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# ISOTHERMAL DEGRADATION AND THERMOOXIDATIVE DEGRADATION OF AN EPOXY POWDER COATING

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Thermogravimetry was used to study the kinetics of isothermal degradation of an epoxy thermoset powder coating in a nitrogen atmosphere and in oxidising atmospheres of air and pure oxygen. An integral isoconversional procedure was used to analyse how the activation energy varies depending on the degree of conversion and depending on the atmospheres used. In the case of degradation in a nitrogen atmosphere, in addition to the activation energy, the kinetic triplet was completed using an Avrami reaction model and the pre-exponential factor. With this atmosphere, the conclusion was reached that the isothermal and non-isothermal kinetics are equivalent. It was shown that the thermooxidative degradation process is more complex and consists of a two-stage process. The first stage of degradation is similar whether nitrogen, oxygen or air are present. Chain scission occurs and it seems that there is formation of thermally more stable compounds. The second stage of degradation, involving several phenomena, occurs only in the presence of oxygen or air and leads to the total disappearance of the organic material by thermooxidation. These stages are very similar under non-isothermal or isothermal conditions.

***Keywords:*** *isoconversional method, kinetics, thermal analysis*

## Introduction

Thermoset powder coatings attain their final state through polymerisation and cross-linking of their components. The study of the kinetics of degradation and of the behaviour of these materials at high temperatures in inert or oxidising atmospheres is of interest from different standpoints: knowledge of thermal stability is valuable in itself and is used to study the mechanisms of ageing and to predict the useful life of the material. It is also a means of checking a posteriori the degree of curing or cross-linking and therefore the quality of a coating once it has been formed. There are many standardised tests to determine the stability and useful life of a given material. All of them share the aim of using experiments lasting a short time or carried out under extreme conditions to predict what will happen over longer times or under less demanding service conditions. Although not all the procedures are standardised, techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TG) have been used for some time now for this purpose, since they have the advantage of providing results much more quickly than in the case of other standardised procedures [1–7].

In the study of the kinetics of degradation by means of either DSC or TG, it is normal to use non-isothermal procedures, even though the information that is eventually of the greatest interest has to do with isothermal kinetics. Non-isothermal procedures have the advantage that they take less time. In addition, the limitations of the instruments used in isothermal experiments give rise to a potential loss of data at the start or end of the process that can complicate the subsequent kinetic analysis. This is why degradation studies based on the results of isothermal experiments are much rarer than studies based on the assumption that non-isothermal data on kinetics can be used to give a reasonably accurate description of the kinetics of isothermal degradation [8–10]. Certain authors have also expressed their doubts in this regard or warn that reliable results require a very careful choice of the procedure to be used [11, 12].

In this study we have examined the kinetics of isothermal degradation of an epoxy thermoset powder coating in an inert atmosphere (nitrogen) and in oxidising atmospheres (air and pure oxygen). We chose an integral isoconversional procedure to analyse how the activation energy varies depending on the degree of conversion and on the different atmospheres used.

In the case of degradation in an inert atmosphere, in addition to the activation energy, a kinetic model of the Avrami–Erofeev type was found that provides a reasonable reproduction of the experimental curves and the kinetic triplet was completed, with calculation of the pre-exponential factor. It was also shown that the kinetic parameters found are interchangeable with those obtained in a non-isothermal kinetics study; those results are not set out in this work, but can be found in previous articles [13, 14]. The equivalence

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of these parameters has been verified through analysis of the compensation effect of the different pairs of $E$ and $A$ obtained from both the isothermal and non-isothermal analyses, observing that the non-isothermal data provide a reasonably accurate reproduction of the isothermal curves.

On the other hand, in the isothermal experiments in thermooxidative atmospheres, a coherent kinetic triplet could not be completed for the different stages of the degradation process, since at some of those stages decomposition reactions are superimposed on oxidation reactions, giving rise to highly complex kinetics. Nevertheless, the isoconversional procedure and the changes arising in the apparent activation energy allow the processes to be tracked qualitatively. Likewise, we observe that the non-isothermal analysis and the isothermal analysis both show that the degradation process occurs basically in two stages, one of them involving strictly thermal degradation, and the other involving thermooxidative degradation. Nevertheless, the kinetic parameters obtained through non-isothermal means do not reliably reproduce the isothermal processes.

## Experimental

### *Materials*

An epoxy powder coating, E3-0007/V, manufactured by Ferro Enamel Española, S.A., was used. The reactive components of this product are epoxy bisphenol A (with a molecular mass between 14 000 and 15 000 g $\text{mol}^{-1}$) and dicyandiamide, which are found in a proportion of 95/5. This coating also contains 30% of colouring additives: $TiO_2$, $BaSO_4$, $SiO_2$ and MgO (the latter two in a proportion of less than 1%).

### *Thermogravimetric analysis (TG)*

The thermogravimetric analyses were carried out on a Mettler TG50 thermobalance connected to a Mettler TA4000 thermal analysis system. Isothermal degradation of the samples was carried out for several hours at temperatures of 350, 360, 370, 380, 390 and 400°C in nitrogen, oxygen and air atmospheres. The mass of the samples was approximately 10 mg and the gas flux 200 $\text{cm}^3\ \text{min}^{-1}$ (measured under normal conditions).

## Theoretical background

The rate of degradation or conversion, $\mathrm{d}\alpha/\mathrm{d}t$, in isothermal thermogravimetric experiments can be defined as the variation of the degree of conversion with time. The degree of degradation or conversion is calculated in terms of mass loss as:

$$\alpha = \frac{M_0 - M}{M_0 - M_\infty} \tag{1}$$

where $M_0$, $M$ and $M_\infty$ are, respectively, mass at the beginning, actual mass at each point of the curve and the final mass measured at the end of the degradation process.

Accepting the Arrhenius equation, the kinetics of the reaction are usually described by the rate equation:

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

where $t$ is time, $A$ is the pre-exponential factor, $E$ is the activation energy, $T$ is the absolute temperature, $R$ is the gas constant and $f(\alpha)$ is the differential conversion function.

Integrating the rate equation, Eq. (2), under isothermal conditions we obtain:

$$\ln t = \ln\left[\frac{g(\alpha)}{A}\right] + \frac{E}{RT} \tag{3}$$

where $g(\alpha)$ is the integral conversion function defined as:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} \tag{4}$$

According to Eq. (3), the activation energy and the constant $\ln[g(\alpha)/A]$ can be obtained, respectively, from the slope and the intercept of the linear relationship $\ln t$ *vs.* $T^{-1}$ for $\alpha$=const.

In this work, the kinetic analysis has been carried out using an integral isoconversional method. The basic assumption of this method is that the reaction mechanism, $g(\alpha)$, at constant conversion, does not vary with temperature [15–17].

Another possible procedure is to take Eq. (2), rearranging and taking logarithms to give

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln[Af(\alpha)] - \frac{E}{RT} \tag{5}$$

According to Eq. (5), the activation energy and the constant $\ln[Af(\alpha)]$ can be obtained, respectively, from the slope and the intercept of the linear relationship $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $T^{-1}$ for $\alpha$=const. However, use of Eq. (5) (an isoconversional differential method) requires evaluation of the experimental curve $\mathrm{d}\alpha/\mathrm{d}t$ *vs.* $\alpha$ for each isotherm, which gives rise to substantial errors (Fig. 1), therefore making it recommendable to use an integral method as in Eq. (3) [8].

On the other hand, by combining Eqs (2) and (3) without logarithms, we can obtain master curves of the type:

$$z(\alpha)=f(\alpha)g(\alpha)=(\mathrm{d}\alpha/\mathrm{d}t)t \qquad (6)$$

The left side of Eq. (6), $[f(\alpha)g(\alpha)]$, is a theoretical curve that is characteristic of each reaction mechanism, whereas the right side of the equation can be obtained from experimental data. The master curves of different models listed in Table 1 can then be obtained using this function. Comparing the plots of $z(\alpha)$ calculated by experimental data (right side of Eq. (6)) with the master curves, we can determine the form of the functions $f(\alpha)$ and $g(\alpha)$ that can be associated with the process being analysed.

## Results and discussion

### *Isothermal degradation in nitrogen, oxygen and air atmospheres*

Figure 1 shows the degree of degradation, depending on time and its derivative, for each experimental temperature in the tests in a nitrogen atmosphere. We observe that a relatively rapid process of degradation and volatilisation occurs, associated with chain scission, after which the material is not degraded any further, even after a long time, leaving approximately 10% of the organic material undegraded. This behaviour agrees with the non-isothermal degradation results obtained in previous studies [13, 14] and with the results obtained by other authors in the degradation of similar systems [18, 19]. This is explained by assuming that during this stage there is formation of thermally more stable compounds through molecular rearrangement, these compounds being relatively stable at high temperatures. With non-isothermal degradation [13], it was found that temperatures higher than 700°C were required to attain their total volatilisation.

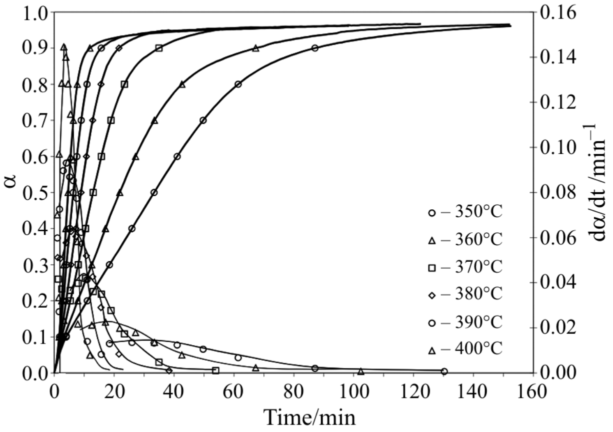

**Fig. 1** Degree of conversion (α) and rate of degree of conversion (dα/d*t*) *vs.* time in a nitrogen atmosphere, for different isothermal experiments

This behaviour changes where the isothermal degradation is carried out in a thermooxidative atmosphere, i.e. air or pure oxygen. Figure 2 compares the mass loss associated with degradation in a nitrogen atmosphere over time with the mass loss obtained in air and oxygen atmospheres at the extreme temperatures studied. We observe that during the initial stage the degradation process is very similar, both in the presence of air and oxygen and in the inert atmosphere. However, after this initial stage, in the case of the experiments in oxidative atmospheres, the rate of degradation slows considerably for a certain time, after which the degradation process

**Table 1** Expressions for $f(\alpha)$ and $g(\alpha)$ functions for the most common mechanisms operating in the solid-state reactions

| Mechanism | Symbol | $f(\alpha)$ | $g(\alpha)$ |
|---|---|---|---|
| reaction order model, first-order kinetics | $F_1$, $A_1$ | $(1-\alpha)$ | $-\ln(1-\alpha)$ |
| three-halves order kinetics | $F_{3/2}$ | $2(1-\alpha)^{3/2}$ | $-1+(1-\alpha)^{-1/2}$ |
| second-order kinetics | $F_2$ | $(1-\alpha)^2$ | $\alpha(1-\alpha)^{-1}$ |
| | $F_3$ | $(1/2)(1-\alpha)^3$ | $-1+(1-\alpha)^{-2}$ |
| power law | $P_n$ | $n\alpha^{(n-1)/n}$ | $\alpha^{1/n}$ |
| random nucleation and growth of nuclei (Avrami–Erofe'ev equation) | $A_{3/2}$ | $(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$ | $[-\ln(1-\alpha)]^{2/3}$ |
| | $A_2$ | $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ | $[-\ln(1-\alpha)]^{1/2}$ |
| | $A_3$ | $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ | $[-\ln(1-\alpha)]^{1/3}$ |
| | $A_4$ | $4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$ | $[-\ln(1-\alpha)]^{1/4}$ |
| one-dimensional diffusion (parabolic law) | $D_1$ | $(2\alpha)^{-1}$ | $\alpha^2$ |
| two-dimensional diffusion (bidimensional particle shape) | $D_2$ | $[-\ln(1-\alpha)]^{-1}$ | $(1-\alpha)\ln(1-\alpha)+\alpha$ |
| three-dimensional diffusion (Jander equation) | $D_3$ | $(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$ | $[1-(1-\alpha)^{1/3}]^2$ |
| three-dimensional diffusion (Ginstein–Brouhnstein equation) | $D_4$ | $(3/2)(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$ | $[1-(2/3)\alpha]-(1-\alpha)^{2/3}$ |
| phase boundary reaction | $R_1$, $P_1$, $F_0$ | $(1-\alpha)^0$ | $\alpha$ |
| contracting area | $R_2$ | $2(1-\alpha)^{1/2}$ | $1-(1-\alpha)^{1/2}$ |
| contracting volume | $R_3$ | $3(1-\alpha)^{2/3}$ | $1-(1-\alpha)^{1/3}$ |
| autocatalytic reaction $(n+m)=2$ | $n=1.9$ | $\alpha^{0.1}(1-\alpha)^{1.9}$ | $[(1-\alpha)\alpha^{-1}]^{-0.9}0.9^{-1}$ |

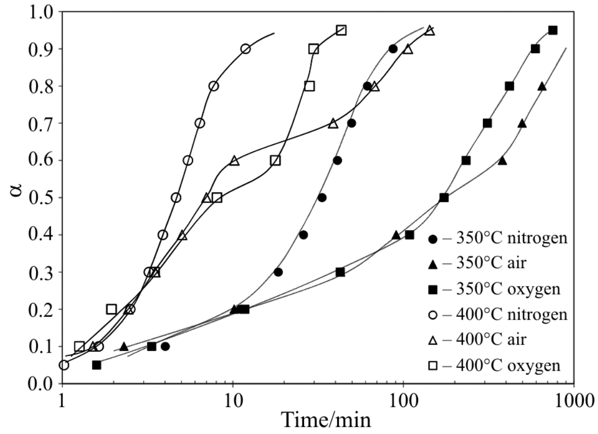

**Fig. 2** Degree of conversion (α) *vs.* time in nitrogen, air and oxygen atmospheres, for 350 and 400°C isothermal experiments

continues at a similar or higher rate in comparison with the initial stage. Furthermore, in contrast with what occurs in the inert atmosphere, here all degradable organic material is eventually volatilised. We can deduce from these experiments that, in an oxidative atmosphere, during the initial stage where degradation occurs through thermal analysis there are also other chemical processes of oxidation that can incorporate oxygen into the degraded materials, giving rise to a local minimum of the rate of mass loss through volatilisation. Subsequently, either because the material that can be oxidised has been exhausted or because the oxidised material eventually volatilises along with the rest, the degradation rate attains a value similar to the initial rate until the process stops due to the disappearance of all organic material. One interesting result observed in Fig. 2 is that, during the initial stage of degradation, the type of oxidative atmosphere, whether air or oxygen, has practically no effect at all on the rate of degradation, which depends exclusively on the temperature. On the other hand, during the second thermooxidative stage, behaviour is different, depending on whether the oxidant is air or pure oxygen. As can be expected, either because the oxidised products formed are of a different type or because the presence of oxygen accelerates the volatilisation process more than the presence of air, at the same temperature the material is degraded faster in oxygen than in air.

### *Kinetics of degradation*

In the case of the kinetics of degradation in a nitrogen atmosphere, applying Eq. (3) to the data obtained in Fig. 1, we can find the activation energy as a function of the degree of conversion. To obtain the pre-exponential factor, we need to elucidate the form of the function $g(\alpha)$. To do so, using the master curves procedure and Eq. (6), we have compared the experimental results with those curves derived from the models in Table 1. Figure 3 shows the experimental results along with a selection of the curves associated with the models of Table 1. We note that model $A_{3/2}$, fits the results for the different isotherms reasonably well, so that $g(\alpha)=[-\ln(1-\alpha)]^{2/3}$ is the function that was used to find the values of the pre-exponential factor $A$, on the basis of the term $\ln[g(\alpha)/A]$ of Eq. (3). Table 2 shows the values for $E$ and $A$ obtained for conversions between 0.1 and 0.9 and the degree of correlation upon application of Eq. (3), which, we note, is very good in all cases. The activation energies found are somewhat lower than those found using non-isothermal procedures [13] and than those reported with systems similar to the ones used here [18, 19].

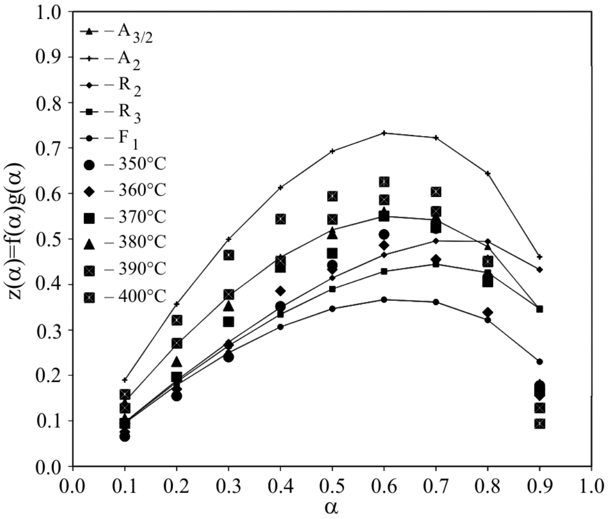

**Fig. 3** Master curves of different kinetic models and experimental data in different isothermal experiments calculated by Eq. (6)

**Table 2** Isothermal kinetic parameters at different degrees of conversion, obtained using Eq. (3) and $A_{3/2}$, Avrami model[a], from experiments in nitrogen atmosphere

| α | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|---|
| $E$/kJ mol$^{-1}$ | 65.3 | 105.7 | 124.5 | 134.0 | 139.1 | 142.7 | 145.5 | 148.2 | 147.7 |
| $\ln[g(\alpha)/A]$/s | –7.1 | –13.9 | –17.1 | –18.6 | –19.3 | –19.8 | –20.1 | –20.4 | –19.9 |
| $\ln A$/s$^{-1}$ | 5.6 | 12.9 | 16.4 | 18.1 | 19.0 | 19.7 | 20.2 | 20.7 | 20.5 |
| R$^2$ | 0.982 | 0.993 | 0.994 | 0.995 | 0.995 | 0.995 | 0.995 | 0.994 | 0.983 |

[a] $g(\alpha)=[-\ln(1-\alpha)]^{2/3}$; R$^2$ – regression coefficient of Eq. (3)

The results of Table 2 show that the activation energy increases with the degree of conversion, as does the pre-exponential factor. From this, we can deduce that the increase of the activation energy will not give rise to a decrease of the rate constant, since it will be compensated by an increase of the pre-exponential factor. This is known as the kinetic compensation effect (KCE) and could be caused either by the changes in the reactive process and the reacting species present, or by experimental causes or comparison of different kinetic models. In this last case, it is known as a pseudo KCE or false KCE [20–22].

The manner of studying the compensation effect is to examine the linear relation that can be established between the pre-exponential factor *A* and the activation energy *E*.

$$\ln A = a + bE \tag{7}$$

where *a* and *b* are constant coefficients for a series of related rate processes.

If two parameter sets (*E*, *A*) satisfy two different KCE relations like Eq. (7), then different kinetics may be correlated with them. On the other hand, even though two sets (*E*, *A*) satisfy the same KCE relation we cannot conclude on that basis that they satisfy the same kinetic expressions. However, analysis of the compensation effect on a kinetic triplet ($f(\alpha)$, $E_\alpha$, $A_\alpha$) obtained through any other procedure (in this case, isoconversional), allows us to determine whether or not it is a reasonable kinetic description of the process and to analyse the effects of experimental factors on kinetic parameters [23–25].

Figure 4 shows the fitting straight line obtained not only by plotting the values of Table 2 obtained through the integral isoconversional process, but also those obtained on the basis of Eq. (5) (differential method) and those obtained in non-isothermal tests in previous studies [13, 14]. As mentioned and as seen in Fig. 4, the activation energies obtained in non-isothermal tests show values higher than those obtained in this study. Nevertheless, when they are 'compensated' with their respective pre-exponential factors, all of them fall on the fitting straight line, which, in addition, shows a very good regression coefficient. These results are convincing evidence that the variations in kinetic parameters are due to experimental effects and that the kinetics of isothermal degradation are essentially the same as the kinetics of degradation studied by means of non-isothermal procedures.

If we compare Eq. (7) with the Arrhenius equation

$$\ln A = \frac{E}{RT} + \ln k \tag{8}$$

we see that we can find the so-called isokinetic point defined by $T_{\text{iso}}=1/Ra$ and $\ln k_{\text{iso}}=b$ representing the point of intersection of Arrhenius lines [i.e. $\ln k(T)$ *vs.* $T^{-1}$]. In other words, for all the rate processes whose kinetic parameters are in the parameter set that satisfies Eq. (7), the corresponding Arrhenius lines have a common point of intersection ($T_{\text{iso}}$, $\ln k_{\text{iso}}$). From the values for *a* and *b* deduced from Fig. 4, we can have $T_{\text{iso}}$=380°C and $\ln k_{\text{iso}}$=–6.2 $s^{-1}$, both values falling within the range of the experimental values used.

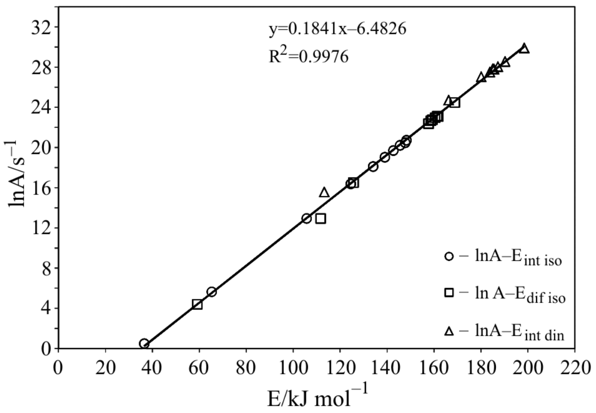

**Fig. 4** Compensation plot of kinetic parameters from
○ – isoconversional integral method (Table 2),
□ – isoconversional differential method using Eq. (5),
△ – isoconversional integral method using non-isothermal data from [13]

Using the same procedure as described so far to analyse the kinetics of degradation in a nitrogen atmosphere, we were unable to obtain similar results associated with the degradation processes in oxygen and air atmospheres. Thus, for example, none of the kinetic models of Table 1 come close to a good fit with the experimental data. Using the integral isoconversional procedure (Eq. (3)), we were able only to find the apparent values for the activation energy for each degree of conversion of the thermooxidative degradations in air and oxygen. In this case, being unable to complete the kinetic triplet with the pre-exponential factor and the model function, we believe that its value is of little interest. The activation energies are much higher than those found in the inert atmosphere and this is surely a reflection of the fact that here, at the same degree of conversion, reactive process as different as degradation, partial volatilisation of degraded products and formation of new products with the incorporation of oxygen due to oxidation can be occurring at the same time.

Figure 5 shows the activation energies found for each degree of conversion in the experiments in air and oxygen atmospheres along with the activation energies of Table 2 (in nitrogen atmosphere). Although the values for the activation energies associated with the thermooxidative processes are difficult to interpret, we can see that their changes with the degree of conversion provide a faithful image of the kinetic complexity to which the material is submitted at the different

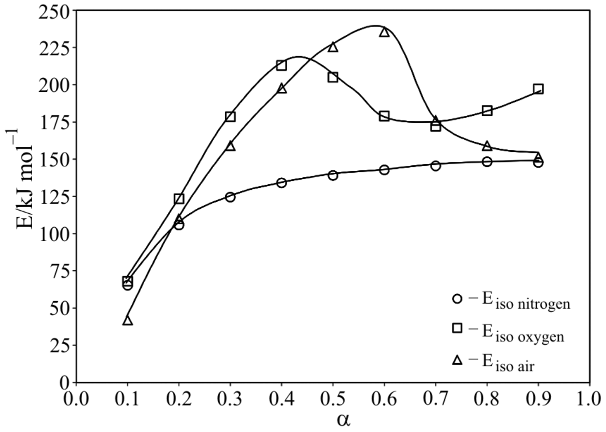

**Fig. 5** Apparent activation energy *vs.* degree of conversion in nitrogen, air and oxygen atmospheres

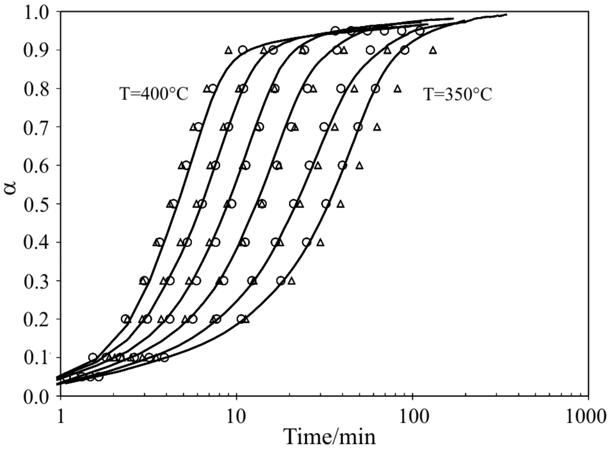

**Fig. 6** Experimental and simulated degrees of conversion *vs.* time for samples degraded at 350, 360, 370, 380, 390 and 400°C; — – experimental isothermal curves, ○ – simulated points calculated with kinetic parameters obtained from Table 2 and △ – simulated points calculated with kinetic parameters obtained from non-isothermal data from [13]

stages of degradation that it passes through. Thus, in the initial stage, up to approximately $\alpha$=0.2, the activation energies in the inert atmosphere and in the oxygen and air atmospheres are very similar. The leap that occurs in the activation energies of the processes with oxygen and air in comparison with nitrogen, from $\alpha$=0.2 to $\alpha$=0.4 in the case of oxygen and from $\alpha$=0.2 to $\alpha$=0.6 in the case of air, corresponds to the stage at which the oxidation process is superimposed on the degradation process. Subsequently, at higher conversions, owing surely to the fact that all the material capable of oxidation has undergone that process, the system returns to a state in which the predominant process is once again thermal degradation and the activation energies return to being similar regardless of the ambient atmosphere. This behaviour is very like the behaviour described by other authors for the degradation of similar epoxidic systems [18, 19, 26].

Referring back to the results obtained in the study of kinetics in a nitrogen atmosphere, in order to check our statement that kinetic parameters obtained in isothermal tests are equivalent to the parameters obtained in non-isothermal experiments, we simulated the experimental isothermal curves on the basis of the non-isothermal parameters. We will not detail the procedure here, since it is described sufficiently in other works [26]. Figure 6 compares the experimental isothermal kinetic curves with those obtained on the basis of the non-isothermal kinetic parameters found in previous studies [13, 14]. Also shown are the results obtained with the kinetic parameters obtained in this study (Table 2). Although the simulation based on non-isothermal experiments is not as good that deduced from isothermal experiments, it can be accepted that in both cases the experimental results are reproduced reasonably well.

This comparison, which gave such good results in the work with the nitrogen atmosphere, could not be repeated with the oxidising atmospheres of pure oxygen and air. Owing to the complexity of the thermo-oxidative processes, although in qualitative terms the isothermal and non-isothermal degradation tests show the same stages, the kinetic parameters obtained are difficult to interpret and are not interchangeable.

## Conclusions

We have seen that the isothermal and thermooxidative degradation process of an epoxy powder coating is a two-stage process. The first stage of degradation is similar whether nitrogen, oxygen or air are present. Chain scission occurs and it seems that there is formation of thermally more stable compounds. Without oxygen, these compounds are relatively stable at the temperatures investigated. The second stage of degradation, involving several phenomena, occurs only in the presence of oxygen or air and leads to the total disappearance of the organic material by thermooxidation. These stages are very similar under non-isothermal or isothermal conditions.

Through use of an integral isoconversional procedure with an Avrami model, we have characterised the isothermal degradation processes in a nitrogen atmosphere and obtained the values for the kinetic triplet [$f(\alpha)$, $E_\alpha$ and $A_\alpha$], verifying that they fit well with the experimental results. We have also seen that the isothermal kinetics coincide with the non-isothermal kinetics examined in a previous study. The equivalence of the two kinetics was determined through the analysis of the compensation effect of different pairs of $E$ and $A$ obtained through both the isothermal and non-isothermal analyses; and the observation that the isothermal curves were reproduced reasonably well on the basis of the non-isothermal data.

On the other hand, due to the complexity of the kinetics of isothermal degradation in thermooxidative atmospheres of air and oxygen, we were unable to find a coherent kinetic triplet for all stages. However, the isoconversional process and the changes occurring in the apparent activation energy allow us carry out qualitative monitoring and detect the differences between the air and oxygen atmospheres. The kinetic parameters obtained by non-isothermal means do not reliably reproduce the isothermal kinetic.

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