Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 3, 797–802

TRANSFORMATION OF DYNAMIC DSC RESULTS INTO ISOTHERMAL DATA FOR THE CURING KINETICS STUDY OF THE RESOL RESINS

M. V. Alonso[1]*, *M. Oliet*[1], *J. García*[1], *F. Rodríguez*[1] *and J. Echeverría*[2]

[1]Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain
[2]Hexion Ibérica, Carretera a Navarra, Epele 39, 20120 Hernani, Guipúzcoa, Spain

Kinetics of thermosetting polymers curing is difficult to study by isothermal methods based on the differential scanning calorimetry (DSC) technique. The difficulty is due to the low sensitivity of the equipment for total reaction heat measurements during high temperature process. The aim of this paper is to display the equivalence between a dynamic model, the Ozawa method, and an isothermal isoconversional fit, which allows predicting the isothermal behavior of the resol resins cure through dynamic runs by DSC. In this work, lignin–phenol–formaldehyde and commercial phenol–formaldehyde resol resins were employed. In addition, the isothermal kinetic parameters for both resins were performed by means of transformation of the data obtained from the dynamic Ozawa method.

Keywords: *curing kinetics, phenolic resin, thermal analysis*

Introduction

Phenol–formaldehyde (PF) resol resins are usually used as adhesive for the manufacture of boards, but the high cost of these polymers have given arise to new alternatives such as the partial replacement of phenol by natural products (lignin, lignosulfonate, tannin, etc.) [1–4]. The physical properties of both polymers depend on the molar ratio of reagents, the catalyst type, and the operating conditions. In order to obtain a resin with high performance applications other important factors should be also considered as the curing degree, time, and temperature of curing process. For this reason, the curing kinetics of these materials is necessary to study.

Different methods for the determination of the curing kinetics of thermosetting polymers have been developed. In most cases, it is difficult to derive a mechanistic model because the resin cure reaction is very complex. Thus, empirical models are preferred to study the cure kinetics [5]. One of the main problems when a resol resin is cured lies in the difficulty of finding a method that encompasses a wide experimental range of temperatures. If isothermal methods are used it is not possible to conduct the reaction at very high temperatures, since part of the total reaction heat is lost during the stabilization time and so high conversions can not be attained. If the reaction is carried out at very low temperatures, some of this heat is likewise lost, since the sensitivity threshold of the appliance is low [5, 6]. Dynamic methods do not usually present these problems, but in some cases they are not equivalent to isothermal ones. The kinetic parameters of polymers curing can vary greatly according to the method used.

The activation energy not only changes with the method employed but also with the conversion degree, which indicates that no single kinetics can be used for the overall curing process. It has been observed that of all the kinetic methods used, the isoconversional ones are the most accurate, since they reveal changes in the resins curing kinetics [7–10]. Among isoconversional methods, the most reliable results are obtained using the Arrhenius law and Ozawa method for isothermal and dynamic curing, respectively [11]. The aim of this paper is to show that both methods are equivalent. Thus, the Ozawa's fits at different curing degrees of resins allowed obtaining data, which were then fitted to Arrhenius law. The isothermal adjustments with the Arrhenius expression (Eq. (7)) were calculated and compared the data obtained by this way with those attained by isothermal experiments. Dynamic Ozawa model presents as main advantages: its both capability to reach high conversions (α=100%) at high temperatures and to detect the total reaction heat.

Kinetic model

Ozawa isoconversional method was employed to calculate the kinetic parameters of lignin–phenol–formaldehyde (LPF) and phenol–formaldehyde resol resins. The Ozawa method, which was the model chosen from among the different isoconversional methods, is based on the following expression:

$$\log\beta = A' - 0.4567\frac{E_a}{RT} \tag{1}$$

---

* Author for correspondence: valonso@quim.ucm.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

where, β is the heating rate (K min^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant (8.31 J mol^{-1} K^{-1}), T is the temperature (K), and A' can be expressed as:

$$A' = \log\left[\frac{k_0 E_a}{g(\alpha)R}\right] - 2.315 \tag{2}$$

where α is the degree of cure, k_0 is the pre-exponential factor of Arrhenius law, and $g(\alpha)$ is a function of curing degree.

From A' and E_a values obtained from Eq. (1) for different resins curing degrees are possible to determine a new constant, A, which can be written as:

$$A = \ln\left[\frac{g(\alpha)}{k_0}\right] \tag{3}$$

The source of Eq. (1) is based on a typical reaction rate expression that can be expressed as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{4}$$

where t is the time, α is the degree of conversion, $k(T)$ is the rate constant, that depends on temperature according to Arrhenius law, and $f(\alpha)$ is a function of curing degree, which depends on the kinetic model applied. The integral form of the Eq. (4) can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k_0 e^{-E_a/RT} dt \tag{5}$$

If the Eq. (5) is integrated from a curing time of t=0 where α=0 to a time t for a curing degree of α, the expression obtained is:

$$g(\alpha) = k_0 e^{-E_a/RT} t \tag{6}$$

In order to determine the kinetic parameters by means of isothermal runs and to transform the dynamic data into isothermal results, the Eq. (6) can be rearranged and expressed as:

$$\ln t = A + \frac{E_a}{RT} \tag{7}$$

The parameter 'A' of the Eq. (7) is the same of the Eq. (3), accepting equal kinetics in dynamical and isothermal experiments. In both equations, A is a function of $g(\alpha)$ and k_0 and consequently, only a function of resin curing degree.

Experimental

Materials

Phenol–formaldehyde commercial resol resin tested was supplied from Hexion Ibérica (Spain). This product was obtained by the polymerization between phenol and formaldehyde in alkaline medium (sodium hydroxide). The softwood ammonium lignosulfonate employed for the partial replacement of phenol in the lignin–phenol–formaldehyde resin was provided by Borregaard Deutschland.

Preparation of lignin-phenolic resin

Lignin–phenol–formaldehyde resin was synthesized in the laboratory with a methylolated softwood ammonium lignosulfonate. The optima conditions of methylolation and formulation of lignin–phenolic resins were reported in previous works [12, 13].

Methods

The calorimetric measurements of both resins (PF and LPF) were performed on a Mettler Toledo DSC 821^e calorimeter. The pressure medium pans (ME-26929), with a volume of 120 μL, can withstand vapour pressures up to 10 MPa. To minimize the effect of mass variations of the sample, the different curves were normalized, by the calorimeter, at 1 g. Later, the baseline 'spline' was subtracted from the original curve. Thus, it is possible to calculate the total and partial heats, the cure degrees and the reaction rates for the curing process of both resins.

The Ozawa's isoconversional method was applied with nine heating rates (2, 4, 6, 8, 10, 12, 14, 16, and 20°C min^{-1}) in a scanning temperature range from 30 to 250°C. Then, the results determined by dynamic DSC were mathematically transformed for obtaining the isothermal data. These results, degree of conversion *vs.* time, were compared with direct isothermal data.

The isothermal DSC runs were carried out at the following temperatures: 110, 120, 130, 135 and 140°C for 30 min. Later, the sample was cooled below 0°C and as under these circumstances the resin was not fully cured, it was necessary to realize a scan second in the same operating conditions to obtain the total curing heat for each sample.

Results and discussion

As mentioned above, the samples of the LPF and PF resol resins were cured at different heating rates by DSC. The typical curves of both resins are exhibited in Fig. 1. The values of constant A' and activation energy at different curing degrees of both resol resins were calculated through the Ozawa isoconversional method (Eq. (1)). The results obtained for both resins have been employed as starting point in this study.

The data of A', A and E_a for the resol resins studied at different conversion degrees are shown in Table 1. The values of A', E_a, and A were obtained by the Ozawa isoconversional method (dynamic DSC). From E_a and A, it can be established by the Eq. (7) isothermal fits of these starting data for the LPF and PF resins cure. The results obtained are plotted in Figs 2 and 3, which show the conversion degree *vs.* the curing time at different temperatures for the LPF and PF resol resins, respectively. The curing temperature values were selected according to the usual range employed (110–140°C) in order to cure the resol resins as adhesive in the plywood manufacture [14–16].

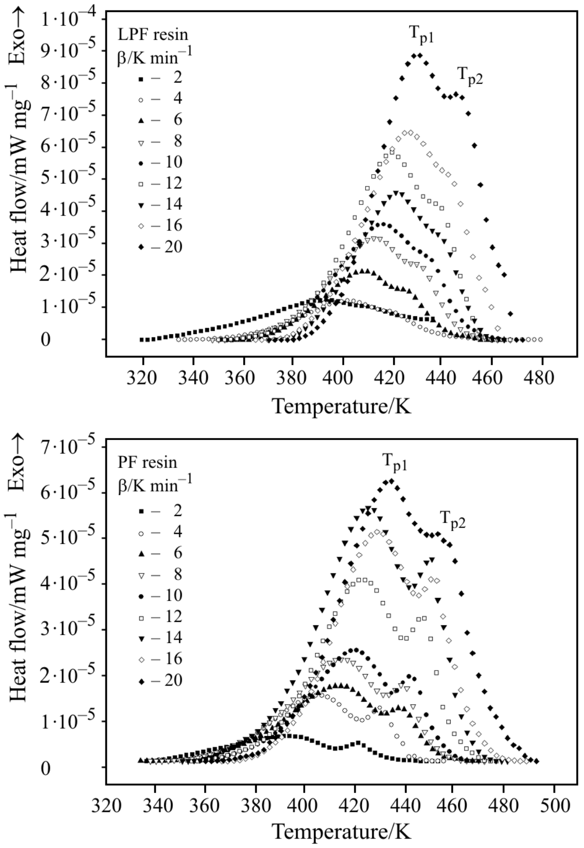

Fig. 1 Typical DSC curves of LPF and PF resol resins

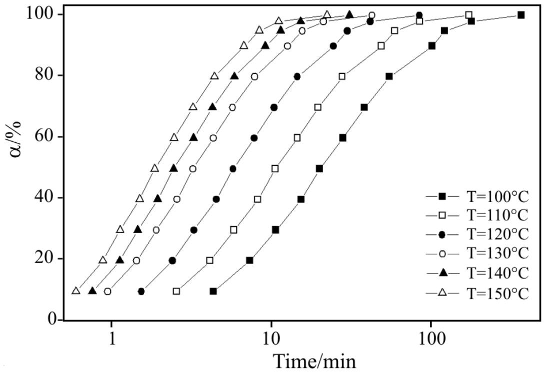

Fig. 2 Conversion degree of LPF resol resin cure *vs.* operating time

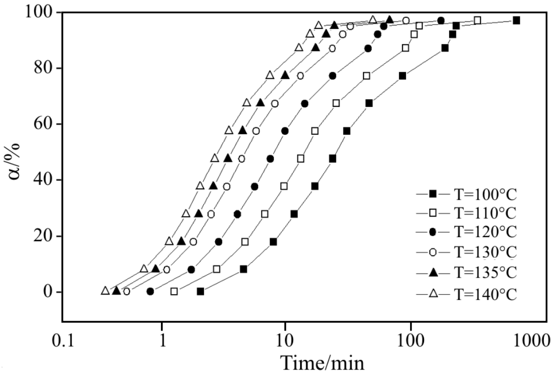

Fig. 3 Conversion degree of PF commercial resol resin cure *vs.* operating time

Table 1 Kinetic parameters of the LPF and PF resol resins cure determined by the Ozawa's dynamic method

α/%	LPF resin				PF resin			
	A'	E_a/kJ mol^{-1}	A^*	R^2	A'	E_a/kJ mol^{-1}	A^*	R^2
2	707.54	2258.2	–	0.997	9.46	58.42	–18.26	0.973
10	9.80	63.33	–18.96	0.989	9.54	61.42	–18.39	0.984
20	10.23	67.80	–19.88	0.995	9.71	64.25	–18.73	0.992
30	10.67	71.93	–20.83	0.994	9.88	66.61	–19.09	0.992
40	10.93	74.76	–21.38	0.992	10.32	70.80	–20.04	0.993
50	11.02	76.20	–21.58	0.995	10.48	72.90	–20.38	0.990
60	11.13	77.95	–21.81	0.994	10.36	72.90	–20.10	0.990
70	11.20	79.37	–21.96	0.994	10.60	75.84	–20.62	0.993
80	11.28	80.99	–22.12	0.987	11.18	81.71	–21.88	0.994
90	11.87	86.90	–23.41	0.990	12.07	90.30	–23.83	0.990
95	11.62	85.70	–22.84	0.993	11.68	88.05	–22.96	0.986
98	11.94	89.07	–23.54	0.991	11.18	84.79	–21.84	0.983
100	11.72	89.74	–23.04	0.959	11.23	88.61	–21.91	0.948

The main advantage of transforming the dynamical data for resol resins into isothermal data is the possibility to obtain the curves α–*t* (Figs 2 and 3) at any curing temperature of interest. So that it facilitates the calculation of the curing kinetics for a wide range of temperatures. This is not always possible using isothermal methods [6, 17]. Moreover, this procedure saves time as it requires fewer trials compared to isothermal methods.

From the isothermal data obtained for LPF and PF resins cure, the kinetic parameters of this process were calculated. Thus, the calculus was based on the general equation of reaction rate, Eq. (4). The assumption made in this expression is that during the resins cure a first-order reaction takes place, i.e., $f(\alpha)=1-\alpha$. Then Eq. (4) can be easily integrated from a curing time of $t=0$ min, where $\alpha=0$, to a time *t* with a conversion degree α. The linear fits between the logarithm of $(1-\alpha)$ and the curing time at different temperatures of the LPF and PF resol resins are shown in Figs 4 and 5, respectively. Figure 4 displays linearity between $\ln(1-\alpha)$ and time at practically all conversions Fig. 5 does not. This different behavior has its origin in the curves represented in Fig. 1, where both resins exhibit two exothermic peaks. First peak (T_{p1}) appears by the condensation of hydroxymethyl groups with phenol to form methylene bridges and/or condensation of two hydroxymethyl groups to form dibenzyl ether bridges. The second peak (T_{p2}) appears in superior temperatures, which is attributed the condensation reactions of dibenzyl ether to obtain methylene bridges with formaldehyde emissions. The curves display that the second peak of PF resin is shifted to higher temperatures relative to LPF resin because PF resin losses mobility, which makes the condensation of dibenzyl ether bridges more tough. Thus, Fig. 5 does not exhibits linearity at high conversions because of the changes in resin mobility during curing process, which is attributed to diffusion effect as a result of the variation in the free volume [18–20]. On the other hand, the chemical reactions in both systems are different. So, during the reaction between phenol and formaldehyde in alkaline medium, hydroxymethyl groups are introduced to the *ortho* and/or *para* positions of phenyl groups. However, the lignin is defined mainly by phenyl propane units, with this configuration the formaldehyde is incorporated as hydroxymethyl group in the aromatic ring free positions and/or side-chain of the lignin. Thus, the condensation and polymerization stages are given in both systems, but lignin presents some free positions that phenol does not.

From each slope of the different fits of Figs 4 and 5, the kinetic constants, $k(T)$, are determined. The fits obtained (since the correlation coefficient, R^2, values are 0.99 for both resins) are satisfactory. The $k(T)$ values for the resins studied are shown in Table 2. It can be seen that the increment of the temperature gives arise to an increase in the kinetic constant. Moreover, it is observed that the $k(T)$ values for the lignin–phenol–formaldehyde resin cure in comparison with those of the phenol–formaldehyde resin cure are not so high, which is caused by the lignosulfonate incorporated in its structure, given that this natural polymer is less reactive than the substituted phenol in principle [17, 21].

The dependence of the rate constant $k(T)$ on the temperature follows the Arrhenius law, which allows calculating the kinetic parameters of the isothermal curing process of both resol resins. The isothermal data fit of both resins is favorable, since the correlation coefficient, in both resins, is higher than 0.99 in all cases. The activation energy values obtained are 90.4 and 89 kJ mol^{-1} for the LPF and PF resins, respectively. The pre-exponential factor of lignin–phenolic ($\ln k_0=25.3$) and commercial ($\ln k_0=24.4$) resins cure is also similar. The results of both resins exhibit excellent agreement. The kinetic parameters obtained from Ozawa's method for the LPF and PF resins cure at curing degree above 90% are based on those calculated by isothermal fits.

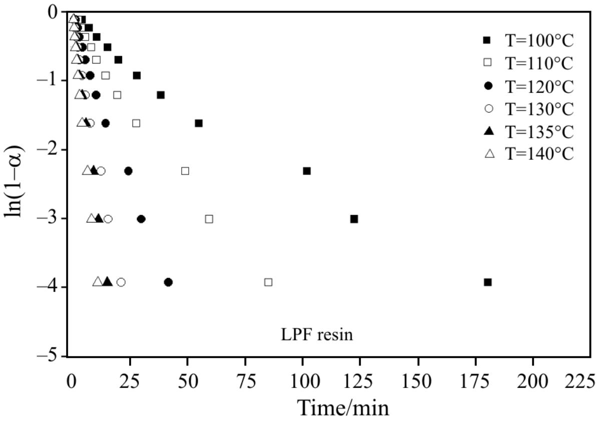

Fig. 4 ln(1–α) *vs.* curing time of LPF commercial resol resin

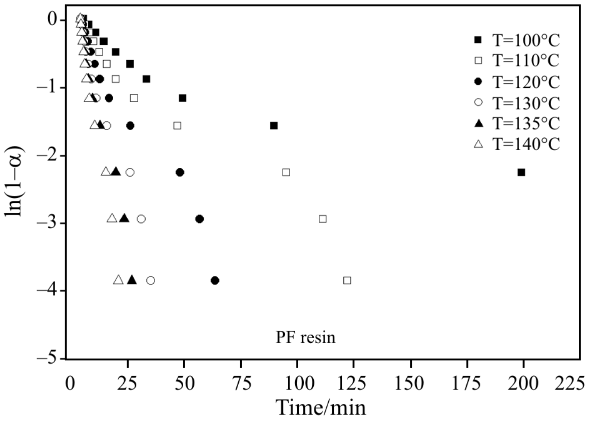

Fig. 5 ln(1–α) *vs.* curing time of PF commercial resol resin

Table 2 Determination of kinetic constant of the LPF and PF resins cure from Arrhenius' isothermal method

Temperature/°C	LPF resin		PF resin	
	k/s^{-1}±standard error	R^2	k/s^{-1}±standard error	R^2
100	0.0214±0.0008	0.993	0.0128±0.0009	0.972
110	0.0456±0.0015	0.995	0.0270±0.0018	0.978
120	0.0935±0.0026	0.997	0.0551±0.0032	0.984
130	0.1853±0.0040	0.998	0.1083±0.0052	0.988
135	0.2576±0.0049	0.998	0.1500±0.0066	0.990
140	0.3554±0.0059	0.999	0.2061±0.0081	0.992

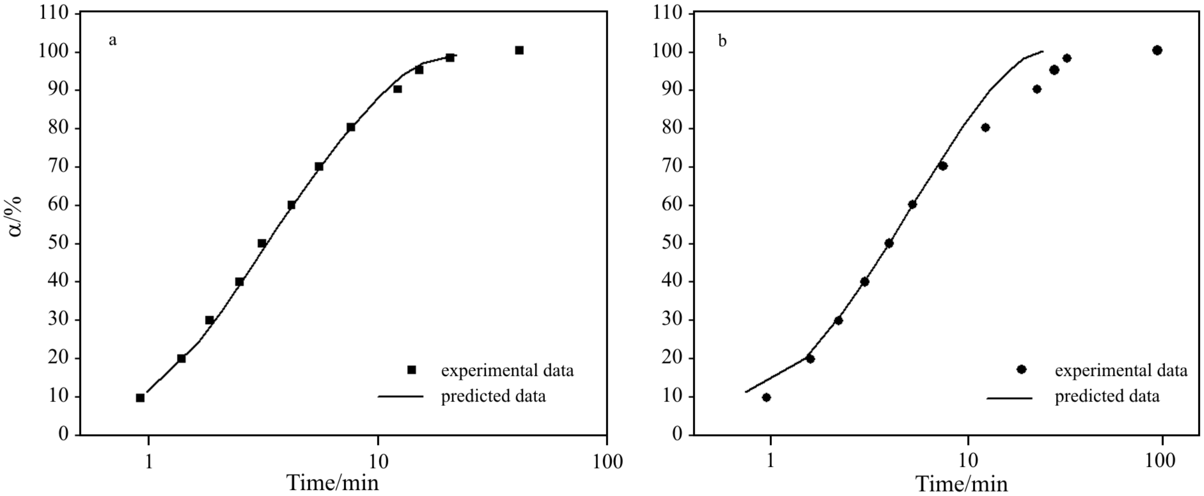

Fig. 6 Comparison between experimental and predicted kinetic data of a – LPF resol resin and b – PF commercial resol resins cure at 140°C

Thus, it can be affirmed that there is an isothermal dependency of the conversion on time, which can be predicted from dynamic differential scanning calorimetry data. All this seems to indicate that the Ozawa isoconversional method provides equivalent data to those obtained by transformation of these data into isothermal results. Isothermal values of both resol resins were compared with dynamical data of Ozawa isoconversional method, and the results are summarized in Fig. 6. Isothermal data of commercial resol resin cure (T=140°C) are deviated with respect to dynamic values for high conversion values (α=80%). This deviation is attributed to the reduction of mobility of the functional groups of phenolic resin and so the curing process rate is controlled by diffusion rather than by chemical reaction. Lignin–phenolic resin cure exhibits isothermal data similar to dynamic values by DSC runs, excepting when the curing degrees is higher than 95%. It should be pointed out, that it is difficult to establish the isothermal kinetic for the curing of phenolic and lignin–phenolic resins at high curing temperatures, because part of the total reaction heat is lost during stabilization time required for the DSC before each scan. The same phenomenon occurs with other types of thermosetting polymers such as epoxy resins and unsaturated polyester resins [22–24]. Thus, the utilization of this dynamic procedure to establish the isothermal kinetics of the curing process, as discussed above, can be useful for wide ranges of temperature and resins with similar issues.

Conclusions

The kinetic parameters obtained in the curing processes of LPF and PF resol resins through the dynamic Ozawa method are equivalent to those determined by the isothermal method used, which is based on the assumption that the curing processes of both resins comply with the isoconversional principle. The activation energies of LPF and PF resins cure are 90.4 and 89 kJ mol^{-1}, respectively, whereas the lnk_0 values are 25.3 and 24.4. Thus, when the resin curing presents a high reaction rate, the isothermal DSC technique is not suitable to determine kinetic data. The measurement of initial isothermal data is not sufficiently accurate. However, a suitable transformation of dynamic scanning data into isothermal data give better results for phenolic and lignin–phenolic resol resins faster curing.

The methodology developed makes it possible to obtain the isothermal kinetic parameters for the resol resins cure using only calorimetrical data obtained by dynamic DSC runs. Although it has been employed for the curing phenol–formaldehyde and lignin–phenolic resol resins, this methodology could be extended to the curing of other thermosetting polymers.

Acknowledgements

Thanks are due to the ‘Ministerio de Ciencia y Tecnología’ for financial support under the project CTQ2004-02032-PPQ.

References

1 G. Vázquez, J. González, S. Freire and G. Antorrena, Bioresour. Technol., 60 (1997) 191.
2 B. Danielson and R. Simonson, J. Adhes. Sci. Technol., 12 (1998) 923.
3 A. R. Gonçalves and P. Benar, Bioresour. Technol., 79 (2001) 103.
4 G. Vázquez, F. López-Suevos, J. González-Álvarez and G. Antorrena, J. Therm. Anal. Cal., 82 (2005) 143.
5 M.-K. Um, Compos. Sci. Technol., 62 (2002) 29.
6 R. B. Prime, Thermosets. In: Thermal Characterization of Polymeric Materials. Ed. E. A. Turi, Academic Press, New York 1997.
7 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340–341 (1999) 53.
8 T. Ozawa, Thermochim. Acta, 356 (2000) 173.
9 D. Rosu, C. N. Cascaval, F. Mustata and C. Ciobanu, Thermochim. Acta, 383 (2002) 119.
10 J. E. K. Schawe, Thermochim. Acta, 388 (2002) 299.
11 X. Ramis and J. M. Salla, J. Polym. Sci., Part B: Polym. Phys., 35 (1997) 371.
12 M. V. Alonso, J. J. Rodríguez, M. Oliet, F. Rodríguez, J. García and M. A. Gilarranz, J. Appl. Polym. Sci., 82 (2001) 2661.
13 M. V. Alonso, M. Oliet, F. Rodríguez, G. Astarloa and J. Echeverría, J. Appl. Polym. Sci., 94 (2004) 643.
14 K. G. Forss and A. Fuhrmann, Forest Prod. J., 29 (1979) 39.
15 T. Sellers Jr., ‘Plywood and Adhesive Technology’. Marcel Dekker, Inc., New York 1985.
16 A. Gardziella, L. A. Pilato and A. Knop, ‘Phenolic Resins’, Ed. Springer, 2000.
17 N. Sbirrazzuoli and S. Vyazovkin, Thermochim. Acta, 388 (2002) 289.
18 G. He, B. Riedl and A. Aït-Kadi, J. Appl. Polym. Sci., 87 (2003) 433.
19 Y. Meng and S. L. Simon, Thermochim. Acta, 437 (2005) 179.
20 F. Shokrolahi, M. Sadi and P. Shokrolahi, J. Therm. Anal. Cal., 82 (2005) 151.
21 T. U. E. Enkvist, (1975), U.S. Patent 3,864,291.
22 S. H. Lee, M. Yoshioka and N. Shiraishi, J. Appl. Polym. Sci., 77 (2000) 2901.
23 J. M. Kenny, G. Pisaniello, F. Farina and S. Puzziello, Thermochim. Acta, 269/270 (1995) 201.
24 F. Y. C. Boey and W. Qiang, Polymer 41 (2000) 2081.

Received: August 2, 2005
Accepted: March 2, 2006
OnlineFirst: May 23, 2006

DOI: 10.1007/s10973-005-7277-4