

NON-ISOTHERMAL DEGRADATION OF A THERMOSET POWDER COATING IN INERT AND OXIDANT ATMOSPHERES

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Abstract

This paper studies the thermal stability of an epoxy powder coating. The study was carried out in a thermobalance at various heating rates and in different atmospheres: nitrogen, air and oxygen. Degradation in air and oxygen leads to a kinetic process which is clearly different from degradation in an inert atmosphere. To characterise each process, the DTG signal peaks were separated and kinetic parameters were associated to each by means of the isoconversional method and other standard methods. The results obtained were compared with the experimental results.

Keywords: isoconversional kinetics, powder coating, thermosets

Introduction

Interest in thermoset powder coatings is rising continuously due their environmental advantages, such as low emission of volatile products. The final product is obtained by means of polymerisation and cross-linking of their components [1, 2]. Thermal stability studies by TG permit analysis of the quality of the material formed (the degree of cure or the degree of cross-linking) [3] and enables quantification of the proportion of additives. Differences in thermal stability, due either to differences in chemical structure or to differences in degree of cure, using an inert, oxygen or air atmosphere, have also been used to predict physical and chemical ageing and lifetime [4]. Obtaining the kinetic parameters of these degradation processes enables us to analyse them on a scale of times and temperatures not necessarily limited to those employed to obtain the experimental results.

The literature includes many studies of the thermal degradation of thermoset and thermoplastic materials which show the difficulty of kinetic studies, due to the heterogeneity of the substances and the fact that the degradation process consists of various stages. The latter problem implies superposition of different reactive processes which are difficult to characterise with a single activation energy [5–8].

The aim of this paper is to show the results of kinetic study of non-isothermal thermal degradation of an epoxy powder coating, in an inert atmosphere and in

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oxygen and air atmospheres. To obtain a kinetic triplet, ($f(\alpha)$, A and E , where $f(\alpha)$ is a function of the degree of conversion, A , the preexponential factor and E , the activation energy) which is representative of each degradation process, the processes manifested as peaks in the DTG signal were separated and treated as independent reactions, and kinetic parameters were associated to them by the standard methods. Specifically, in this work the differential and integral isoconversional methods [6, 9] are compared with the results obtained with Coats–Redfern [10] and Ozawa [11] equations. With the first two methods an activation energy (E) and a second kinetic parameter is obtained for each degree of conversion (A_{int} for the integral and A_{dif} for the differential) which includes the preexponential factor, without the need for presupposition of a kinetic model. In order to apply the Coats–Redfern and Ozawa equations to the entire reactive process, it is necessary to presuppose a kinetic model, and a single activation energy (E) and a single preexponential factor (A) are obtained. A variation on the so-called Kissinger method [12] was also employed which only uses the temperature shift of the peaks at different rates, to obtain the kinetic parameters. The results obtained through all these methods were compared with the experimental results.

Theoretical considerations

In the non-isothermal experiments carried out with a thermobalance, the mass of a substance is measured as a function of temperature. The degree of conversion [13] is defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where m is the mass corresponding to a temperature T , m_0 is the initial mass and m_∞ is the mass at the end of the experiment.

Variation of the degree of conversion with time ($d\alpha/dt$) is proportional to a function of the degree of conversion: $f(\alpha)$ [14]. The proportionality constant (k) is known as rate constant and depends on the temperature, according to the Arrhenius equation, where A is the preexponential factor and E is the activation energy.

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

The integral of the inverse of $f(\alpha)$ between the start of the reaction ($\alpha=0$) and a given degree of conversion α , is represented by $g(\alpha)$:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (3)$$

$f(\alpha)$ can take different forms [13, 15]. Table 1 indicates those used here.

The variation of the degree of conversion with temperature ($d\alpha/dT$) is obtained in dynamic experiments. Replacing the heating rate ($\beta=dT/dt$) in Eq. (2):

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

Coats and Redfern [10] obtained that:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (5)$$

For a given experiment (if $2RT/E \ll 1$), representing $\ln(g(\alpha)/T^2)$ vs. the inverse of the temperature we obtain a straight line. The activation energy can be obtained from its slope and the preexponential factor value from the intercept.

Another expression allowing us to obtain these values is the Ozawa expression [11]:

$$\log[\beta g(\alpha)] = \log\left[\frac{AE}{R}\right] - 2.315 - 0.4567 \frac{E}{RT} \quad (6)$$

in which $\log[\beta g(\alpha)]$ is represented vs. the inverse of the temperature.

In the so-called isoconversional method [6, 9] it is presupposed that the reaction mechanism is independent of the temperature. This procedure can be applied to the Ozawa equation (integral isoconversional method), thereby obtaining for different degrees of conversion, activation energy and A_{int} values, the latter depending on the preexponential factor:

$$\log\beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - 0.4567 \frac{E}{RT} = A_{\text{int}} - 0.4567 \frac{E}{RT} \quad (7)$$

In the so-called differential isoconversional method, neperian logarithms are used on both sides of Eq. (4):

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E}{RT} = A_{\text{dif}} - \frac{E}{RT} \quad (8)$$

From this expression, we obtain activation energy and A_{dif} , which also depends on the preexponential factor.

Table 1 Expressions of the degree of conversion $f(\alpha)$

Model	Symbol	$f(\alpha)$
Avrami–Erofeev	Am	$m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$
Contracting surface	R2	$2(1-\alpha)^{1/2}$

Once $g(\alpha)$ is known, Eq. (5) can be reordered and applied to the temperature of the peak (maximum reaction rate) as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{g(\alpha_p)E}\right) - \frac{E}{RT_p} \quad (9)$$

If the degree of conversion in the peak, α_p does not vary with heating rate, representation of $\ln(\beta/T_p^2)$ vs. $1/T_p$ for different rates permits us to obtain activation energy and pre-exponential factor. If in Eq. (9) a model of order n is assumed and that $n(1-\alpha_p)^{n-1} \approx 1$, we obtain the well-known Kissinger's equation [12].

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \quad (10)$$

A similar procedure could be followed for Eqs (6) and (8), using $(d\alpha/dt)_p$ instead of T_p .

Experimental

Materials

E3-0007/V powder coating manufactured by Ferro Enamel Española, S.A. was used. The reactive components of this product are epoxy bisphenol A (with a molecular mass between 14000 and 15000 g mol⁻¹) and dicyandiamide, which are found in a proportion of 95/5. This coating also contains 30% of colouring additives: TiO₂, BaSO₄, SiO₂ and MgO (the latter two in a proportion of less than 1%).

Methods

Experimental determination was carried out with a Mettler TG50 thermobalance, linked to a Mettler TA4000 thermal analysis system. Degradation of coating samples with an approximate mass of 10 mg was studied. Dynamic tests were carried out at different rates (1 to 20°C min) between 25 and 900°C (in the experiments carried out at lower rates maximum temperature reached was 700°C) in nitrogen, air and oxygen atmospheres (gases entered at 200 cm³ min⁻¹, measured in normal conditions).

Results and discussion

Figure 1 represents the degree of conversion calculated by means of Eq. (1), where m_∞ is the sample mass at the end of the experiment, vs. the temperature for different heating rates, in a nitrogen atmosphere. Two different stages can be observed in the process, and the lower the heating rate, the lower the temperature at which they occur. The first stage (at lower temperature) is associated with thermal degradation of the polymeric matrix, the second with pyrolysis of the carbon formed in the first stage [16, 17].

Figure 2 shows the derivative of the curve in Fig. 1. A peak appears for each stage of the process. Height and temperature of the peaks increase with heating rate.

The kinetics of the first stage of degradation were studied, considering m_∞ (Eq. (1)) as the mass of the substance at the end of this stage. The results obtained by means of isoconversional analysis, through both the integral (Eq. (7)) and differential (Eq. (8)) methods are shown in Table 2, which sets out activation energy and A_{int} and

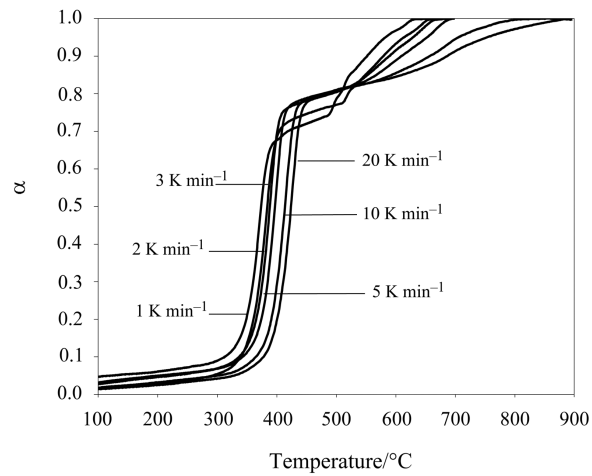


Fig. 1 Degree of conversion (α) vs. temperature in a nitrogen atmosphere, for different heating rates

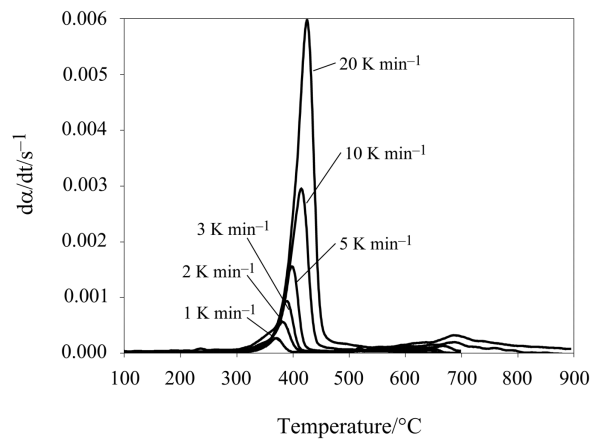


Fig. 2 Rate of degree of conversion ($d\alpha/dt$, DTG curves) vs. temperature in a nitrogen atmosphere for different heating rates

A_{dif} values. It can be seen that activation energy varies with degree of conversion. Both methods lead to similar values in the intermediate area of the degradation stage (between $\alpha=0.2$ and $\alpha=0.9$), where activation energy varies slightly, indicating that this part of the degradation process must be quite similar. The differences observed at the beginning and end of degradation must be interpreted with caution since they could be the result of manipulation of the experimental results.

On the basis of the derivatives of the experimental curves (DTG curves), the peaks were separated, for each heating rate. For separation, the mathematical procedure provided by Jandel Scientific Software program 'Peak.Fit' was used. Among the different functions included in the program, we used the so-called 'log normal 4-parameter (area)'. The corresponding kinetic parameters were obtained by apply-

ing the various methods described to the peaks corresponding to the first stage of degradation. For example, application of Eq. (5) to the curve corresponding to a rate of $10^{\circ}\text{C min}^{-1}$, with Am model with $m=1.5$ (Table 1), gave an activation energy of 128 kJ mol^{-1} and a preexponential factor of $4.92 \cdot 10^5 \text{ s}^{-1}$. Employing Eq. (9), the temperatures of the peaks of rates 1, 3, 5, 10 and $20^{\circ}\text{C min}^{-1}$ and an Am model with $m=1.5$, gave an activation energy of 188 kJ mol^{-1} , very similar to that found with isoconversional methods, and a preexponential factor of $2.48 \cdot 10^{10} \text{ s}^{-1}$.

Table 2 Activation energy and A_{int} , A_{dif} values obtained by integral and differential isoconversional methods in nitrogen atmosphere

Isoconversional integral (Eq. (7))									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
R^2	0.964	0.987	0.988	0.99	0.99	0.989	0.989	0.9888	0.989
$A_{\text{int}}/\text{K s}^{-1}$	7.437	13.61	14.68	15.15	15.14	15.29	15.56	16.539	7.3
$E_{\text{int}}/\text{kJ mol}^{-1}$	113.3	166.2	180.1	185	183.8	185.6	187.2	190.26	198.4
Isoconversional differential (Eq. (8))									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
R^2	0.993	0.993	0.991	0.987	0.979	0.986	0.988	0.9884	0.996
$A_{\text{dif}}/\text{s}^{-1}$	34.59	30.88	31.18	28.42	28.49	28.47	28.36	29.155	30.26
$E_{\text{dif}}/\text{kJ mol}^{-1}$	233.4	208.2	208.1	192.6	193.2	193.3	193.7	200.36	212.2

The models set out in Table 1 were chosen because they are the ones which best reproduce the reduced master curve $Z(\alpha)/Z(0.5)$, where $Z(\alpha)=f(\alpha) \cdot g(\alpha)$. The way in which the reduced function $Z(\alpha)/Z(0.5)$ is used to decide which model best fits the experimental results is described in [18].

Figure 3 shows the experimental degree of conversion vs. temperature (discontinuous lines) for two heating rates (5 and $10^{\circ}\text{C min}^{-1}$) along with the results obtained from the various procedures applied. Although the best simulation is obtained with the integral isoconversional method, the results given by the other methods also fit reasonably well with the experimental data. This would seem to indicate that using the same procedures for kinetic study of the oxidation process with air and oxygen would produce similarly correct results.

Figure 4 compares the experimental curves obtained at $10^{\circ}\text{C min}^{-1}$ in different atmospheres: nitrogen, air and oxygen. The degree of conversion is represented vs. the temperature (m_{∞} is the mass at the end of the experiment). In the oxygen and air atmospheres, the degradation process has an additional stage. Up to a temperature slightly above 400°C , the degradation process is very similar in all three. Therefore, the decomposition process should also be very similar. After this point, mass loss slows down in the presence of oxygen or air. An intermediate oxidation compound may be formed. Then a sharp change occurs in each of these atmospheres, especially oxygen. This stage is clearly one of oxidation (the higher the proportion of oxygen, the more accelerated the

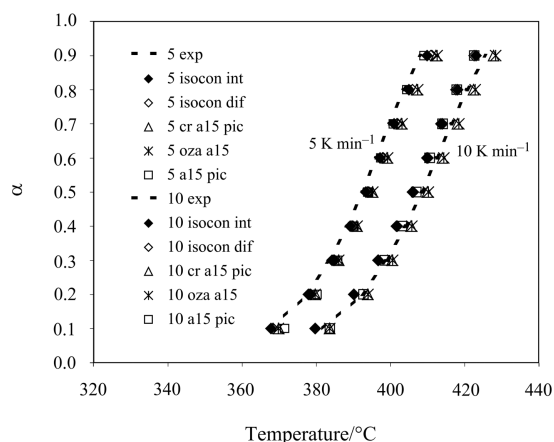


Fig. 3 Comparison of experimental data (discontinuous lines) and the data obtained from different methods (symbols) of the degree of conversion (α) vs. temperature of the first decomposition stage in a nitrogen atmosphere. In the legend, the number on the left is the heating rate in K min^{-1} ; isocon int are the dates obtained from Eq. (7); isocon dif, from Eq. (8); cr a15, from Eq. (5) with Am model and $m=1.5$; oza a15, from Eq. (6) with Am model and $m=1.5$; a15 pic, from Eq. (9) with Am model and $m=1.5$

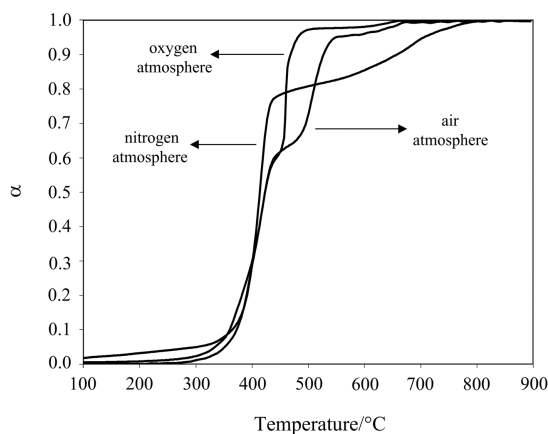


Fig. 4 Comparison of degradation processes in nitrogen, oxygen and air. Degree of conversion (α) vs. temperature at heating rate of 10 K min^{-1}

process). At the same time, the curve corresponding to the nitrogen atmosphere slows down and the coating continues to degrade (carbon pyrolysis). In air and oxygen atmospheres, this last stage of degradation has practically disappeared.

Figure 5 shows the derivative of the curves in Fig. 4, in which the processes described above can be observed. The oxidation taking place in pure oxygen and air is clearly reflected and separated from the degradation processes. The appearance of shoulders in the degradation peaks in the presence of air and oxygen (but not in the

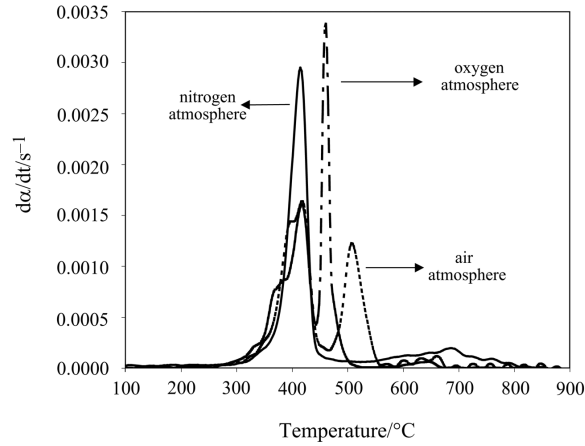


Fig. 5 Comparison of degradation processes in nitrogen, oxygen and air. Rate of the degree of conversion ($d\alpha/dt$) vs. temperature at heating rate of 10 K min^{-1}

nitrogen atmosphere), indicates that the oxydant atmospheres have a catalytic effect on the degradation process.

Figure 6 shows the results of the mathematical procedure described for separation of the peaks of the degradation curve in an air atmosphere at $10^\circ\text{C min}^{-1}$. The discontinuous curve corresponds to the real curve and the continuous curves to the peaks obtained. The sum of all the separated curves provides a highly accurate reproduction of the experimental signal. Similarly good results are obtained for other rates, both in air and oxygen. From the temperature of the peak corresponding to oxidation in air and oxygen associated to each experimental rate ($1, 3, 5, 10$ and $20^\circ\text{C min}^{-1}$), the corresponding kinetic parameters were obtained by using Eq. (9). The models used were the Am model and the R2. With the former and $m=2$, when the atmosphere was air,

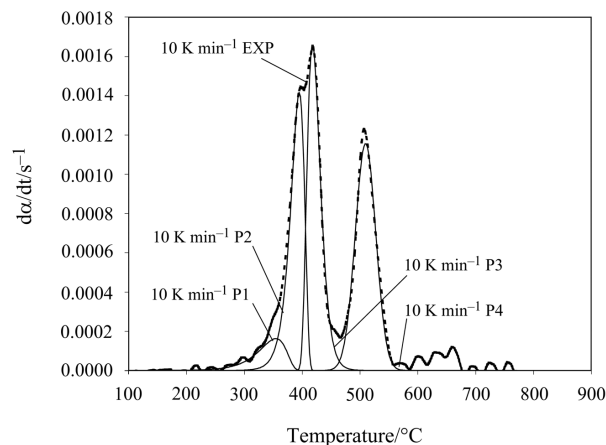


Fig. 6 Decomposition of overall kinetic process in different peaks. Degradation in air at 10 K min^{-1}

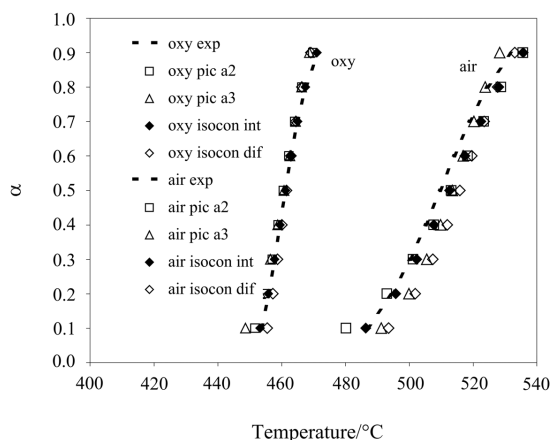


Fig. 7 Comparison of experimental data (discontinuous lines) and data obtained from different models (symbols) of the degree of conversion (α) vs. temperature of the oxidation process in air (air in the legend) and oxygen (oxy in the legend) at heating rate of 10 K min^{-1} pic a2 are the data from Eq. (9) with Am model and $m=2$; pic a3 from Eq. (9) with Am model and $m=3$; isocon int from Eq. (7); isocon dif, from Eq. (8)

the activation energy and preexponential factor obtained were 129 kJ mol^{-1} and $2.35 \cdot 10^4 \text{ s}^{-1}$, respectively. When the atmosphere is oxygen, the activation energy and the preexponential factor are 217 kJ mol^{-1} and $3.14 \cdot 10^{11} \text{ s}^{-1}$, respectively. The discontinuous line in Fig. 7 represents the degree of conversion vs. temperature, corresponding to the oxidation stage at $10^\circ\text{C min}^{-1}$ in air and oxygen (the degree of conversion of this stage was normalized between 0 and 1) along with the values obtained from the different models. As occurred with the nitrogen atmosphere, the results of the simulation fit reasonably well.

As can be observed in Fig. 6, the catalytic effect produced by the presence of air and oxygen leads to two peaks in the degradation process. One of these is identical to that found for degradation in nitrogen and the other corresponds to lower temperature. Analysis of these peaks in both air and oxygen atmospheres gives an activation energy which is practically identical to the activation energy associated with the first degradation process in nitrogen.

Conclusions

The process of non-isothermal degradation of the thermoset epoxy coating in an inert atmosphere basically occurs in two stages, a decomposition stage which occurs at temperatures of around 400°C and another stage which takes place at a higher temperature and consists of pyrolysis of the carbon residue formed in the first stage.

When degradation takes place in an oxygen or air atmosphere, after the first stage, which again takes place at around 400°C , another process occurs which consists of oxidation of the degraded matter, which takes place at some 50 or 100°C higher, depending on whether the atmosphere is oxygen or air.

In order to characterise the degradation and oxidation processes by means of the corresponding kinetic parameters, it was found that mathematical separation of the DTG signal peaks and then the application of the usual procedures to each peak to determine the kinetic triplet, produced reasonably correct results in comparison with experimental values.

The best results were obtained through the isoconversional method. However, the use of temperature shift of the DTG curve maximums with heating rate, once a model had been established, to determine the activation energy and the preexponential factor of each process is of great interest by virtue of its simplicity and the good results obtained.

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