S. Kim, J. Wood Chem. Technol., 19 (1999) 265.
17 S. Vyazovkin and N. Sbirrazzuoli, Macromolecules, 29 (1996) 1867.
18 S. Vyazovkin and N. Sbirrazzuoli, Macromol. Chem. Phys., 201 (2000) 199.