Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 419 (2004) 181–187

thermochimica acta

www.elsevier.com/locate/tca

Comparative study of the degradation kinetics of three powder thermoset coatings

J.M. Morancho*, J.M. Salla, X. Ramis, A. Cadenato

Laboratori de Termodinàmica i Físico-Química, ETSEIB, UPC, Diagonal 647, 08028 Barcelona, Spain

Received 4 December 2003; received in revised form 4 December 2003; accepted 23 February 2004

Abstract

This paper deals with the thermal stability and thermal degradation kinetics of three powder thermoset coatings that are representative of the most common product families on the market at present: polyester, epoxy and hybrid. The study was carried out in a thermobalance at different rates of heating and using different atmospheres: nitrogen, air and oxygen. The procedure applied for characterising the most significant kinetic processes consisted in separating the peaks of the DTG signal and associating each peak with a kinetic system by means of an isoconversional procedure or the familiar Kissinger method. The results showed that, although all three coatings have high thermal stability, they do not all behave in the same way, particularly in an oxidising atmosphere. The decomposition kinetics of the three systems, although similar in a nitrogen atmosphere, are different in the presence of oxygen or air, allowing each to be characterised individually.

Keywords: Thermal stability; Powder thermoset coating; Isoconversional kinetics

1. Introduction

Powder thermoset coatings, made up of a reactive resin mixed with fillers and pigments, are used for dry finishing processes for which a thin layer of fine powder is deposited on the surface to be coated. The surface coated in this manner is then heated, first to soften and fuse the powder and then to cure it, creating a crosslinked structure that provides a high-quality, durable finish [1]. The most commonly used chemical families at present are epoxy resins, polyester resins, and so-called hybrids, which are formulations where a polyester resin reacts with an epoxy one [2].

In comparison with conventional paints containing solvents, powder coatings generate only small amounts of volatile organic compounds (VOCs). They also have other advantages, such as a shorter drying time, lower energy costs and the absence of waste (solvents) that requires treatment and disposal. All of these factors make them highly competitive in comparison with conventional paints [3].

The end use and durability of the coatings depend on both the formulation of the paint and the coating and curing process. For example, the continuous curing of thermoset powder deposited electrostatically on metal parts requires a hot-air oven with temperatures of between 300 and 400 °C and curing times of between 15 and 60 s. Since the ideal curing temperature can be in the neighbourhood of 200 °C, it is important to avoid exposing the coating to temperatures of over 250 °C, at which point the organic matter can begin to oxidise [4]. In addition, it is known that coatings made from polyester resins provide greater durability and resistance to ultraviolet radiation than epoxy coatings. This makes the former especially suitable for outdoor uses and the latter preferable for indoor uses [5].

There are predictive studies, which are time-consuming, accelerated ageing studies and standardised procedures for the study of durability that have recently been called into question in view of their largely unreliable results [6]. However, some authors claim that the study of the thermodegradation behaviour of coatings and paints at high temperatures provides a ‘fingerprint’ of the material that has to do not only with the characteristics of the original product, but also with its processing and the final quality of the material formed [7]. Furthermore, the study of thermal stability by means of TGA allows us to analyse the degradation response of the sample subjected to different atmospheres (inert or oxidis-

---

* Corresponding author. Tel.: +34-934016531; fax: +34-934017389.
E-mail address: morancho@mmt.upc.es (J.M. Morancho).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.02.011

ing), and to draw conclusions with respect to its useful life and durability [8].

This paper deals with the thermal stability and degradation kinetics of three powder thermoset coatings that are representative of the most common product families on the market at present: a carboxylated polyester using TGIC as a crosslinking agent, an epoxy resin using dicyandiamide as a reticulating agent, and a hybrid system in which an epoxy resin reacts directly with a carboxylated polyester. The study was carried out in a thermobalance at different rates of heating and using different atmospheres: nitrogen, air and pure oxygen. The procedure applied for characterising the most significant kinetic processes consisted in separating the peaks of the DTG signal and associating each peak with a kinetic system by means of an isoconversional procedure [9,10] or the familiar Kissinger method [11]. This procedure was used in a previous study [12] that showed the usefulness of the peaks of the derivative of the thermogravimetric signal for kinetic analysis of degradation processes. Furthermore, the bibliography contains works by numerous authors who have used the DTG signal to study high-temperature degradation processes in a wide range of systems [13–16].

2. Theory

Dynamic experiments carried out using a thermobalance have analysed the mass loss of a system depending on temperature. The degree of conversion is defined as:

$$\alpha = \frac{m_o - m}{m_o - m_\infty} \tag{1}$$

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

As usual with reactive processes in heterogeneous systems, it is assumed that the variation in degree of conversion over time ($\mathrm{d}\alpha/\mathrm{d}t$) is proportional to a function of the degree of conversion, $f(\alpha)$, the form of which depends on the mechanism driving the reaction [17]. The proportionality constant (k) is called the rate constant and it is accepted that it depends only on temperature, according to the familiar Arrhenius equation, where A is the frequency factor and E is the activation energy.

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

In dynamic tests, the integral of the inverse of $f(\alpha)$ between the beginning of the reaction ($\alpha = 0$) and a given degree of conversion α, is represented by $g(\alpha)$ and can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \mathrm{e}^{-(E/RT)}\mathrm{d}T \tag{3}$$

$g(\alpha)$ is known as the integral function of the degree of conversion and β is the rate of heating of the dynamic test.

Eq. (3) can be integrated by means of the Doyle approximation [18]. By rearranging the terms, and set out in logarithmic form, this gives:

$$\log\beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.4567E}{RT} = A_{\alpha,\mathrm{int}} - \frac{0.4567E}{RT} \tag{4}$$

Another way of integrating Eq. (3), assuming that $(2RT/E) \ll 1$, is the so-called Coats–Redfern equation [19], which, by rearranging the terms and set out in logarithmic form, gives:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} = A'_{\alpha,\mathrm{int}} - \frac{E}{RT} \tag{5}$$

Both equations allow the use of the isoconversional procedure to find how E varies with the degree of conversion. Using Eq. (4), the linear representation of $\log\beta$ versus $1/T$ allows us to determine E_α and a kinetic parameter $A_{\alpha,\mathrm{int}}$ (the Ozawa method [20]). Likewise, using Eq. (5), we can represent $\ln[\beta/T^2]$ versus $1/T$, allowing us to determine E_α and the kinetic parameter $A'_{\alpha,\mathrm{int}}$. If we know $g(\alpha)$, using the values $A_{\alpha,\mathrm{int}}$ and $A'_{\alpha,\mathrm{int}}$ we can find the pre-exponential factor for each alpha, A_α.

If in Eq. (5) $g(\alpha) = 1$ and we apply the degree of conversion associated with the temperature of the DTG signal peak T_p, we arrive at the familiar Kissinger equation [11]:

$$\ln\frac{\beta}{T_\mathrm{p}^2} = \ln\left[\frac{AR}{E}\right] - \frac{E}{RT_\mathrm{p}} \tag{6}$$

The use of the Kissinger equation presupposes accepting that the kinetic parameters associated with the degree of conversion of the peak are unique and representative of the set of kinetic processes that can occur in any conversion.

On the basis of experimental results, there are different procedures for assigning the most suitable kinetic model, ($f(\alpha)$ or $g(\alpha)$). In this study, we used the so-called master-curves procedure [21,22], which has been described in at length in another paper [23].

3. Experimental

3.1. Materials

We studied three powder coatings. In the E3-0007/V the reactive components were epoxy bisphenol A (with a molecular mass between 14,000 and 15,000 $\mathrm{g\,mol^{-1}}$) and dicyandiamide, combined in a proportion of 95/5. In the P3-0083/V coating, the reactive components were a carboxylated polyester (molecular mass 20,000 $\mathrm{g\,mol^{-1}}$) and TGIC (triglycidylisocyanurate), combined in a proportion of 93/7. The third coating analysed, H3-0052/V, was of the hybrid type, containing a carboxylated polyester (molecular mass 25,000 $\mathrm{g\,mol^{-1}}$) and epoxy bisphenol A (molecular mass between 14,000 and 15,000 $\mathrm{g\,mol^{-1}}$), combined in a proportion of 6/4. These coatings also contained between 30 and 38% of colouring additives: TiO_2, $BaSO_4$, SiO_2 and MgO (these latter two substances in a proportion of under 1%). The three systems are available on the market and were supplied by the manufacturer, Ferro Enamel Española, S.A.

3.2. *Techniques*

The experiments were carried out in a Mettler TG50 thermobalance coupled to a Mettler TA4000 thermoanalyser. The degradation of samples of the coatings with a mass of approximately 10 mg was studied. Dynamic tests were carried out at different rates (from 1 to 20 °C min^{-1}) between 25 and 900 °C (the experiments carried out at lower rates reached only 700 °C) in atmospheres of nitrogen, air and oxygen (the entry flow of these gases was 200 $cm^3 min^{-1}$, measured under normal conditions).

4. Results and discussion

For each powder resin studied, the tests carried out at different rates in atmospheres of nitrogen, air and oxygen provided the weight loss (TG signal) and the rate of weight loss (DTG signal) depending on the temperature. These data were standardised by means of Eq. (1) to find the degree of conversion α, and the rate of conversion $d\alpha/dt$. Fig. 1 compares the variation in each type of resin, the degree of conversion and rate of conversion with temperature at a rate of 10 °C min^{-1} in an inert atmosphere (nitrogen). The most representative data on the main process of degradation are shown in Table 1. The three systems all show a high degree of thermal stability up to temperatures of around 350 °C, with weight loss of under 8%. Massive thermal degradation occurs in each of the three samples above that temperature, but with a different fingerprint in each case. Degradation of the P3 sample had a shorter temperature interval than the E3 and H3 samples. In addition, at the end of the process, at around 450 °C, while the P3 sample had volatilised by 89%, the E3 and H3 samples had only volatilised by 78.3 and 60.7% respectively. The unvolatilised residue, in a slow degradation process, had to be subjected to very high temperatures before it was fully volatilised. This behaviour is described at length in other works and is explained by the fact that, while breakage of the polyester chains produces volatile substances, breakage of the polymer chains in the epoxy and the hybrid gives rise to solid, carbon-rich by-products that do not volatilise completely until temperatures associated with carbon pyrolysis are reached [24,25]. The fact that the hybrid sample shows a broader degradation temperature interval and volatilises to a substantially lesser extent than the other samples indicates that the thermal stability of these coatings, in addition to depending on chemical functions, can also be influenced by other factors related to

Table 1
Characteristic parameters of the degradation process in a nitrogen atmosphere

	CMO (%)	PP-350 °C (%)	PP-450 °C (%)	T_{i} (°C)	T_{p} (°C)	T_{f} (°C)
TSC-P3	67.0	7.6	89.0	325	413	440
TSC-E3	70.0	8.0	78.3	325	417	451
TSC-H3	62.0	7.5	60.7	325	405–433	463

CMO (%), organic matter content in the samples. PP-350 °C and PP-450 °C (%), weight loss of organic matter up to temperatures of 350 and 450 °C, respectively. T_{i} and T_{f}, temperatures at the start and end of the main degradation process, respectively; T_{p}, maximum temperature of curve $d\alpha/dt$.

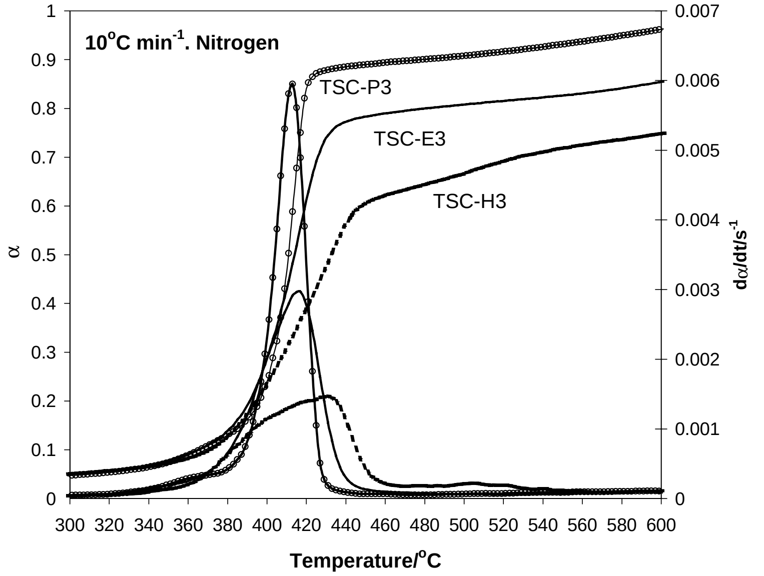

Fig. 1. Degree of conversion (α) and rate of conversion ($d\alpha/dt$) vs. temperature in the nitrogen atmosphere and at a heating rate of 10 °C min^{-1}, for the three powder coatings studied.

the size and distribution of molecular weights, the degree of crosslinking and the effects produced by the additives used as fillers.

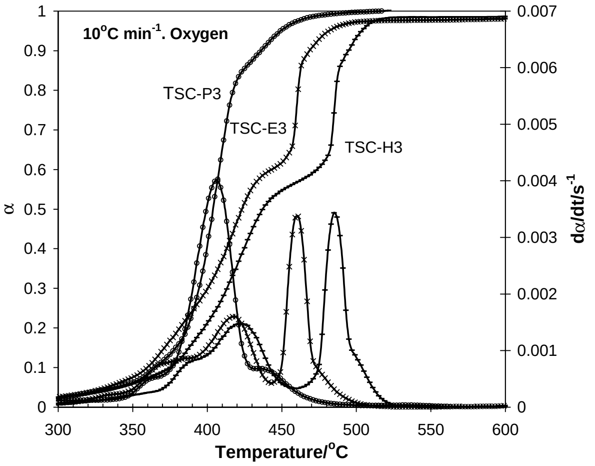

Fig. 2. Degree of conversion (α) and rate of conversion ($d\alpha/dt$) vs. temperature in the oxygen atmosphere and at a heating rate of 10 °C min^{-1}, for the three powder coatings studied.

Table 2
Initial (T_i), peak (T_P) and final (T_f) temperatures of the degradation processes in oxygen and air atmospheres

	$T_{i,P1}$ (°C)	$T_{p,P1}$ (°C)	$T_{f,P1}$ (°C)	$T_{i,P2}$ (°C)	$T_{p,P2}$ (°C)	$T_{f,P2}$ (°C)
Oxygen atmosphere						
TSC-P3	325	407	433	–	–	–
TSC-E3	325	371–419	443	443	461	501
TSC-H3	325	393–423	455	461	487	523
Air atmosphere						
TSC-P3	325	409	435	–	–	–
TSC-E3	325	399–419	465	467	509	561
TSC-H3	325	405–425	467	473	519–543	589

Figs. 2 and 3 compare the degradation processes undergone by the three thermoset systems in atmospheres of oxygen and air, respectively. These figures show the degree of conversion and rate of conversion, $d\alpha/dt$, depending on the temperature. Table 2 shows the initial and final temperatures and the temperature at the maximum rate of degradation for each process. In the case of the P3 system, the degradation process in the oxidising atmosphere is practically identical to the process observed in the nitrogen atmosphere, except for a slight acceleration effect. At a rate of 10 °C min^{-1}, the temperature of the maximum is 413 °C in the nitrogen atmosphere, compared with 409 °C in air and 407 °C in oxygen. On the other hand, degradation of both the E3 and H3 samples in the oxidising atmosphere sets off two clearly distinct degradation processes. We can attribute the first of those processes to the same thermal degradation that occurs in the nitrogen atmosphere. In this case, however, as shown by the appearance of shoulders in the DTG signal and by the shift of the maximum to higher temperatures, the oxidising atmosphere makes the degradation by-products react with the oxygen. This fact is also confirmed, from the quantitative standpoint, by the observation that, for example, at 450 °C in the oxygen atmosphere, the volatilised material represents 61% of the epoxy sample and 55% of the hybrid sample. If compared to the 78.3 and 60.7% volatilisation that occurs in the inert atmosphere at the same temperature, it can be concluded that the lower degree of volatilisation is due to the fact that the degraded material remains in a solid state because of the oxygen atmosphere or because oxygen is incorporated into some of the degraded products. As a consequence, a second degradation process appears in the epoxy and hybrid samples that leads to the disappearance of practically all the organic matter.

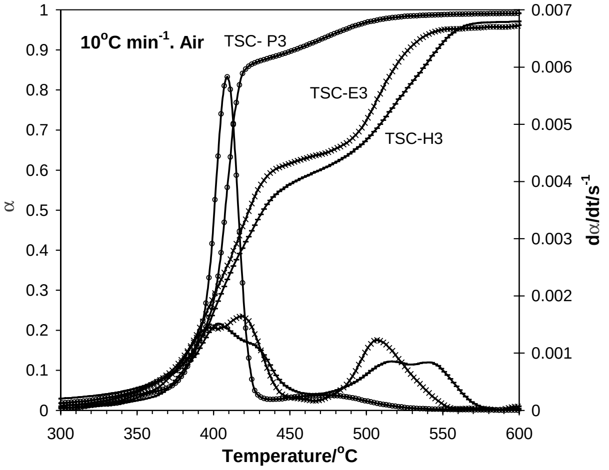

Fig. 3. Degree of conversion (α) and rate of conversion ($d\alpha/dt$) vs. temperature in the air atmosphere and at a heating rate of 10 °C min^{-1}, for the three powder coatings studied.

The effect of each different atmosphere on the degradation of the three types of coating is seen most clearly in Fig. 4, where the rate of degradation is compared for each system depending on the temperature and type of atmosphere used. Fig. 4a shows, as mentioned above, that in the case of the P3 sample, the presence of an oxidising atmosphere does not give rise to any significant change in the degradation process. It merely shifts the process to lower temperatures. In contrast, particularly with oxygen, the rate of degradation associated with the peak temperature is much lower than the rate obtained in an inert atmosphere, and therefore, from the standpoint of kinetics, the presence of oxygen is significant. In addition, we can attribute the small shoulders that appear before and after the degradation peak to a slight oxidising effect, which is more significant in the presence of oxygen than in the presence of air. Fig. 4b and c clearly show the degradation processes arising in the epoxy and hybrid samples in the presence of oxygen and air. In the presence of oxygen, the second degradation process occurs within a narrow temperature band, while in air, the process occurs across a broad temperature interval, with the result that the peak is shifted upwards by approximately 50 °C. For practical purposes, these results show that the recommendation against

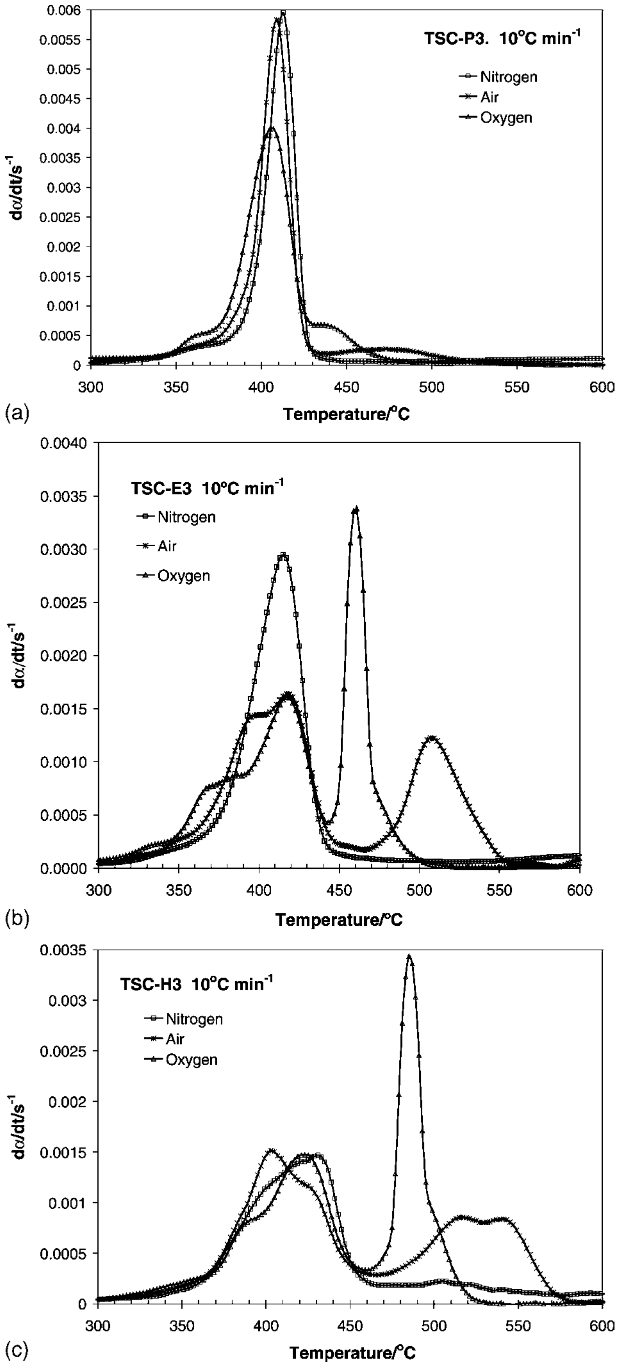

Fig. 4. Rate of conversion ($d\alpha/dt$) vs. temperature at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$, in different atmospheres: (a) P3 coating, (b) E3 coating and (c) H3 coating.

epoxy and hybrid resins for outdoor uses is wholly justified, owing to the photo-oxidation degradation effect that UV radiation can have on them.

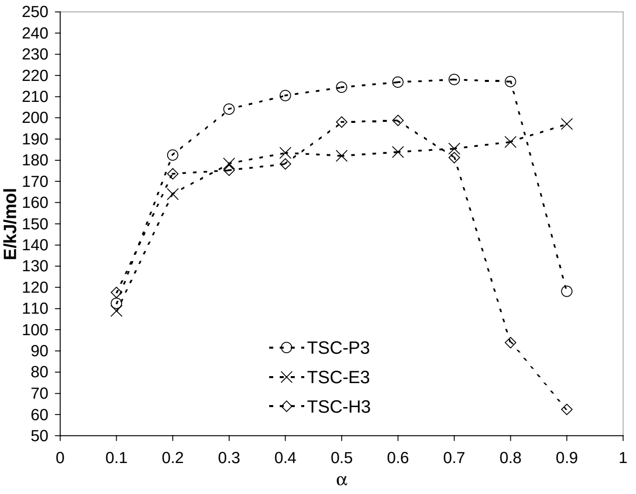

Fig. 5. Activation energy (E) vs. degree of conversion (α) in the nitrogen atmosphere for the three coatings studied.

The dynamic isoconversional kinetics study, using the Eq. (5), applied to the degradation process in an inert atmosphere for the three systems, gives the activation energy shown depending on the degree of conversion in Fig. 5, and in the case of conversion associated with the DTG signal peak, using the Kissinger procedure, in the values given in Table 3. The variation in the activation energy with the degree of conversion for the three systems indicates that the degradation process is a complex one. In the first phase of degradation, up to 20% conversion, the three systems undergo a similar process. Between 20 and 80%, the activation energy varies little, although it remains appreciably higher in the P3 system than in the E3 and H3 systems. In the hybrid system, during the first phase, up to 40% conversion, the activation energy is practically identical to that of epoxy, while above that proportion the values attained and their development tend to approximate the activation energy of the polyester system.

Although a kinetic model that fits the experimental results perfectly was not found, those that work the best are of the Avrami A1.5 and A2 types [12,23]. With these models, the value attained by $g(\alpha_p)$ is around 0.98–0.99, which justifies the additional use in Table 3 of the Kissinger equation to find the pre-exponential factor.

If we define the so-called reduced rate constant, k_r as:

$$k_r = \left(\frac{d\alpha}{dt}\right)\left(\frac{1}{f(\alpha)}\right) \tag{7}$$

and it is compared with Eq. (2), and if the kinetic model used and the Arrhenius equation are valid, k_r is in fact the rate constant, so that representation of $\ln k_r$ depending on the inverse of the temperature must be a straight line from which we can obtain the activation energy and the pre-exponential factor. In this study Eq. (7) was used as the test for verifying the accuracy of the kinetic parameters obtained and for verifying the existence of a single triplet in a broad interval of conversions and rates.

Fig. 6 shows that for the polyester and epoxy systems, in the conversion interval $0.2 < \alpha < 0.8$, the correlation is notably high and therefore the kinetic parameters are very reliable. The results in the case of the hybrid system have not

Table 3
Activation energy and pre-exponential factor of the degradation processes using Kissinger's method

	α_{p1}	E_{p1} (kJ mol^{-1})	$\ln(A_{p1}\,s^{-1})$	R^2
Nitrogen atmosphere				
TSC-P3	0.62 ± 0.03	230.4	35.7	0.994
TSC-E3	0.67 ± 0.02	185.2	27.7	0.995
TSC-H3	0.29 ± 0.02, 0.51 ± 0.01	288.9, 218.8	46.9, 32.5	0.999, 0.999
Oxygen atmosphere				
TSC-P3	0.58 ± 0.04	236.0	37.2	0.998
TSC-E3	0.18 ± 0.04, 0.38 ± 0.02	246.6, 226.6	40.6, 34.8	0.978, 0.956
TSC-H3	0.16 ± 0.03, 0.37 ± 0.01	299.7, 228.7	50.4, 34.9	0.991, 0.999
Air atmosphere				
TSC-P3	0.57 ± 0.01	234.0	36.6	0.994
TSC-E3	0.25 ± 0.06, 0.46 ± 0.05	132.6, 243.1	18.5, 37.5	0.983, 0.997
TSC-H3	0.23 ± 0.01, 0.45 ± 0.05	218.6, 277.5	34.6, 43.3	0.991, 0.996
	α_{p2}	E_{p2} (kJ mol^{-1})	$\ln(A_{p2}\,s^{-1})$	R^2
Oxygen atmosphere				
TSC-P3	–	–	–	–
TSC-E3	0.77 ± 0.02	231.0	33.1	0.980
TSC-H3	0.79 ± 0.01	152.3	18.8	0.979
Air atmosphere				
TSC-P3	–	–	–	–
TSC-E3	0.78 ± 0.04	131.1	14.6	0.991
TSC-H3	0.82 ± 0.02	181.7	21.7	0.976

To determine E and A, four speeds from 1, 2, 3, 5, 10 and 20 °C min^{-1} were used. The value of α_p, is the average value of the α of the peak temperatures of each speed. The first value of E and A corresponds to the lowest α_p.

been shown, as the correlation is not good. This confirms that the kinetics are more complex and that the processes observed in Figs. 1 and 4, must be separated if we wish to obtain kinetic parameters that are even minimally representative. Another result that can be deduced from Fig. 6 is that although the activation energy found for the polyester system is higher than for the epoxy system, the rate of degradation of one in comparison with the other will be higher or lower, depending on the temperature.

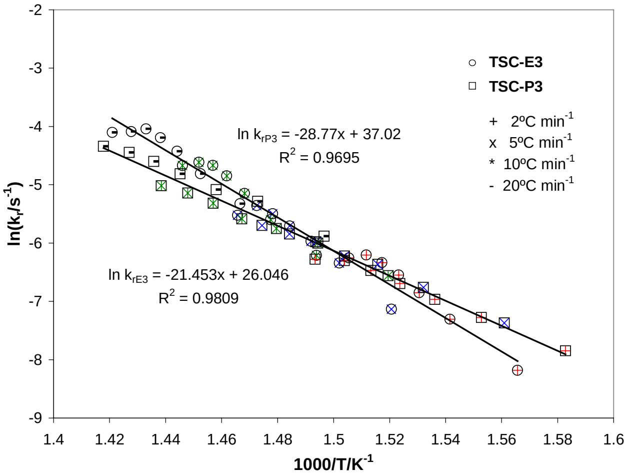

Fig. 6. Logarithm for the reduced rate constant ($\ln k_r$) vs. the inverse of the temperature in the nitrogen atmosphere for the epoxy (E3) and polyester (P3) coatings.

To study the kinetics of the two processes of degradation occurring in the epoxy and hybrid samples in an oxygen and air atmosphere, the peaks of the experimental curves (DTG curves) were separated for each rate tested. To make this separation the mathematical procedure provided by Jandel Scientific Software's Peak.Fit program was used, following the same procedure as described in a previous paper [12]. With the temperature of the peaks obtained in this manner, the Kissinger method to calculate the kinetic parameters shown in Table 3 was applied. The presence of several peaks and the wide variability of the values obtained, once again show the kinetic complexity of these degradation processes, meaning that, in terms of comparison, these values must be used with a great deal of caution. Nevertheless, it can be stated that, in the case of the polyester resin, both the activation energy and the pre-exponential factor associated with the first degradation process remain practically invariable regardless of whether the atmosphere is nitrogen or oxygen or air. However, in the case of the epoxy and hybrid resins, there are overlapping peaks characterised by distinct kinetic parameters, due to the fact that both the thermal degradation and the kinetics associated with oxidation reactions had to be taken into account. The differences observed between the kinetic parameters associated with the second degradation peak would appear to be a result of the fact that the intensity of the oxidation degradation, depending on whether oxygen or air is used, produces different oxidised by-products. Similar results have been recently published by Parra et al. [26].

5. Conclusions

Dynamic thermal degradation at high temperatures of the three coatings studied, i.e. polyester, epoxy and hybrid, produces a characteristic fingerprint in the TG signal and particularly in the DTG signal, allowing us to differentiate them. This fingerprint is also distinct when the atmosphere is oxygen or air.

The dynamic degradation process of the three thermoset coatings in an inert atmosphere occurs basically in the temperature interval between 350 and 450 °C, but while 90% of the organic material in the polyester system volatilises in this interval, the percentage of this volatilisation in the epoxy and hybrid systems is only 78 and 60%, respectively, owing to the formation of a carbonaceous residue. This residue also eventually volatilises, but requires much higher temperatures to do so.

Where degradation occurs in an atmosphere of oxygen or air, the polyester system behaves in a very similar manner to degradation in a nitrogen atmosphere. However, with the epoxy and hybrid systems, in addition to the degradation process that occurs in the nitrogen atmosphere, a second process appears, at temperatures 50 or 100 °C higher, depending on whether the atmosphere is oxygen or air, that can be attributed to the volatilisation of previously oxidised-degraded material.

Using the isoconversional procedure, we found, for each system, the variation in the kinetic parameters of the degradation processes with the degree of conversion, in an inert atmosphere. It was determined that the activation energy of the polyester system is higher than that of the epoxy and hybrid systems. However, at temperatures below 400 °C, the rate constant of the polyester system is lower than that of the epoxy and hybrid systems. This shows that use of activation energy as the only kinetic parameter can give rise to a mistaken interpretation if the pre-exponential factor is not also taken into account.

The use of the Kissinger method allowed us to find the kinetic parameters associated with the degree of conversion of the peak of the most significant degradation processes. The kinetic complexity of the thermal degradation processes, added to the oxidation reactions where the atmosphere is an oxidising one, becomes evident in the variability of the activation energies obtained for the epoxy and hybrid systems. However, with the polyester system, both the activation energy and the pre-exponential factor are practically independent of the atmosphere used for thermal degradation.

Acknowledgements

This work was supported by CICYT project no. MAT2000-1002-C02-02 and by CICYT and FEDER under Grant No. PPQ2001-2764-C03-02. The material used in this work was supplied by Ferro Enamel Española, S.A.

References

[1] T.A. Misev (Ed.), Powder Coatings Chemistry and Technology, Wiley, New York, 1991.
[2] K. Rijkse, Mod. Paints Coat. 91 (2001) 36.
[3] S. Papasavva, S. Kia, J. Claya, R. Gunther, Prog. Org. Coat. 43 (2001) 193.
[4] M. Korhonen, P. Starck, B. Lofgren, P. Mikkila, O. Hormi, J. Coat. Technol. 75 (2003) 67.
[5] G. Bocchi, Adv. Mater. Process. 4 (1999) 23.
[6] G.R. Pilcher, Macromol. Symposia. 187 (2002) 1.
[7] R.B. Prime, J.M. Burns, M.L. Karmin, C.H. Mo, H.T. Tu, J. Coat. Technol. 60 (1988) 55.
[8] C.M. Neag, L. Floyd, S. Manzuk, Polym. Mater. Sci. Eng. 68 (1993) 331.
[9] S. Vyazovkin, W. Linert, J. Sol. State Chem. 114 (1995) 392.
[10] S. Vyazovkin, Int. J. Chem. Kinetics 28 (1996) 95.
[11] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[12] J.M. Salla, J.M. Morancho, A. Cadenato, X. Ramis, J. Therm. Anal. Cal. 72 (2003) 719.
[13] L. Barral, J. Cano, J. López, I. López Bueno, P. Nogueira, C. Ramírez, M.J. Abad, J. Therm. Anal. Cal. 55 (1999) 37.
[14] R.S. Rajeev, S.K. De, A.K. Bhowmick, B. Jhon, Polym. Degradation Stability 79 (2003) 449.
[15] H. Yen, F. Lee, M. Yang, Polym. Testing 22 (2003) 31.
[16] C.N. Cascaval, D. Rosu, L. Rosu, C. Ciobanu, Polym. Testing 22 (2003) 45.
[17] J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis, Elsevier, Amsterdam, 1984.
[18] C.D. Doyle, Nature 207 (1965) 240.
[19] A.W. Coats, J.P. Redfern, Nature 207 (1964) 290.
[20] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[21] J.M. Criado, Thermochim. Acta 24 (1978) 186.
[22] J.M. Criado, J. Málek, A. Ortega, Thermochim. Acta 147 (1989) 377.
[23] X. Ramis, J.M. Salla, A. Cadenato, J.M. Morancho, J. Therm. Anal. Cal. 72 (2003) 707.
[24] P. Jain, V. Chouldhari, I.K. Varma, Eur. Polym. J. 39 (2003) 181.
[25] P. Khurana, S. Aggarwal, A.K. Narula, V. Choudhary, J. Therm. Anal. Cal. 71 (2003) 613.
[26] D.F. Parra, L.P. Mercuri, J.R. Matos, H.F. Brito, R.R. Romano, Thermochim. Acta 386 (2002) 143.