

## CURING KINETICS OF AMINE AND SODIUM HYDROXIDE CATALYZED PHENOL-FORMALDEHYDE RESINS

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The effect of both formaldehyde content and catalyst type used in the synthesis of several resole type phenolic resins has been studied by using differential scanning calorimetry. In this study Kissinger–Akahira–Sunose (KAS), Ozawa–Flynn–Wall (OFW) and Friedman model-free kinetics are applied in order to correlate the dynamic cure behaviour with the mentioned synthesis variables. Strong upward dependency of activation energy on conversion has been detected in all cases up to a maximum value. Lower the formaldehyde content fewer changes in activation energy have been detected, revealing a more homogeneous polymerization. As formaldehyde content increases, stronger variations of energy values have been observed and the maximum value is shifted to lower conversions. By comparing triethylamine and sodium hydroxide catalysts similar behaviour has been observed, with higher energy values and shifting of the maximum in the latter. Friedman approach has been resulted in more convenient and accurate for the energy values determination and KAS method seems useful for the dynamic cure prediction of that type of thermoset.

**Keywords:** catalysts, differential scanning calorimetry, formaldehyde/phenol ratio, model-free kinetics, phenol-formaldehyde resole resins, polymerization prediction

### Introduction

Alkaline phenol-formaldehyde resins are one of the most important adhesives for manufacturing composite wood materials for structural uses [1]. Resins with different molar ratios between phenol (P) and formaldehyde (F) (usually in excess of the latter) can be synthesized, using different alkali types and concentrations and different condensation temperatures, leading to prepolymers with controlled viscosities, degrees of polymerization, pH values, etc. Phenol–formaldehyde reaction proceeds through the formation of hydroxymethylphenol reactive groups (HMP), so that the major part of the cure reactions are attributed to the condensation reactions between them. However, although some papers have been published on the kinetics and mechanisms of condensation reactions of HMP groups as model compounds [2, 3], the reaction pathway of phenol-formaldehyde prepolymers is still no well known [3].

Differential scanning calorimetry (DSC) is the most popular technique for monitoring oligomer curing and has been extensively used in curing studies of phenolic resins, mostly since the appearance of high pressure crucibles [4–8]. Attempting to explain the curing behaviour, mechanistic models application becomes extremely complex in case of the kinetic analysis of phenolic type resins, where multiple and parallel reactions are in competition and their products can

take part in the reaction with the starting reactant [1]. Several authors have applied different approaches based on fitting kinetic data to previously assumed reaction models [9–14]. Nevertheless, this type of approaches has resulted in some inconsistencies as are not effective in explaining complex reactive systems particularities [14]. Therefore, methods based on the isoconversion concept can be considered more appropriated to be used [12]. Model-free kinetics (MFK) is well suited to depict the kinetics of complex reactions such as the cure of PF resins [15, 16]. Several applications of the novel isoconversional method in the curing process of epoxy or polyurethane resins have already been reported but unfortunately few studies have been reported about the kinetic study of the curing process of phenolic resins [14, 17, 18]. In addition, reported literature attempted to explain the cure behaviour of individual resins, without a deep study of the influence of synthesis parameters on it. In order to complete our previous work [19], we report in this paper the results obtained by application of several MFK methods such as Ozawa–Flynn–Wall (OFW), Kissinger–Akahira–Sunose (KAS) and Friedman, to calorimetric experimental data of the curing process of five phenolic resole resins synthesized with different monomer molar ratios and/or catalyst type. KAS method has also being used for predicting the dynamic cure behaviour of one of PF resins. Finally, this work is

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aimed to obtaining kinetic data related to the complex curing of resoles and, in particular, we attempt to explain those activation energy values in order to correlate the effect of both catalyst type and formaldehyde content used in the synthesis with the relative contribution of each reaction to the main curing process.

## Experimental

### Synthesis of prepolymers

Phenol and 37 mass% aqueous solution of formaldehyde commercial products supplied by Hexion Specialty Chemicals were used as monomers without further purification. Several prepolymers (RT series) were synthesized with formaldehyde to phenol molar ratios from 1.0 to 2.2 using triethylamine (TEA) as catalyst. A fixed amount of triethylamine was added in all cases in order to maintain a constant value of TEA/P molar ratio (0.011). On the other hand, another prepolymer was synthesized with sodium hydroxide as catalyst and an F/P value of 1.8 (RN1.8). In this case hydroxide was added as a 50% aqueous solution up to a pH value 8.0. Condensation was carried out at 80°C until prepolymers showed a 1/1 g/g solubility in water. Water extraction was performed under vacuum at 45–48°C until the solid content of resins achieved 72–78%. Samples were stored at –20°C until they were analyzed. Table 1 resumes the starting conditions of each synthesized prepolymer.

### Calorimetry

Calorimetric measurements were used to perform the kinetic study of synthesized prepolymers polymerization. Calorimetric measurements were carried out using a Mettler Toledo DSC-20 calorimeter. Around 3–4 mg of samples were placed in stainless steel crucibles of 120 µL sealed with a Viton® O-ring, which can withstand 2 MPa. Dynamic scans were carried out from 30 to 280°C at 1, 5, 10 and 20°C min<sup>-1</sup> heating rates. Curves were processed with the Mettler Toledo STAR<sup>e</sup> software to extract the degree of cure,  $\alpha$ , reaction rate,  $da/dt$ , and corresponding temperature,

$T_{\alpha}$ , in the  $0 \leq \alpha \leq 0.99$  range. Degree of cure was determined at a specific cure time,  $t$ , as the partial heat of reaction divided by the total heat of reaction as follows:

$$\alpha = \frac{\Delta H(t)_{T_{\alpha}}}{\Delta H} \quad (1)$$

### Model-free kinetics approach

The isoconversional principle was used in the models of Kissinger [9], Ozawa and Flynn and Wall [10, 11]. These models start from a general equation, where the temperature dependent rate constant ( $k(T)$ ) relates the reaction rate ( $v$ ) with the reaction model, which is expressed by a function dependent on the conversion,  $f(\alpha)$ .

$$v = \frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where  $t$  is time,  $T$  the temperature and  $\alpha$  the extent of cure reaction. The explicit temperature dependence of the rate constant is introduced by replacing  $k(T)$  by the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

where  $A$  is the pre-exponential factor and  $E_a$  the activation energy of the process. Dynamic calorimetric runs are useful to perform cure kinetics studies in the whole reaction temperature range. At non-isothermal conditions, the evolution of conversion with temperature is analyzed and the explicit time dependency is removed by the introduction of  $\beta = dT/dt$ , the heating rate term.

$$g(\alpha) = \int_0^{\alpha} \frac{\partial \alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_a}{RT_m}\right) dT \quad (4)$$

Ozawa method relates the activation energy with both heating rate and temperature of the exothermic peak of reaction ( $T_m$ ). By taking natural logarithms in the general expression

$$\ln g(\alpha) = \ln \int_0^{\alpha} \frac{\partial \alpha}{f(\alpha)} = \ln \frac{A}{\beta} + \ln \left[ \int_{T_0}^{T_m} \exp\left(-\frac{E_a}{RT_m}\right) dT \right] \quad (5)$$

**Table 1** Physical and chemical properties of phenolic prepolymers

	RT1.0	RT1.4	RT1.8	RT2.2	RN1.8
$\eta_{25^\circ\text{C}}/\text{mPa s}$	165	432	550	621	560
$n_D$	1.552	1.559	1.561	1.559	1.555
$\rho_{20^\circ\text{C}}/\text{g cm}^{-3}$	1.183	1.212	1.214	1.206	1.228
H <sub>2</sub> O solubility/mg mg <sup>-1</sup>	1.48	1.82	1.94	2.21	1.85
pH	7.70	7.53	7.5	7.45	7.79
H <sub>2</sub> O/mass%	8.67	8.75	5.48	6.64	9.123
Solid content/mass%	72.2	78.8	78.4	73.8	78.1

Doyle [13] defined the polynomial function  $p(E_a/RT_m)$  as follows:

$$p\left(\frac{E_a}{RT_m}\right) = \frac{R}{E_a} \int_{T_0}^{T_m} \exp\left(-\frac{E_a}{RT_m}\right) dT \quad (6)$$

For  $(E_a/RT)$  values between 20 and 60 this polynomial function can be approximated to the following expression:

$$\ln\left[p\left(\frac{E_a}{RT_m}\right)\right] = -5330 - 1.0516\left(\frac{E_a}{RT_m}\right) \quad (7)$$

Thus, Eq. (5) gives for the heating rate  $(\beta)$  the expression:

$$\ln\beta = C - 1.0516\left(\frac{E_a}{RT_m}\right) \quad (8)$$

where

$$C = \ln\frac{g(\alpha)E_a}{AR} - 5330$$

takes a constant value at each extent of reaction.

Besides, Kissinger [9] reported a different expression for the determination of pre-exponential factor in case of  $n$  order reaction. The pre-exponential factor is evaluated on the assumption of a first-order reaction. This expression also relates activation energy with heating rate and temperature of the exothermic peak in a dynamic temperature scan.

$$-\ln\left(\frac{\beta}{T_m^2}\right) = \frac{E_a}{RT_m} - \ln\frac{AR}{E_a} \quad (9)$$

Both Ozawa and Kissinger simple methods assume that cure reactions are not dependent on the cure temperature and provide a single activation energy value which maintains constant along the cure process.

On the other hand, the basic assumption of model-free isoconversional methods is that reaction model is not dependent on the heating rate. The application of both OFW and KAS methods within the whole range of conversion allows the activation energy to be determined as a function of conversion, without a forced fitting of non-isothermal data to a hypothetical unique reaction model. Thus, Eqs (8) and (9) can be expressed for each extent of reaction within the whole temperature range along the dynamic scan.

$$\ln\beta = C_\alpha - 1.0516\left(\frac{E_\alpha}{RT_\alpha}\right) \quad (10)$$

$$-\ln\frac{\beta}{T_\alpha^2} = \frac{E_\alpha}{RT_\alpha} - \ln\frac{A_\alpha R}{E_\alpha} \quad (11)$$

where

$$\ln\frac{A_\alpha R}{E_\alpha} = C_k(\alpha)$$

Activation energy values at each conversion have been calculated from the slope of the plot of  $\ln\beta$  or  $-\ln(\beta/T_\alpha^2)$  vs.  $(1/T_\alpha)$ , respectively. At the same time values of  $C_\alpha$  and  $C_k(\alpha)$  have been obtained from the intercept in each case.

On the other hand, for various heating rates,  $\beta_i$ , the Friedman method directly evaluates Eq. (3) at a specific degree of cure  $\alpha$ :

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = C_f(\alpha) - \frac{E_\alpha}{RT_{\alpha_i}} \quad (12)$$

being

$$C_f(\alpha) = \ln[A_\alpha f(\alpha)] \quad (13)$$

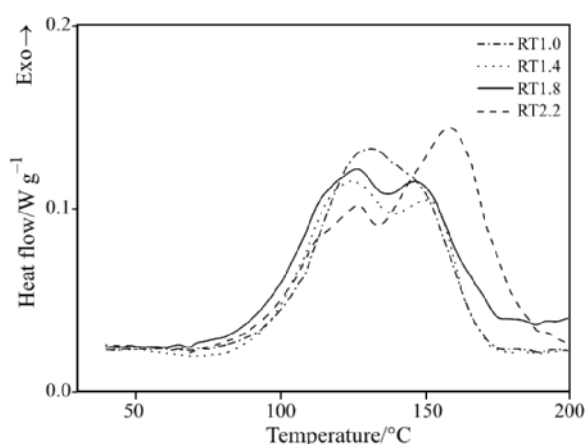
For a specific  $\alpha$  and at several heating rates, pairs of  $(d\alpha/dt)_{\alpha_i}$  and  $T_{\alpha_i}$  can be determined experimentally from DSC curves. Activation energy values at each conversion have been calculated from the slope of the plot  $\ln(d\alpha/dt)_{\alpha_i}$  vs.  $1/T_{\alpha_i}$  and  $C_f(\alpha)$  from the intercept. Friedman method does not introduce any approximations and the method is not restricted to the constant heating rate mode as in case of OFW and KAS methods, which use Doyle's approximation, so that only provide estimate values of activation energies. However, as in the case of any kinetic methods involving the differential term  $(d\alpha/dt)$ , the Friedman method is subjected to significant numerical instability and noise interference [20].

Assuming the hypothesis that cure reactions are not dependent on the temperature, the application of MFK methods allows to determine time, temperature and extent of cure without the introduction of a fixed form of  $f(\alpha)$  function [14, 21]. By representing obtained activation energy values against conversion, the nature of the reaction can be deduced from the shape of the curve [22], e.g. competitive, consecutive, reversible, diffusion controlled, etc. In the present work, the different kinetic models above mentioned have been applied to calorimetric measurements carried out during nonisothermal curing.

## Results and discussion

### Dynamic cure of phenolic resins

Figure 1 presents the dynamic calorimetric scans of synthesized prepolymers at  $1^\circ\text{C min}^{-1}$ . Two exothermic peaks can be observed. During decades, the diversity in resin composition and employed conditions variations for resole synthesis has derived in an incomplete under-



**Fig. 1** DSC dynamic scans for amine catalyzed prepolymers at  $1\text{ }^{\circ}\text{C min}^{-1}$ . The curves have been normalized by taking into account the mass of each sample

standing of the thermal behaviour of those resins attending to recently reported literature [23]. In general, it is assumed that the first exothermic peak at  $120\text{--}140^{\circ}\text{C}$  (peak I) corresponds to the condensation reaction, involving the formation of both methylene and dimethylene ether bridges. The second peak at highest temperatures (peak II) is related to subsequent reactions, e.g. dimethylene ether bridges breakage [4, 7, 24]. The higher the formaldehyde amount the greater second exothermic peak intensity. Both dimethylene ether bridge concentration and oxidation products increase as formaldehyde to phenol molar ratio does [17, 23]. Table 2 includes the average enthalpy of reaction of synthesized prepolymers. RT1.4 labelled prepolymer showed the maximum value, decreasing as the formaldehyde content increased up to 2.2. In our previous report [19] we had demonstrated that at initial states of the cure process, residual addition reactions are possible in cases of lack of formaldehyde since the achieved degree of substitution of phenolic rings during synthesis is low, allowing to remaining formaldehyde to be added to free reactive sites. Those residual addition reactions were probably affecting the values of curing enthalpies at low formaldehyde content resoles, decreasing as the formaldehyde to phenol molar ratio increased due to the absence of reactive free aromatic sites.

**Table 2** Enthalpy of reaction of synthesized phenolic prepolymers

Prepolymer	$\Delta H/\text{J g}^{-1}$
RT1.0	260.0
RT1.4	274.3
RT1.8	233.4
RT2.2	232.5
RN1.8	234.4

On the other hand, enthalpy of reaction also seemed to be independent on the catalyst type used in the synthesis. This fact is surprising since it had been demonstrated that the type of catalyst affects the reaction pathway [3, 19, 25, 26], being studied mainly the effect of hydroxide type catalysts on addition reactions both in *para* and *ortho* positions. In general, it had been reported that sodium hydroxide favours the addition on *para* free sites in contrast of the preference of amine type catalysts to create hydroxymethyl groups on *ortho* free sites [3, 19, 25]. Higher effect on addition reactions had been observed with amine type catalysts, suggesting higher degree of substitution in cases of amine catalyzed resoles [19, 24, 25]. Besides, some authors have concluded that the use of amines in phenolic resin synthesis leads to a higher dimethylene ether concentration [19, 24, 25]. However, few studies have been developed about the catalyst role in condensation reactions and calorimetric studies carried out suggest that either formaldehyde to phenol molar ratio or water amount are important parameters that affect to the overall reaction enthalpy. Therefore, the preference of catalyst type to the methylene or dimethylene ether formation seems not to be affecting since curing reaction involves the participation of several independent reactions that are not possible to be evaluated as individual processes. Those apparent limitations in elucidating the cure behaviour and detecting the influence of all parameters solely by the analysis of enthalpy values make essential an accurate analysis in terms of curing kinetics.

#### Application of kinetic models

With the aim to evaluate and compare the curing behaviour of synthesized prepolymers, several kinetic approaches had been carried out. Assuming that the cure reaction pathway does not change with the heating rate, both Ozawa and Kissinger simple methods, Eqs (8) and (9) respectively, had been applied for the fitting of experimental data. Values of activation en-

**Table 3** Activation energies obtained by Ozawa and Kissinger methods ( $\text{kJ mol}^{-1}$ )

		I	II
RT1.0	Ozawa	79.7	81.2
	Kissinger	76.7	78.0
RT1.4	Ozawa	79.8	94.4
	Kissinger	77.0	91.8
RT1.8	Ozawa	79.7	94.5
	Kissinger	77.9	92.7
RT2.2	Ozawa	75.5	111.5
	Kissinger	72.3	109.8
RN1.8	Ozawa	64.1	170.7
	Kissinger	60.1	171.7

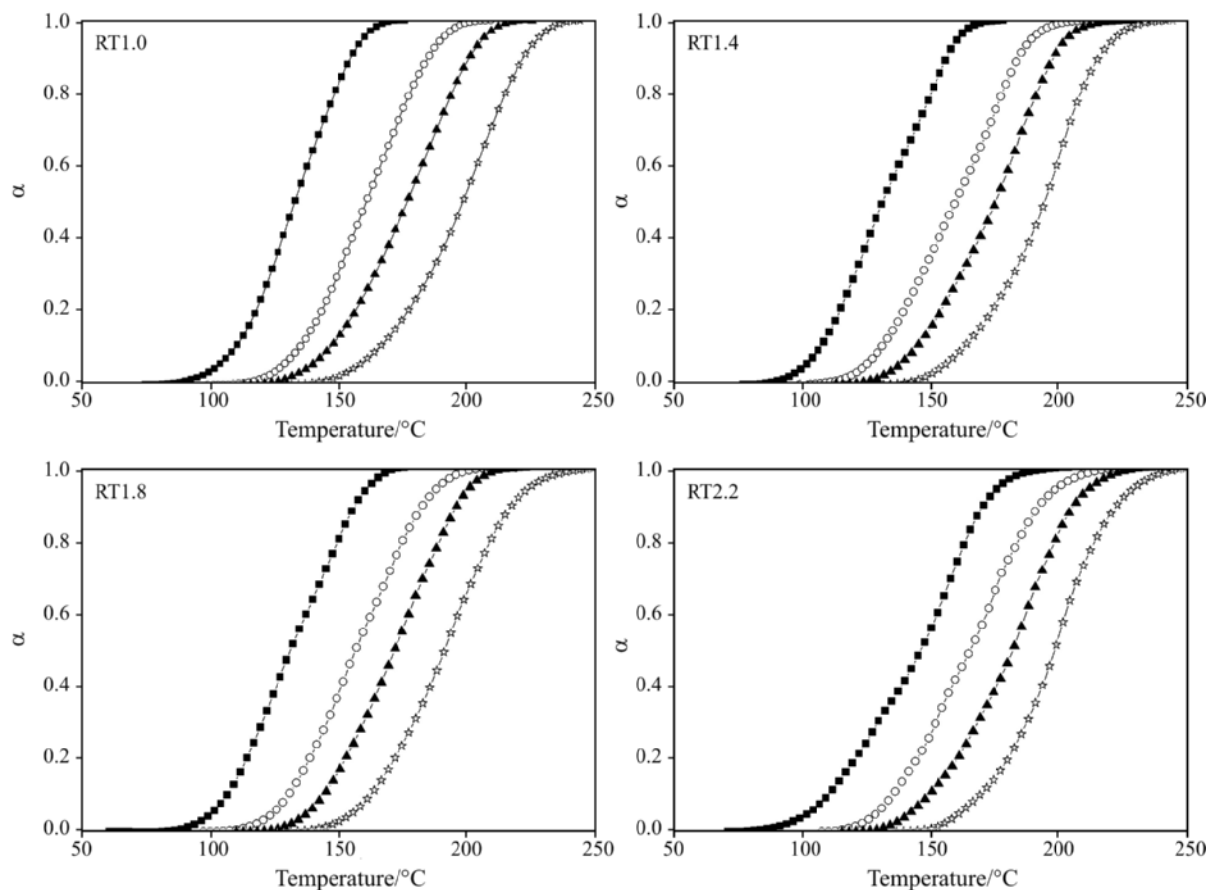


Fig. 2 Conversion profiles of amine catalyzed prepolymers at several heating rates; ■ – 1, ○ – 5, ▲ – 10 and \* – 20°C min<sup>-1</sup>

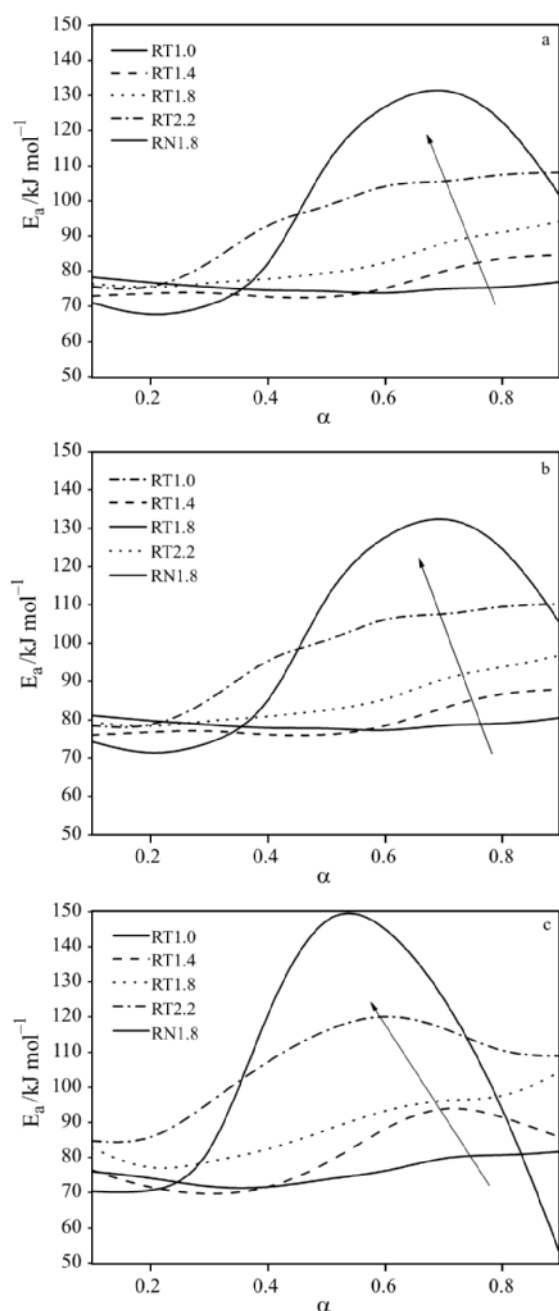
ergy of each reaction (peaks I and II) obtained by those methods are summarized in Table 3.

Park *et al.* [6] reported an activation energy value of 85.3 kJ mol<sup>-1</sup> as studied by differential scanning calorimetry. In our case, both Ozawa and Kissinger methods offered similar values for all resoles. According to values of activation energy of the first peak, related to the polycondensation reaction, one should consider that resoles catalyzed with triethylamine present in general a similar behaviour. RT2.2 resole presented a lower activation energy value as the presence of higher amount of hydroxymethyl groups would activate aromatic rings towards the polycondensation [27]. However greater differences were observed in case of the second reaction (II) which is related to the evolution of first formed dimethylene ether bridges and/or parallel reactions involving oxidized groups. It seems that differences in activation energy values were greater with the increase of formaldehyde content, while RT1.0 resole presented similar value of activation energies in both cases. The lower value of activation energy of the RN1.8 resole could be a consequence of a different reaction pathway derived from the effect of hydroxide in the curing process. Therefore, although those simple methods result in a good fitting of exper-

imental data, it is obvious that those single activation energy values offer limited information about characteristics of the reactive process, and any change derived from the singularity of those systems can not be detected by the sole application of simple kinetic models. Therefore, model-free isoconversional methods had been applied, in particular, OFW, KAS and Friedman methods.

As shown in Fig. 2, conversion profiles in the whole range of temperatures can be plotted for each resole resin at different heating rates. According to OFW, KAS and Friedman methods, Eqs (10)–(12), respectively, applied for each heating rates, the activation energy dependence on conversion for each resole resin had been obtained. Figures 3a–c show the dependence of  $E_a$  on degree of cure by fitting using each of the three methods.

The overall range of values is in concordance with values reported in literature for phenolic resole resins [6]. Energy values obtained by the application of KAS and OFW methods were very similar, while Friedman method application yielded to higher activation energy variations. On the other hand, both KAS and OFW methods presented curves shifted to higher conversion by comparing with those from Friedman. Those effects have been previously ob-



**Fig. 3** Activation energy dependency on degree of cure by applying a – OFW, b – KAS and c – Friedman isoconversional models

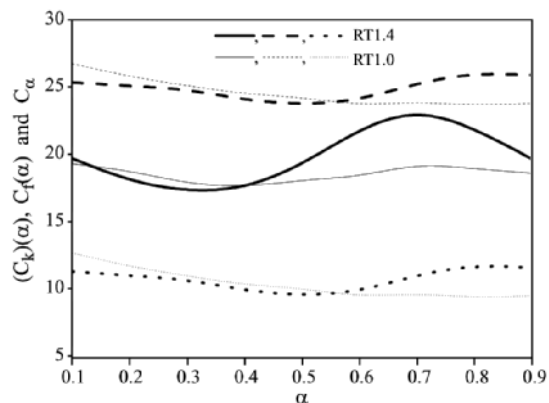
served and recently reported literature suggests [20] that they could be attributable to the fact that both KAS and OFW methods are derived by the use of Doyle's approximation (Eq. (6)), while Friedman method is not based in any approximation. Therefore, the accuracy of energy values obtained from Friedman method is greater, being more sensitive to changes in mechanism.

However, whatever the method was, activation energy presented strong dependence on the degree of cure, increasing as conversion did after a period of a

concave decrease, especially for low-formaldehyde content systems. This behaviour was also described by Li *et al.* [14] with acid catalyzed resole resins. According to literature [28], an upward tendency is characteristic of a reactive process which involves multiple, parallel and competitive reactions. Activation energy showed the cited upward curve up to a maximum value where it started to decrease with a convex shape. Vyazovkin *et al.* [28] have reported that a convex shaped decrease of the activation energy with the increase of degree of cure is related to the transition from the kinetic to the diffusive regime.

Within triethylamine catalyzed resoles the energy value at the maximum increased as F/P molar ratio did and the maximum value of energy shifted to lower conversion values. RT2.2 presented a maximum energy value of  $120 \text{ kJ mol}^{-1}$  near 60% of reaction while in case of RT1.4 activation energy increased up to  $90 \text{ kJ mol}^{-1}$  at a degree of cure of 70%. In contrast, activation energy of RT1.0 resin presented small changes upon conversion as the complexity of curing decreases [21]. Figure 4 shows the value of the combined complex parameters  $C_f(\alpha)$ ,  $C_k(\alpha)$  or  $C_\alpha$  of RT1.4 and RT1.0 prepolymers. Also this parameter is dependent on degree of cure, so that reflects the changes in mechanism as a function of initial monomer molar ratios, since RT1.0 prepolymer presented an almost constant value along the reaction. Both  $C_k(\alpha)$  and  $E_\alpha$  were then introduced for the modelling of dynamic cure of RT1.4 as we present below. Once more, in case of  $C_f(\alpha)$  higher differences were observed as in case of activation energy variations.

It seems evident that in case of amine catalyzed systems, higher the formaldehyde, and in consequence the hydroxymethyl reactive groups concentration, earlier the transition to a diffusive control of the reaction is. In the case of lower formaldehyde content resins, the value of activation energy is found to decrease at initial stages of reaction.

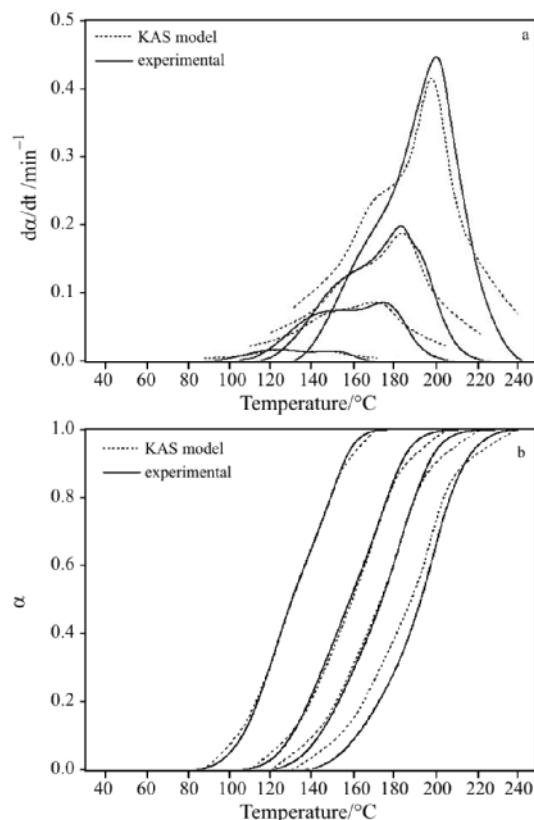


**Fig. 4** Combined complex parameters for RT1.4 and RT1.0 prepolymers: ... –  $C_k(\alpha)$ , — –  $C_f(\alpha)$  and --- –  $C_\alpha$

A concave form decrease upon conversion is related to the presence of reversible reactions [21, 28]. As we previously reported [19], addition reactions of remaining formaldehyde are likely to occur in case of RT1.0 and RT1.4 resoles as enough free aromatic reactive sites are able to react. New hydroxymethyl groups could lead to a decrease in the activation energy value due to the activation effect of the alcohol groups over the aromatic ring. He *et al.* [21] detected the same behaviour in the analysis of the reaction between phenol and formaldehyde, attributing it to the influence of intermediate products derived from reversible formaldehyde addition reaction. The concave decrease occurs in a narrow range of conversion, as addition takes place mainly in the previous synthesis process. In case of higher formaldehyde to phenol molar ratio, remaining addition reactions could also be possible during the polycondensation since formaldehyde becomes reactant as is released as by-product of some condensation reactions. However, there is no evidence of this fact in activation energy values of those systems.

The comparison between RT1.8 amine catalyzed resin and sodium hydroxide catalyzed RN1.8 is very interesting. As we describe above no relevant differences have been observed in those cases in terms of enthalpy of reaction. However, the activation energy curve shape presented important differences in both cases. In case of sodium hydroxide catalyzed resin activation energy seems to be more affected by the increase of degree of cure and, in addition, energy reached the maximum value at lower conversion, near 50%.

He *et al.* [21] also detected this effect in resoles catalyzed with sodium hydroxide, while for resoles catalyzed with acid catalyst Li *et al.* [14] did not describe similar behaviour. It must be taken into account that two transitions are presented during curing process: one from the liquid-viscous state to the rubbery state (gelation) and another from the rubbery to a glassy state (vitrification). The molecular mobility is reduced due to network formation between both transitions, and the kinetic control gives way to a diffusive control of the reaction. Both the increase of temperature and the degree of cure, along with molecular structure phenomena (linear or branched chains formation, network formation) affect directly to diffusion [21, 29]. Besides, higher amount of water detected in RN1.8 resole could be also responsible of the decrease in the activation energy at higher values of degree of cure by plasticization effects [30]. Observed differences reveal a serious effect of catalyst type onto the curing process of resins, which corroborates the fact that enthalpy values or single activation energy value do not clarify the curing behaviour of those complex reactive systems.



**Fig. 5** Comparison of both a – experimental dynamic cure and b – conversion profiles vs. KAS predictions for RT1.4 resole resin

#### Modelling of dynamic cure

KAS method was used to predict the dynamic cure of phenolic RT1.4 prepolymer. The model was developed using 1, 5 and 10°C min<sup>-1</sup> values of heating rates and the dynamic prediction corresponds to curing at 20°C min<sup>-1</sup>. By using Mathcad 12.0 program and by the application of Eq. (11), theoretical relationships between temperature and degree of cure were obtained at specific heating rates, as shown in Figs 5a and b.

Dotted curves correspond to KAS predictions while continuous lines had been used for experimental curves. Although it is noted that there is a slight shift at the initial stages of reaction, KAS model seems to be effective to describe the dynamic cure of this system at 20°C min<sup>-1</sup>, especially at higher conversions.

#### Conclusions

The kinetic study of different phenolic resole resins was carried out using differential scanning calorimetry and activation energies of those systems were obtained by application of model-free kinetics. Synthesized systems presented two exothermic peaks related to polycondensation and ether bridge decomposition

and oxidative processes, respectively. The relative intensity of both peaks changed as formaldehyde content increase. Resoles synthesized with low content of formaldehyde presented a higher value of enthalpy as a consequence of addition residual reactions. KAS, OFW and Friedman model-free kinetic methods were selected to be applied for the kinetic study of the cure development of those systems. Model-free kinetic methods had been found to be more convenient and reliable than other model fitting approaches applied commonly in literature in case of phenolic resins. An upward dependency of activation energy on conversion was observed in all cases, indicating a complex reaction pathway that involves multiple and competitive polymerization reactions. The Friedman method had been found to be more sensitive to activation energy changes than KAS or OFW methods where the use of Doyle's approximation reduced their accuracy and shifted the maximum value to lower conversions. However, three methods revealed that the complexity of the process increased as the initial formaldehyde content did, so that changes in activation energy were determined to be less considerable for low formaldehyde resoles. Furthermore, activation energy reached the maximum value at lower conversion as formaldehyde content increased. In addition, an initial decrease of energy values was observed for low F resoles, probably derived from residual addition reactions. The presence of sodium hydroxide in the systems leads to higher energetic processes in comparison with that for triethylamine. Above a fixed value of conversion the reaction is diffusion controlled and thereby activation energy depends on the molecular structure and plasticization effects in each system. Finally, KAS algorithm was found to be suitable for the dynamic cure prediction of resole type prepolymers, whereas Friedman method presented higher consistency and accuracy in the activation energies determination.

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