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# ISOCONVERSIONAL KINETIC ANALYSIS OF RESOL-CLAY NANOCOMPOSITES

*M. López[1], M. Blanco[1], A. Vazquez[1], J. A. Ramos[1], A. Arbelaiz[1], N. Gabilondo[1], J. M. Echeverría[2] and I. Mondragon[1]**

[1]Materials and Technologies' Group, Escuela Politécnica, Department of Chemical & Environmental Engineering, Universidad País Vasco/Euskal Herriko Unibertsitatea, Pza. Europa 1, 20018 Donostia-San Sebastián, Spain
[2]Hexion Specialty Chemicals Ibérica Ctra. Navarra, Epele 39, 20120 Hernani (Gipuzkoa), Spain

The curing kinetics of nanocomposites based on phenolic resol cured with triethylamine (TEA) containing different amounts of organic montmorillonite was analyzed by differential scanning calorimetry. Kissinger–Akahira–Sunose (KAS) model-free kinetics has been applied to correlate the dynamic cure behaviour in the presence of modified montmorillonite. The effect in the curing of the use of different clay modifiers has also been studied. A commercial clay with hydroxyl groups (Cloisite 30B) and a customized montmorillonite (PheMMT) whose reactive groups induce condensation reactions with the resol matrix have been used. Strong dependency of activation energy on apparent conversion has been observed for all compounds.

***Keywords:*** *curing, kinetics, montmorillonite, nanocomposites, resols*

## Introduction

Polymer clay nanocomposites (PCN) are novel composite materials that have received a lot of attention during the last decade due to the significant improvement in mechanical, thermal, barrier, and flame-retardant properties. These enhanced properties are presumably a result of the nanometer size, large aspect ratio and large surface area of the silicate layers [1–9].

Montmorillonite (MMT) clays are usually used owing to their nano-dispersible character. MMT has platelet geometry. Each MMT layer is composed of two tetrahedral layers sandwiching an alumina octahedral sheet. There is a cation deficiency on the surface of the clay layers that is compensated by the exchangeable metal ions (e.g. $Na^+$) which are in the interlayer. Since natural clays are hydrophilic, they are generally modified by short chain molecules to make them more compatible with the host polymer, thereby making the clay organophilic. These organic modifiers can participate in the reaction(s) with resin components and improve the miscibility of the clay with resin. By diffusing host polymer chains into the layers of intercalated clay, the individual clay layers can be intercalated or exfoliated [10–12].

Phenolic resins are the polycondensation products of reaction of phenol with formaldehyde which have been widely used owing to their high heat resistance, high char yield, solvent resistance and moderate flame resistance that make them appropriate for thermal insulation materials, adhesives, abrasives, coating applications, molding compounds, laminates and in other composite materials. Resol resins are synthesized under basic conditions using an excess of formaldehyde [13–16].

On the other hand, only a few studies have been performed with phenolic resins in the nanocomposite field. Their three-dimensional molecular structure even prior to cure and the formation of water as a by-product of cross-linking may avoid the exfoliation of the clay even when they are not crosslinked [17–22].

In a previous study [22], resol type phenolic resin/layered silicate nanocomposites were synthesized by monomer intercalation to overcome the structural problem of MMT dispersion and exfoliation into phenolic resin matrix. Thereby, MMT was modified by using an amino acid, *L*-phenyl alanine, in order to induce condensation reactions between the carboxyl end group of the *L*-phenyl alanine and the hydroxyl groups of the formaldehyde and enhance the compatibility with the phenolic resin matrix. From X-ray diffraction (XRD) analysis and atomic force microscopy (AFM), we have shown [22] that the silicate layers of clay achieve an intercalated/exfoliated state in the resol matrix. Moreover a slight improvement in thermal stability of the resin system has also been observed by the incorporation of the organically modified clay. Overall, for thermosetting systems in industrial applications, it is important to know the curing behaviour in order to obtain the desired prop-

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* Author for correspondence: inaki.mondragon@ehu.es

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

erties of the final product. Thus, the study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the final material.

There are two approaches to study the cure kinetics, namely mechanistic and phenomenological. In the case of phenolic resins, it is difficult to apply mechanistic model due to multiple and parallel reactions in competition. Thus, phenomenological models are more suitable to study the cure kinetics of these polymers [23].

Thereby, model-free kinetics (MFK), such as Ozawa or Kissinger's models [24–26] are appropriated to portray the kinetics of complex reactions such as the cure of phenolic resins [27–32]. These models relate the heating rates (β) to the peak exothermic temperatures ($T_p$) of dynamic curves to obtain the activation energy of overall cure process. MFK does not assume any definite form of the reaction and allows for variations in activation energy as the reaction progresses.

On the other hand, the curing kinetics of polymers during nanocomposites formation has been less studied [33–39] and for phenolic resins it does not exist.

Thus, in order to complete our previous work [22, 40], the main aim of this paper is to report the results obtained by application of the MFK method of Kissinger–Akahira–Sunose (KAS) to calorimetric experimental data of the curing process of five montmorillonite modified phenolic resol resins. KAS method has also been used for predicting the dynamic cure behaviour of one of the composites. Finally, this work is aimed to obtaining kinetic data related to the complex curing of resols in order to correlate the effect of montmorillonite on the main curing process.

## Experimental

Phenol was kindly supplied by Hexion Specialty Chemicals Ibérica, and formaldehyde (35–40% aqueous solution) and triethylamine (TEA) were purchased from Panreac and used without further purification. Untreated $Na^+$MMT and Cloisite 30B, a MMT organically treated with methyl tallow bis-2-hydroxylethyl quaternary ammonium, were obtained from Southern Clay Products. *L*-phenyl alanine (Phe) was purchased from Aldrich and used for modifying $Na^+$MMT.

*L*-phenyl alanine modified montmorillonite (PheMMT) was prepared through the ion exchange of $Na^+$MMT with *L*-phenyl alanine in acidic environment according to the extended method included in a previous paper [22]. The operating conditions of curing and formulation of composites have been reported elsewhere [22, 40].

Neat resol (Res) was synthesised following the same conditions than for the modified resins. Samples with montmorillonite were designed as Phe-*i*, C*i* being *i* the mass content of modified montmorillonite.

Differential scanning calorimetry (DSC), Perkin-Elmer DSC-7, was used to perform dynamic and isothermal experiments. Sample masses were between 3 and 5 mg and medium pressure/ Viton 120 μL pans were used. Dynamic temperature scans were conducted at five heating rates 5, 10, 15, 20 and 25°C $min^{-1}$ from 30 to 280°C. Isothermal DSC runs were performed at 110°C during 180 min and then the residual heat of reaction was obtained from a subsequent ramp scan at 10°C $min^{-1}$ from 30 to 280°C.

Apparent extent of cure was determined as the isothermal reaction enthalpy divided by the total enthalpy of reaction calculated as the addition of the enthalpy from the isothermal mode to the residual one. Nitrogen was used as purge gas at a flow rate of 40 mL $min^{-1}$.

### *Isoconversional methods*

Isoconversional methods are based on dynamic kinetics analyses by DSC [41]. In the reaction rate equation (Eq. (1)) used to study the resins curing kinetics, the extent of cure (α) is proportional to the heat generated during the reaction rate and the reaction is expressed by a function of conversion.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \qquad (1)$$

where $t$ is time, $k$ the rate constant and $f(\alpha)$ is a model function that depends on reaction mechanism. The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ by the Arrhenius equation, which gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (2)$$

where $A$ is the pre-exponential factor, $E_a$ the activation energy of the process, which is independent of conversion and $R$ the gas constant. Therefore, at non-isothermal conditions and considering that $\mathrm{d}\alpha/\mathrm{d}t=\beta(\mathrm{d}\alpha/\mathrm{d}T)$ where $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate term, the integral form of the rate equation can be expressed as:

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (3)$$

In order to compute Arrhenius parameters at dynamic conditions, there are some relationships depending on the approximate form of the temperature integral that have been based on Eq. (3). The Kissinger–Akahira–Sunose's model-free [42] is one of them, where the reaction order is taken into account. The pre-exponential factor is evaluated on the assumption of a first-order reaction. In the KAS method, $E_{\alpha}$ is evaluated by using Doyle's integral approximations [43] when $20<E/RT<60$:

$$\int_{0}^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\approx\frac{ART^2}{\beta E}\exp\left(-\frac{E}{RT}\right) \quad (4)$$

Thereby, applying logarithms, the expression for each extent of cure reaction within the whole temperature range along the dynamic scan, is the following:

$$-\ln\frac{\beta_i}{T_{\alpha_i}^2}=\frac{E_{\alpha}}{RT_{\alpha_i}}-C_k(\alpha) \quad (5)$$

being:

$$C_k(\alpha)=\ln\frac{A_{\alpha}R}{E_{\alpha}} \quad (6)$$

For each extent of cure $\alpha_i$, the corresponding $T_{\alpha_i}$ and heating rate are used to plot $\ln(\beta_i/T_{\alpha_i}^2)$ *vs.* $1/T_{\alpha_i}$. The parameters $E_{\alpha}$ and $C_k(\alpha)$ are then determined from the regression slope and intercept, respectively.

Taking into account the hypothesis that cure reactions are not dependent on temperature, the application of isothermal methods allows to determine time, temperature and extent of cure without the introduction of a fixed form of $f(\alpha)$ function [28, 30]. By representing obtained activation energy values *vs.* conversion, the nature of the reaction can be deduced from the shape of the curve [44], e.g. competitive, consecutive reversible, diffusion controlled, etc. Therefore, the effect of the addition of the organoclay in the main curing process can be studied.

## Results and discussion

### *Kinetic parameters from MFK methods*

After synthesis and curing of phenolic resol resin, four different composites have been prepared. When using PheMMT as clay, at low percentages (Phe-1 and Phe-2 composites), an intercalated/exfoliated state has been achieved, but increasing the amount of modified MMT (Phe-4 composite), an intercalated composite with some agglomerates of clay results [22]. On the other hand, using Cloisite 30B (C2 composite), thick agglomerated clay particles are observed, indicating poor dispersion of this MMT in the resol matrix [22].

The cure pathway of phenolic resol resins is mainly based on two reaction types [13, 28, 32]. First, addition reactions of hydroxymethyl groups to ortho- and para-free positions of phenol (or/and *L*-phenyl alanine in the case of PheMMT modified composites [22]). Secondly, condensation reactions of methylol phenols with phenol and/or methylol phenols lead to the final resin [13, 28, 32]. Figure 1a presents dynamic calorimetric scans of synthesized composites and neat resol at 10°C min$^{-1}$. As can be observed, neat resol (Res) exhibits two major exothermic peaks that shift to higher temperatures with increasing heating rate (Fig. 1b). In general, it is assumed that the first exothermic peak at 150–170°C is related to residual addition reactions (mostly of addition reactions were completed during synthesis of resol resin) and condensation reactions of resols giving as a result methylene and ether bridges [32, 45, 46]. The second exothermic peak, centered around 200°C, is related to subsequent reactions, such as the break of ether bridges to methylene bridges and/or oxidation reactions at high temperatures [32, 40]. As reported in a previous work [40], the behaviour of the composites can change in the presence of modified MMT. Increasing PheMMT content, both exothermic peaks merge in only one. Depending on the clay content and the used surfactant, it was observed that modified montmorillonite can lead to acceleration of reactions that usually occur in the second step [40].

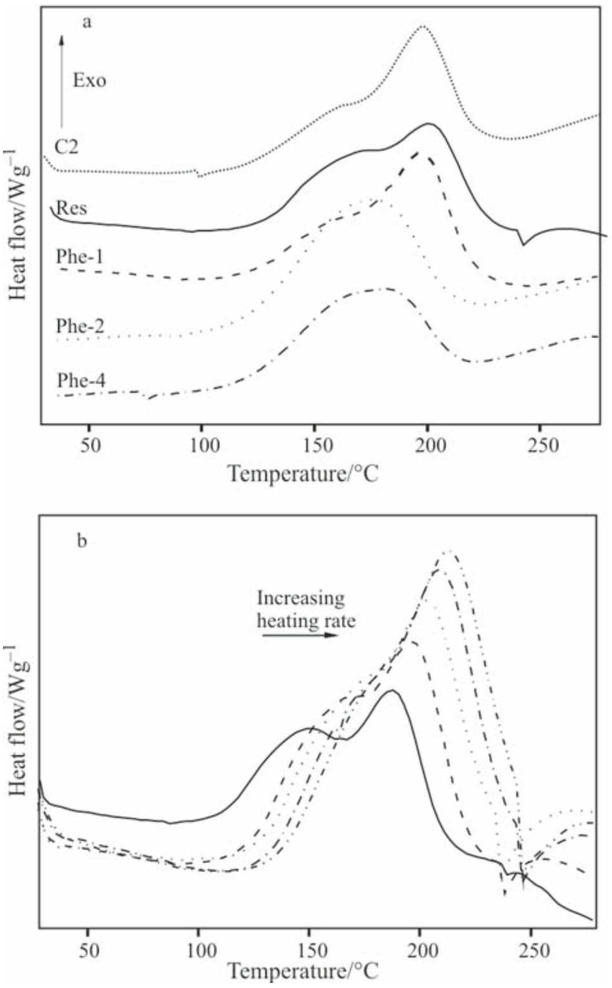

**Fig. 1** DSC dynamic scans for a – composites and neat resol at 10°C min$^{-1}$ and b – resol matrix cured at 5, 10, 15, 20 and 25°C min$^{-1}$

Thereby, with the aim to evaluate and compare the curing behaviour of synthesized composites, Figs 2a–e display the curves of extent of cure *vs.* temperature for all the composites and neat resol at different heating rates. As can be observed, when comparing the curves of conversion-temperature profiles of different composites with this one of resol at same conversion, the presence of PheMMT accelerates cure reactions. On the other hand, curves for C2 composite are in general slightly delayed at high conversion, overall at higher heating rates, while its behaviour at 5°C $\text{min}^{-1}$ is fairly similar to this one of the neat resol. For example at 160°C and 10°C $\text{min}^{-1}$, if the conversion for neat resol is 0.25, for Phe-2 is 0.33 and for Phe-4 is 0.36, while for C2 is 0.20.

Isoconversional method of Kissinger–Akahira–Sunose was applied to determine the kinetic parameters. Figure 3 show the dependence of $E_a$ on extent of cure for all the composites and neat resol. The overall range of $E_a$ values is similar to other values reported for phenolic resol resins [27, 29, 32]. For neat resol, the observed upward tendency of $E_a$ values is characteristic of a reactive process which involves multiple, parallel and competitive reactions [45]. Therefore, an increase in activation energy is observed up to over 70% extent of cure. Above this extent of cure, $E_a$ changes the upward tendency and it starts to decrease, that Vyazovkin *et al.* [47] reported as a kinetic transition from a chemical to a diffusion-controlled process. As can be observed, at extents of cure around 20–30%, there is a slight $E_a$ decrease related to the presence of reversible reactions [28, 32, 47]. Addition reactions of remaining formaldehyde are likely to occur in the case of RT1.4 resols because enough free aromatic reactive sites able to react do exist. Thereby, new hydroxymethyl groups could lead to a decrease in the activation energy value as a result of the activation effect of the alcohol groups over the aromatic ring. The decrease occurs in a narrow range of conversion because addition takes place mainly in the previous synthesis process.

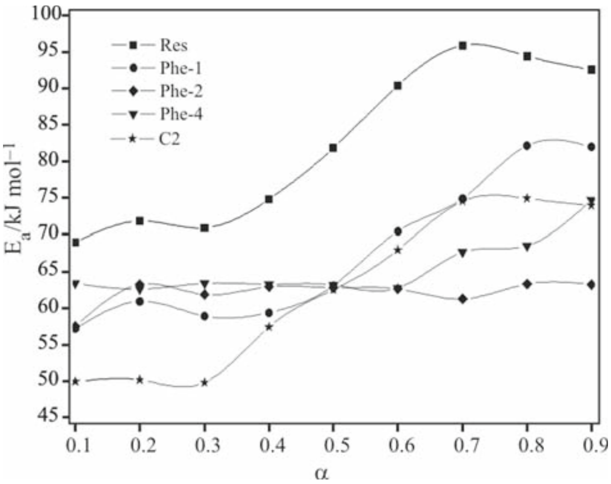

**Fig. 3** Activation energy variation upon extent of cure obtained by KAS method for: neat resol, Phe-1, Phe-2, Phe-4 and C2 composites

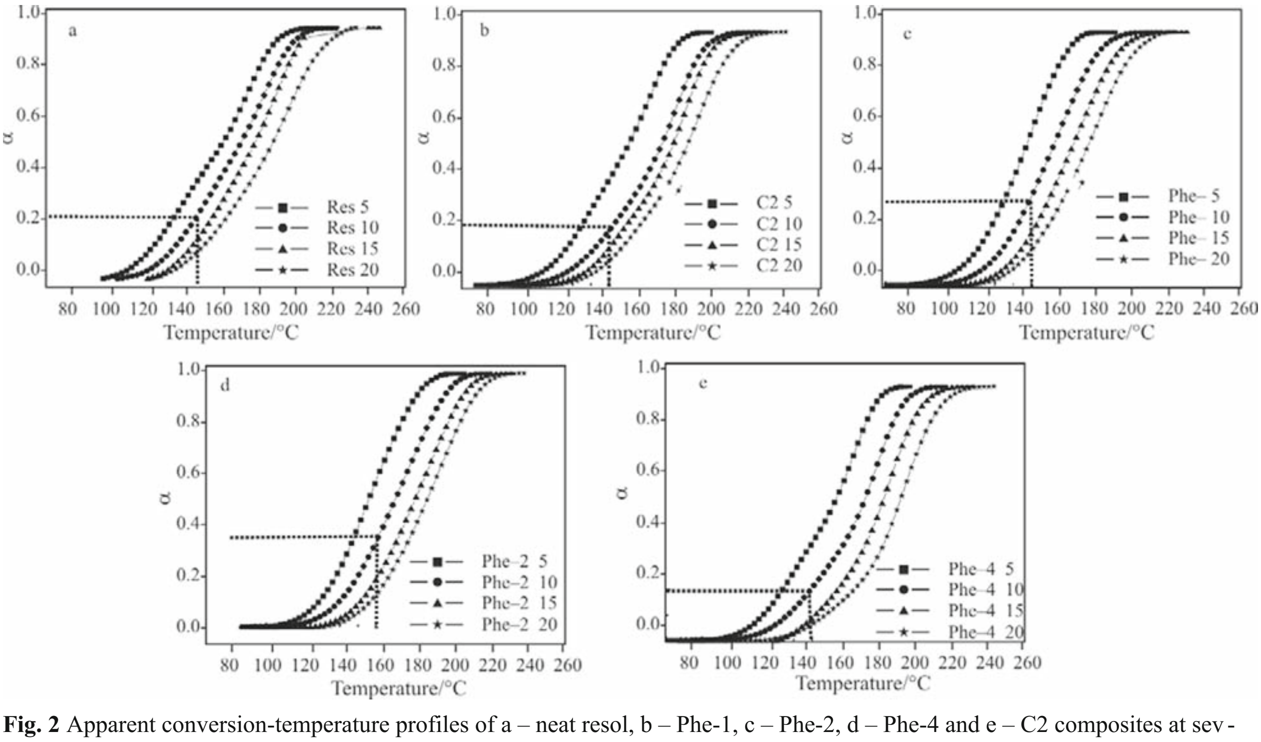

**Fig. 2** Apparent conversion-temperature profiles of a – neat resol, b – Phe-1, c – Phe-2, d – Phe-4 and e – C2 composites at several heating rates indicated in the figure c

Therefore, the reaction of phenolic resins is a complex process, which includes addition and condensation reactions going through gelation and vitrification stages [13, 32]. On the other hand, the curing reactions of phenolic resins, when mixed with organoclay, may become more complicated because of interactions between resol and modified clay and the presence of the clay during the curing, as it was also observed in a previous study [40].

Thus, significant variations are observed in $E_a$ values in modified clay resins. For montmorillonite modified phenolic system, a balance between the intragallery and the extragallery polymerisation rates is required in order to exfoliate the clay into the matrix [22]. For exfoliated/intercalated composites as Phe-1 and Phe-2, this balance seems to be achieved. In the case of Phe-4 or C2 composites, the extragallery polymerisation seems to be more favourable, remaining part of the added modified clay as agglomerates [22].

When PheMMT is used, the presence of the amino acid group in the intragallery of the MMT could lead to condensation reactions between carboxyl (–COOH) end group of *L*-phenyl alanine and –OH groups of formaldehyde in aqueous acidic solution, thus acting like an anchorage point between the layers and the resin. This fact could catalyze cure reactions [33, 34, 37, 40] as a result of the reactive effect of the *L*-phenyl alanine groups, as above shown in Fig. 2. On the other hand, as previously reported [40] the presence of modified PheMMT could accelerate the oxidative reactions that naturally occur at higher temperatures. The largest oxidation was seen for composite Phe-2 where acid nature of MMT and phenylalanine could favour oxidation reactions. On the other hand, in the case of Cloisite 30B, the presence of long alkyl chains of the surfactant seems to decrease the acid nature of the montmorillonite, thus avoiding the acceleration of these oxidation reactions at the used temperatures.

Furthermore, the lack of interactions in composite C2 between the montmorillonite modifier and the reactive groups of resol along with the low extent of cure achieved due to the steric barrier of the unreactive clay that remains in large agglomerates, observed in a previous study [22], results in the decrease in the $E_a$ values.

On the other hand, Table 1 provides the apparent extent of cure values at a specific cure time for isothermal curing at 110°C and dynamical curing at 10°C $\text{min}^{-1}$ [40] for the different composites. As can be seen, when increasing the clay content for PheMMT composites, the apparent extent of cure at this time, decreased from 0.76 to 0.55. Thereby, higher clay contents seem to hinder the curing reactions as a result of the clay providing a steric barrier [36], although in the case of PheMMT composites, apparent conversion values could be lower than real because in scans used to obtain residual enthalpies higher temperatures are reached and so, more affected by oxidation reactions [40]. Thus, at initial stage of curing, the presence of reactive groups of MMT modifier could catalyse the curing reactions but the clay can also create a steric barrier at further stages of reaction. Moreover, the presence of oxidation reactions in the case of PheMMT composites seems also to affect the cure.

When Cloisite 30B was used, as it does not contain reactive groups, curing reactions were retarded possibly due to the presence of montmorillonite agglomerates as observed in a previous study [22].

### *Modelling of dynamic cure of Phe-2 composite*

KAS method was also used to predict the dynamic cure of Phe-2 composite [27]. This model was developed using 5, 10, 15°C $\text{min}^{-1}$ values of heating rates and the dynamic prediction corresponds to curing at 20°C $\text{min}^{-1}$. At a selected heating rate $C_k$ ($\alpha$) (defined in Eq. (6)) and $E_\alpha$, both were substituted into Eq. (5) to predict the apparent extent of cure *vs.* temperature behaviour. By using Mathcad 12.0 and by application of Eq. (5), theoretical relationships between extent of cure *vs.* temperature curves have been obtained, as shown in Figs 4a–b for Phe-2 composite. Symbol curves correspond to KAS predictions, while continuous lines are experimental curves. Despite a slight shift at the initial and the final stages of reaction, KAS model seems to be effective to predict the dynamic cure of this system at 20°C $\text{min}^{-1}$.

**Table 1** Extent of cure and area (J $\text{g}^{-1}$) under the exothermic peak for the different composites for isothermal (110°C) and dynamic measurements (10°C $\text{min}^{-1}$)

| Composite | Isothermal reaction enthalpy | Residual enthalpy | Total enthalpy | Apparent extent of cure |
|---|---|---|---|---|
| Res | 170 | 55 | 225 | 0.76 |
| Phe-1 | 177 | 100 | 277 | 0.64 |
| Phe-2 | 185 | 122 | 307 | 0.60 |
| Phe-4 | 161 | 129 | 290 | 0.55 |
| C2 | 104 | 146 | 254 | 0.41 |

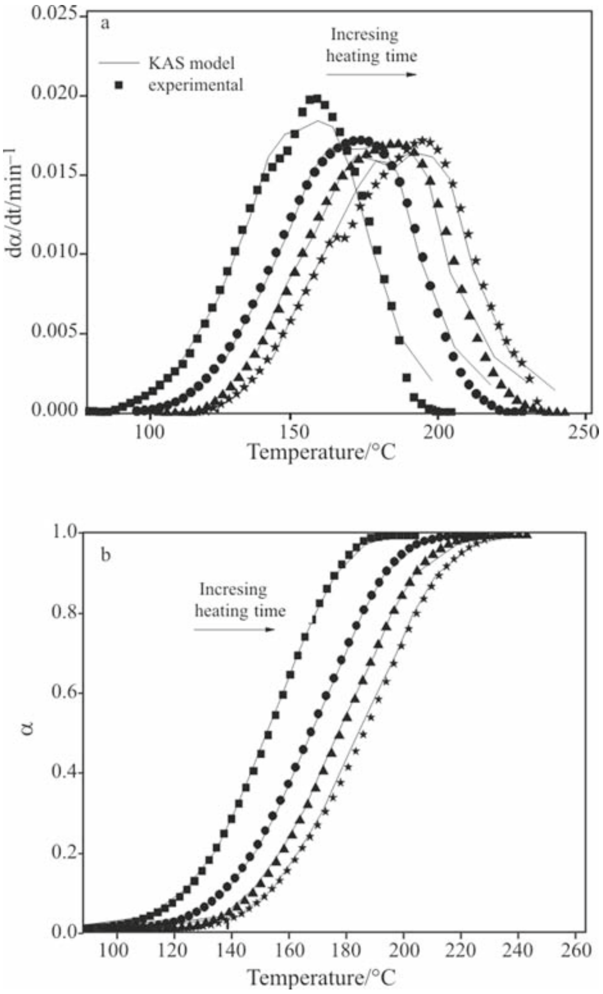

**Fig. 4** Comparison of experimental data and KAS predictions at 5, 10, 15 and 20°C min$^{-1}$ for: a – reaction rate and b – extent of cure profiles for Phe-2 composite

### *Acquisition of apparent rate constant values for composites and neat resol*

From the kinetic values obtained from isoconversional method, apparent rate constants can also be studied for different extents of cure (Fig. 5). No significant changes in apparent rate constant values for neat resol and C2 composite were observed. On the contrary, when using PheMMT as modified clay, at early stages of curing a slight increase in rate constant values is detected. PheMMT modified composites present not only ring reactive positions but also other reactive sites as a result of the presence of the *L*-phenyl alanine modifier [22, 48, 49] that can result in this increase in rate constant values. At the final stage of curing, all the composites seem to have similar apparent rate constants.

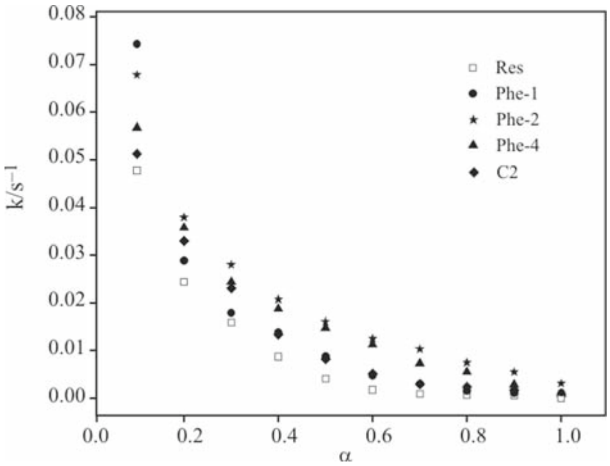

**Fig. 5** Evolution of apparent rate constant with extent of cure for neat resol and all the composites

## Conclusions

A kinetic study of different composites based on phenolic resol resins and modified montmorillonites was carried out using differential scanning calorimetry. Activation energies of those systems were obtained by application of Kissinger–Akahira–Sunose model-free kinetics. An upward dependency of activation energy on conversion was observed for neat resol, indicating a complex reaction pathway that involves multiple and competitive polymerization reactions. On the other hand, when all the composites were analyzed, a different behaviour was observed. When using PheMMT, changes in $E_a$ values during curing process of composites can be the result of two different factors: on one side, the presence of possible additional reactions because of the reactive modifiers of MMT and on the other, the clay providing a steric barrier. On the contrary, using Cloisite 30B, only small changes in apparent rate constant with conversion were observed because of the poor dispersions of this clay in the matrix. On the other hand, kinetic parameters obtained from KAS method indicate that neat resol and composites present different cure reactions depending on the load of clay and the kind of modifier, concluding that PheMMT modified composites react more easily than neat resol due to the presence of modified montmorillonite. Furthermore KAS algorithm also was found to be suitable for the dynamic cure prediction of these polymer clay nanocomposites.

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## References

1 A. Usuki, M. Kawasumi and Y. Kojima, J. Mater. Res., 8 (1993) 1174.
2 K. Wang, L. Chen, J. Wu, M. L. Toh, C. He and A. F. Yee, Macromolecules, 38 (2005) 788.
3 B. Chen and J. R. G. Evans, Polym. Int., 54 (2005) 807.
4 D. García-López, I. Gobernado-Mitre, J. F. Fernández and J. M. Pastor, Polymer, 46 (2005) 2758.
5 C. H. Dan, M. H. Lee, Y. D. Kim and J. H. Kim, Polymer, 47 (2006) 6718.
6 R. Pucciariello, V. Villani, F. Langerame, G. Gorrasi and V. Vittoria, J. Polym. Sci.: Part B: Polym. Phys., 42 (2004) 3907.
7 T. X. Liu, Z. H. Liu, K. X. Ma and C. B. He, Compos. Sci. Technol., 63 (2003) 331.
8 T. McNally, W. R. Murphy, C. Y. Lew and G. P. Brennan, Polymer, 44 (2003) 2761.
9 O. Becker, R. Varley and G. Simon, Polymer, 43 (2002) 4365.
10 Y. Lee and S. J. Kim, Colloids Surf., 211 (2002) 19.
11 Y. Kim and J. L. White, J. Appl. Polym. Sci., 96 (2005) 1888.
12 T. Kollár, I. Pálinkó, Z. Kónya and I. Kiricsi, J. Mol. Struct., 335 (2003) 651.
13 A. Gardziella, L. A. Pilato and A. Knop, 'Phenolic Resins', 2nd Ed., Springer Verlag, Berlin 2000, p. 29.
14 G. Astarloa-Aierbe, J. M. Echeverría, M. D. Martín, A. M. Etxeberria and I. Mondragon, Polymer, 43 (2002) 2239.
15 G. Astarloa-Aierbe, J. M. Echeverría, M. D. Martín, A. M. Etxeberria and I. Mondragon, Polymer, 41 (2000) 3311.
16 G. Astarloa-Aierbe, J. M. Echeverría, M. D. Martín, A. M. Etxeberria and I. Mondragon, Polymer, 41 (2000) 6797.
17 L. B. Manfredi, D. Puglia, J. M. Kenny and A. Vázquez, J. Appl. Polym. Sci., 104 (2007) 3082.
18 H. Y. Byun, M. H. Choi and I. J. Chung, Chem. Mater., 13 (2001) 4221.
19 H. Wang, T. Zhao, L. Zhi and Y. Yan, Macromol. Rapid Commun., 23 (2002) 144.
20 H. Wang, T. Zhao and Y. Yan, J. Appl. Polym. Sci., 92 (2004) 791.
21 Z. Wu, C. Zhou and R. Qi, Polym. Compos., 23 (2002) 634.
22 M. López, M. Blanco, J. A. Ramos, A. Vázquez, N. Gabilondo, J. J. del Val, J. M. Echeverría and I. Mondragon, J. Appl. Polym. Sci., 106 (2007) 2800.
23 H. L. Friedman, J. Polym. Sci., C6 (1965) 183.
24 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
25 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
26 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
27 J. Wang, M. G. Laborie and M. P. Wolcott, Thermochim. Acta, 439 (2005) 68.
28 G. He, B. Riedl and A. Aït-Kadi, J. Appl. Polym. Sci., 87 (2003) 433.
29 M. V. Alonso, M. Oliet, F. García, J. Rodríguez and J. M. Echeverría, Chem. Eng. J., 122 (2006) 159.
30 S. Li and P. Järvelä, J. Polym. Sci.: Part B: Polym. Phys., 39 (2001) 1525.
31 G. He, B. Riedl and A. Aït-Kadi, J. Appl. Polym. Sci., 89 (2003) 1371.
32 N. Gabilondo, M. López, J. A. Ramos, J. M. Echeverría and I. Mondragon, J. Therm. Anal. Cal., 90 (2007) 229.
33 M. Ivankovic, I. Brnardic, H. Ivankovic and H. J. Mencer, J. Appl. Polym. Sci., 99 (2006) 550.
34 W. Xu, S. Bao, S. Shen, W. Wang G. Hang ang P. He, J. Polym. Sci.: Part B: Polym. Phys., 41 (2003) 378.
35 D. S. Kim and K. M. Lee, J. Appl. Polym. Sci., 92 (2004) 1955.
36 D. Yei, H. Fu, W. Chen and F. Chang, J. Polym. Sci.: Part B: Polym. Phys., 44 (2006) 347.
37 M. Shen, M. Lu, Y. Chen and C. Ha, J. Appl. Polym. Sci., 96 (2005) 1329.
38 C. J. Pérez, V. A. Alvarez, P. M. Stefani and A. Vázquez, J. Therm. Anal. Cal., 88 (2007) 825.
39 L. Abate, I. Blanco, F. A. Bottino, G. Di Pasquale, E. Fabbri, A. Orestano and A. Pollicino, J. Therm. Anal. Cal., 91 (2008) 681.
40 M. López, M. Blanco, A. Vazquez, A. Arbelaiz, N. Gabilondo, J. M. Echeverria and I. Mondragon, Thermochim. Acta, 467 (2008) 73.
41 R. B. Prime, in: E. A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York 1997, pp. 1380–1744.
42 T. Akahira and T. Sunose, Joint Convention of Four Electrical Institutes. Research Report Chiba Institute Technology, (1971) no. 246.
43 C. D. Doyle, Anal. Chem., 33 (1961) 77.
44 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340 (1999) 53.
45 T. Holopainen, L. Alvila, J. Rainio and T. T. Pakkanen, J. Appl. Polym. Sci., 66 (1997) 1183.
46 J. M. Kenny, G. Pisaniello, F. Farina and S. Puzzielo, Thermochim. Acta, 269/270 (1995) 201.
47 S. Vyazovkin and A. Lesnikovich, Thermochim. Acta, 165 (1990) 273.
48 C. Peña, M. Larrañaga, N. Gabilondo, A. Tejado, J. M. Echeverría and I. Mondragon, J. Appl. Polym. Sci., 101 (2006) 2034.
49 C. Peña, M. D. Martin, A. Tejado, J. Labidi, J. M. Echeverría and I. Mondragon, J. Appl. Polym. Sci., 100 (2006) 4273.

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