

Kinetics of curing process in carbon/epoxy nano-composites

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Abstract. Epoxy resins are routinely used as adhesives, coatings, encapsulates, casting materials, and as matrix in composites. Their high crosslinking supposes too much rigidity, resulting in low toughness. Nano-filled addition could modify toughness, but it could also modify the curing process of the resin. Quality requirements of nano-composite (NC) imply a control of their curing process to ensure the mechanical properties of the material. Therefore, the aim of this work is to study the influence of carbon-based nano-fillers in the kinetics of curing of an epoxy resin. Three different methods are used in this work, Kissinger, Kamal and Model Free (MFK). The methods are complementary and provide information on the curing process of the nano-composites.

1. Introduction

Polymer matrix composite (PMC) are materials which provide a good compromise between properties and weight. These properties depend on the filler used, so additives can be found in several geometries, for example natural fibres [1], carbon fibres [2], glass fibres [3], natural particles [4] or inorganic particles as carbon black [5], silicon carbide [6], boron carbide [7], silica [8], polyhedral oligomeric silsesquioxanes (POSS) [9], etc. All these additives can change the mechanical, tribological, thermal, electric or magnetic properties. This design strategy allows obtaining materials with on-demand properties.

Epoxy resins are the most versatile of the structural adhesives being strong but also brittle. They are usually used as polymer matrix to manufacture composites. Epoxy resins are a thermosetting polymer which possesses an oxirane group. This oxirane group is opened and it accelerates curing reaction. Polyaddition reactions with amines or polyamides are well known curing reactions, through which a primary or secondary amines added to the epoxy produce tertiary amine. The presence of particles or nanoparticles can promote or prevent the curing reactions [10,11] since other types of hydroxyl groups with different reactivity can activate the oxirane rings [12]. Amine type affects to curing reactions, so aliphatic amines cure epoxies at room temperature, whereas aromatic amines require higher temperatures.

The main purpose of this work is to study the curing process in an epoxy resin that cures at room temperature (Araldite 2020) modified with nano-carbon particles. For this purpose graphene, graphene oxide, multi-walled carbon nano-tubes and chemically exfoliated graphite nano-platelets were added in wt. 0.5% to the epoxy resin.

Differential scanning calorimetry (DSC) is an efficient method to analyse curing processes of



thermoset resins. Kinetic parameters were calculated by non-isothermal scans.

2. Materials and experimental procedure

2.1. Materials

Epoxy resin used to manufacture the nanocomposite was Araldite 2020 by Hunstman (Barcelona, Spain). The rate epoxy: hardener was 100:30 by weight. This resin has a low viscosity and cure at room temperature for 24 hours. The used nano-carbon materials were graphene (G) of 1-2 layers by Avanzare Innovación Tecnológica S.L. (Logroño, Spain), graphene oxide (GO) and graphite nanoplatelets (GKOH) from Nanoinnova Technologies (Madrid, Spain); and multi-walled carbon nanotubes (CNT) by Nanocyl (Sambreville, Belgium).

2.2. Experimental process

A differential scanning calorimetry (DSC) 822e instrument was used and 40 μ l aluminium crucibles were filled with approximately 8 mg of composite for each test. Different types of nano-carbon materials were added in 0.5 wt% and mixed mechanically for 10 min to 120 rpm, and then 8 mg approximately of this mixture was brought into pan to carry out the test by DSC. Nitrogen (80 ml/min flow) was used as purge gas. The non-isothermal scans were programmed from 0 to 200°C with a heating rate of 5, 10 and 20°C min⁻¹. For each composition, test was repeated three times.

2.3. Kinetic analysis

To analyse the cure kinetics of specimens, with and without nano-particles, non-isothermal (dynamic) DSC tests were performed. The kinetic analysis is based on the curing rate and it is proportional with the rate of heat flow at any time. So the rate of reaction can be described as equation (1).

$$d\alpha/dt = dH/dt \times 1/\Delta H = k(T)f(\alpha) \quad (1)$$

Being ΔH the total heat of reaction determined from integration of the DSC curve, H the total heat released between start of reaction and time t , α the conversion degree, and $d\alpha/dt$ and dH/dt stand for curing rates and the heat flow. The $k(T)$ is a temperature-dependent parameter and $f(\alpha)$ is a conversion degree function.

Kinetics and calculi of curing activation energy were carried out under three different methods. Empirical methods were performed to calculate the kinetic parameters. At the first method the experimental data were adjusted to a model for heterogeneous reactions, using two kinetic mechanisms: autocatalytic and n -order. The autocatalytic mechanism is characterized by a maximum reaction rate at about 30–40% reaction curing progress. For the calculation of the kinetic parameters the Kamal's method was used [13], according to equation (2) where the two mechanisms are included:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2)$$

Kamal M R and Sourour [13] explained these parameters. While the chemical kinetic controls the reaction, the rate constants (k_1 and k_2) depend on temperature following an Arrhenius dependence, according to equation (3).

$$K = Ae^{-(E_a/RT)} \quad (3)$$

The pre-exponential constant or frequency factor (A), in the Arrhenius equation, is an empirical relationship between temperature and rate coefficient. It depends on the quantity of molecules or groups in the reaction and their orientation [14].

The model free kinetic (MFK) [15,16] gives reliable predictions about conversions degree of chemical reactions under simulated conditions and allows calculate an E_a which depends on the conversion degree. The E_a was obtained using STARE Software of Mettler Toledo GmbH.

In addition other empirical models (such as Kissinger and Flynn–Wall–Ozawa models) can be used

for dynamic kinetic studies. They have already been used to study epoxy based nanocomposites [17]. This model keeps in mind the curing peak temperature and heating rates, it is applying an Arrhenius type equation, according to equation (4), where β is heating rates.

$$\beta/T_p^2 = Ce^{-E/RT_p} \quad (4)$$

3. Results and discussion

When non-isothermal scans are integrated at three heating rates, the curing heat (ΔH) and the temperature (T_p) of curing peak are known. These values are shown in table 1. As it is logical whereas rate increases the curve is moved to the right and temperature increases with the heating rate. The addition of nano-particles produces a descent of the curing heat, this effect is more significant when GKOH or GO is added, mainly with GO. In the nano-composite with GO a decrement of the peak temperature is also noted.

Table 1. Influence of heating rate on peak temperature (T_p) and total reaction heat (ΔH)

β (°C/min)	5	10	20	$\Delta H \pm 1$ (J/g)
	$T_p \pm 1$ (°C)			
Araldite	99	114	130	346
+0.5CNT	99	115	131	338
+0.5G	97	115	131	339
+0.5GKOH	97	113	130	319
+0.5GO	95	111	127	289

According to equation (1) the conversion degree for all heating rates of each nano-composite and clear resin is calculated.

3.1. Kamal kinetic model

From the DSC curves, the conversion degrees versus the temperature or time can be obtained; figure 1 shows conversion degree at three heating rates for nano-composite with 0.5% CNT. Conversion degree plot is the average of three scans and its error is not more than $\pm 1\%$. Figure 2 shows the curves (figure 1) derived with respect to time and plotted versus the conversion degree. Fitting these curves (figure 2) according to Kamal model equation (2) (see figure 3) then the kinetic parameters are obtained.

In this case reaction constants (k_1 and k_2) are obtained, which provide information about the reaction rates of n -order and autocatalytic respectively, together the order reaction (n and m). The table 2 shows the kinetic parameters for all nano-composites and clear resin.

The reaction constants increase with heating rate, k_2 is greater than k_1 , so the autocatalytic reaction is always faster than the n -order. Additions of nano-particles decrease the reaction rate thus slowing the curing reactions consequently. Reaction order also decreases, which implies fewer particles present in the medium to produce the curing reaction.

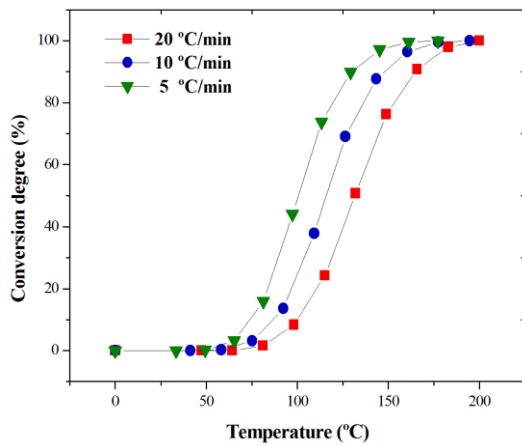


Figure 1. Conversion degree versus temperature of Araldite + 0.5CNT.

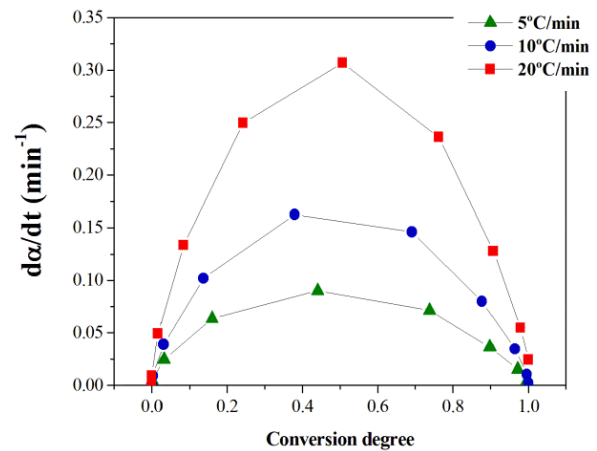


Figure 2. Reacting rates ($d\alpha/dt$) versus conversion degree Araldite + 0.5CNT.

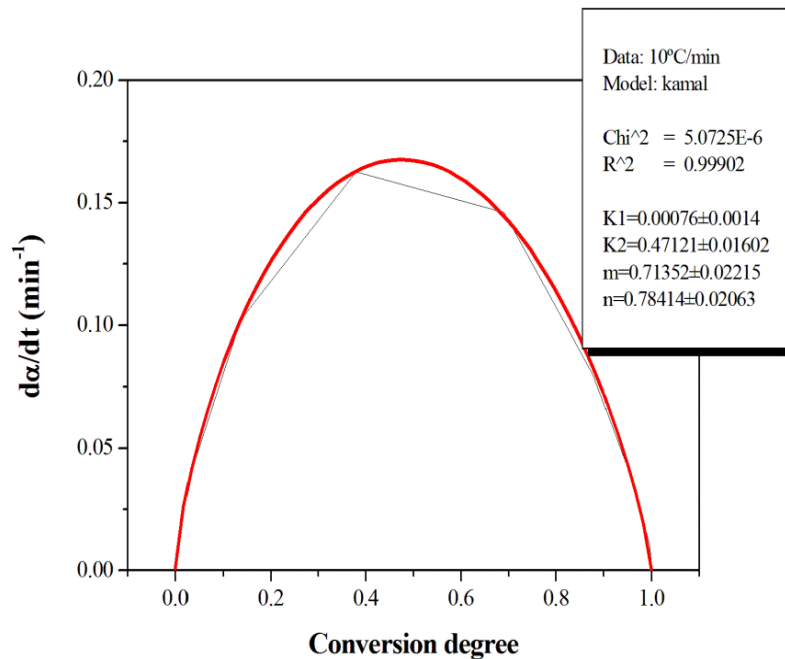


Figure 3. Fit to Kamal model: Reacting rates ($d\alpha/dt$) versus conversion degree Araldite + 0.5CNT at 10 °C/min.

Table 2. Kinetic parameters obtained by kamal model equation (1).

	K_1 (min^{-1})			K_2 (min^{-1})			m+n			R^2		
β ($^{\circ}\text{C}/\text{min}$)	5	10	20	5	10	20	5	10	20	5	10	20
Araldite	0.0102	0.0229	0.0345	0.6010	1.1039	1.6574	2.6	2.6	2.4	0.9919	0.9868	0.9650
+0.5G	0.0004	0.0022	0.0021	0.2662	0.3703	0.8607	1.5	1.3	1.5	0.9993	0.9970	0.9941
+0.5CNT	0.0005	0.0008	0.0034	0.2456	0.4712	0.8270	1.5	1.5	1.4	0.9991	0.9990	0.9937
+0.5GKOH	0.0014	0.0016	0.0035	0.2459	0.4633	0.7712	1.4	1.5	1.4	0.9977	0.9989	0.9923
+0.5GO	0.0008	0.0019	0.0021	0.2292	0.4690	0.6905	1.5	1.5	1.5	0.9987	0.9989	0.9954

3.2. Activation energy

The activation energy was calculated from k_1 and k_2 and equation (3), and from heating rates and equation (4). Figure 4 shows how the equations are applied, plotting $\ln(k \text{ or } \beta/T_p^2)$ versus $1000/T$ then the data is adjusted to a line whose slope allows to calculate the activation energy and table 3 shows linear regression (R^2) of these adjustments.

In figure 5 the activation energy values are observed, for clear resin, and nano-composites with graphene and nano-tubes. The activation energy from k_1 (constant of n -order reaction) is greater than k_2 , being greater for nano-composites. As the n -order reaction initially has a maximum rate, the curing reaction of these nano-composites needs more energy at the beginning and in the end than clear resin. However nano-composites with graphene oxide and graphite nano-platelets need less energy than the clear resin. This effect may be due to the presence of OH groups which could catalyse the reaction that favours the beginning of the reaction. The OH groups on the surface of nano-fillers could produce a catalytic effect [18], then the oxirane ring does not need to open, the catalytic reaction would start earlier than the autocatalytic, which has a maximum rate at about 30-40% of the reaction progress. In this case, activation energy from k_2 is similar at all nano-composites.

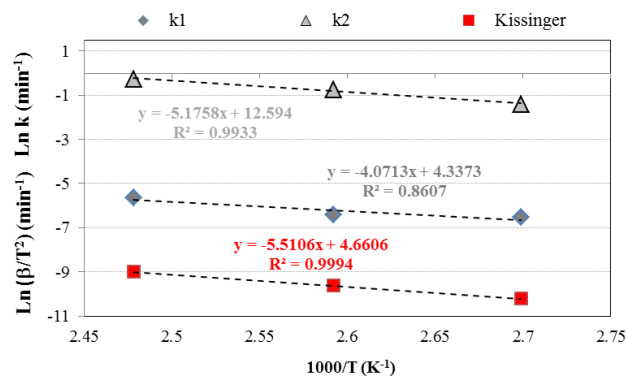


Figure 4. Adjustment for calculation of the activation energy from equations (3) and (4) for nano-composite Araldite + 0.5%GKOH.

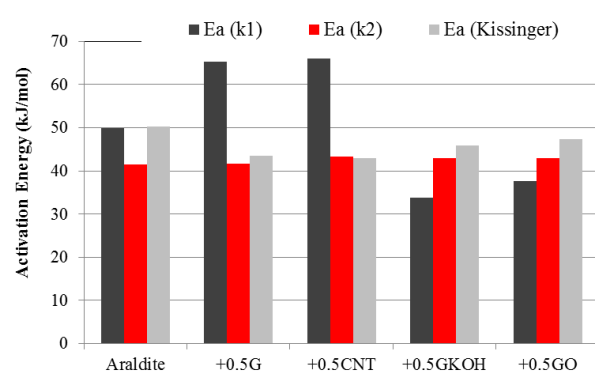


Figure 5. Activation energy obtained from reaction constants of Kamal model (equation (3)) and Kissinger model (equation (4)).

Table 3. R^2 values of the adjustments to a line of Arrhenius equation.

	R^2		
Araldite	0.9574	0.9983	1
+0.5G	0.8787	0.9100	0.959
+0.5CNT	0.8545	0.9994	0.9942
+0.5GKOH	0.8607	0.9933	0.9994
+0.5GO	0.8889	0.9807	0.9987

When Kissinger model is used, activation energy is always higher for the clear resin than the nano-composites, in this case according to equation (4), the heating rates are only taken into account; therefore the reaction mechanisms do not have influence.

When MFK is used, the activation energy depends on conversion degree. Taking into account only the beginning of the reaction, from figure 6 it is clearly appreciable that the clear resin (Araldite) needs more energy than the nano-composites. Activation energy is higher for graphene and nano-tubes than for the other nano-fillers. Therefore at the beginning the nano-fillers favour the curing reaction, specially GO and GKOH. However, in the middle of reaction clear resin and nano-composites have similar activation energy, although nano-composite with graphene needs slightly less energy than the

rest. At the end of reaction nano-composite with graphene needs less energy to finish its curing reaction than any other materials; on the other hand the nano-composite that contains graphene oxide needs more energy than every else. This effect could be due to a fast initial reaction in which the graphene oxide could react with the OH groups of oxirane rings. After that, the crosslinking between the chains would be slowed and the last 5% curing takes much more time than in the other nanocomposites.

Others researchers explained these types of effect, thus kinetic models are based on a fast-pre-equilibrium step which happens due to hydrogen bonding between the oxygen of the epoxide ring and OH groups, as proton donor [19-24]. The reaction is also participated by amine-hydroxyl complexes [19]. Nevertheless in amine-hydroxyl complexes the amine is the proton acceptor, thanks to the greater dipolar moment of OH groups. According to Rozenberg [20] when amine loses its nucleophilic character, the oxirane ring reaction does not happen. Beside a compensation effect amine-amine and hydroxyl-hydroxyl reaction can be slighted.

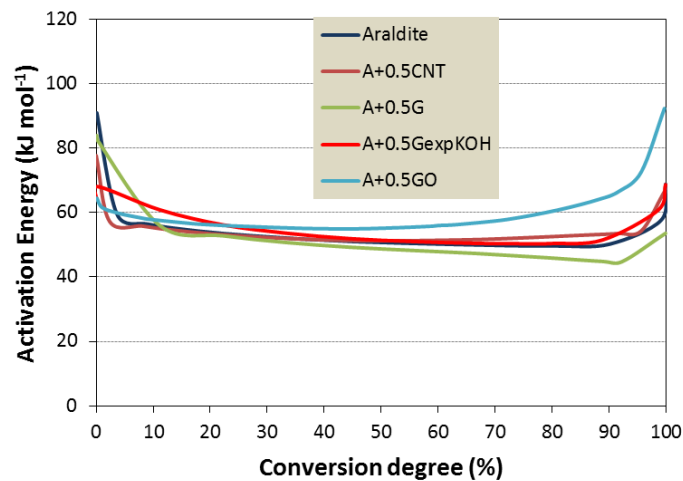


Figure 6. Activation energy obtained by MFK.

4. Conclusions

The empiric models complement each other and give information about the curing mechanisms that are being produced.

The Kamal and MFK models provide similar information, noting that there are two mechanisms: n -order at the beginning and end of the reaction and autocatalytic when oxirane group is opened and following while these are present in the medium.

The nano-carbon particles have an influence on the curing of the studied composites, this influence is greater when the nano-particles contain OH groups. These groups catalyse the reaction, but they can also delay its completion.

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