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Curing of a thermosetting powder coating by means of DMTA, TMA and DSC

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Abstract

The curing of a thermosetting powder coating made up of carboxyl-terminated polyester and triglycidylisocyanurate (TGIC) was studied by means of dynamic mechanical thermal analysis (DMTA), thermal mechanical analysis (TMA) and differential scanning calorimetry (DSC). On the basis of isothermal curing of the coating on different supports with DMTA and TMA, we determine the degree of mechanical curing. The degree of chemical conversion is determined by curing the material isothermally and dynamically by DSC. In both cases, curing kinetics were established by means of isoconversional analysis and it was observed that both the technique and the support used appreciably modify the kinetics of the reaction process. Gelation was determined on the basis of the maximum for the loss tangent (tan δ) and in TMA as the point at which the shrinkage rate drops to zero and the dimensions of the material show no appreciable change. The relationship between the glass transition and the conversion ($T_g - \alpha$) was established by means of DSC, DMTA and TMA. It is demonstrated that the degree of mechanical curing, determined on the basis of dynamic mechanical measurements, is an indicator of the progress of the reaction and up to gelation is always higher than the chemical curing level. The relationship between mechanical and chemical conversion serves as a point of connection between results obtained by means of TMA and DMTA and those obtained by means of DSC. Lastly, using the calorimetric kinetic data, the $T_g - \alpha$ relationship and conversion at gelation, we construct the TTT diagram for the curing of the coating.

Keywords: Thermosetting powder coating; Curing; Kinetic analysis

1. Introduction

Polymer powder coatings attain their maximum properties through a curing process involving heat or ultraviolet light. The preparation process of powder coatings and the chemical structure of the polymer binders have an influence on curing temperatures. To ensure its stability, solid resin must be stored at a temperature lower than its glass transition temperature (T_g). Therefore, the T_g of the powder coating prior to crosslinking, T_{go}, must be at least 50 °C, approximately. For preparation of the powder coating, the fused raw materials with the appropriate viscosity are passed through an extruder. The extrusion temperature is generally around 100 °C and the curing temperature must be no lower than the extrusion temperature. Viscosity during fusion (impregnation time of support) and prior to gelation strongly affects the adhesion of a powder coating to the support and also the quality of the coating. The T_g, fusion temperature and viscosity of the coating strongly limit curing temperatures, which are generally between 140 and 220 °C [1,2].

The curing of thermosetting powder coatings is complex, as is the curing of any thermoset, owing to the existence of changes in physical properties (gelation and vitrification) along with chemical transformations [3]. Vitrification is a thermo-reversible process in which the T_g of the material becomes equal to the curing temperature and involves cessation of the reactive process. With powder coatings, vitrification is not generally a phenomenon that needs to be taken into consideration, since curing temperatures, T_c, are normally higher than the glass transition temperature of the fully cured material, $T_{g\infty}$.

Vitrification can be detected either by means of calorimetric techniques, such as DSC [4–6] and temperature modulated differential scanning calorimetry (TMDSC) [7–9], or by means of techniques detecting changes in

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dynamic mechanical properties [3,9,10–13] or dielectric techniques [14,15].

Gelation occurs when the molecular weight of the crosslink tends to infinity and the material becomes insoluble and non-fusible, and therefore non-processable (molecular gelation). The macroscopic consequences of gelation are that viscosity tends to infinity and the material acquires elastic properties not present in the pre-gel state (macroscopic gelation). Gelation is an irreversible phenomenon that is determinant in the curing of powder coatings and if it occurs too soon the system will not have had sufficient time to fluidise, making the quality and appearance of the coating unsatisfactory.

Gelation occurs at a certain conversion level and does not involve any change in the reaction kinetics. Therefore, it cannot be observed by calorimetry and must be detected by means of the methods that measure changes in mechanical, electrical and viscoelastic properties. Many methods for detecting gelation have been published. Some of these methods are not equivalent and show inconsistencies. Accurate detection of gelation requires coincidence of macroscopic and microscopic gelation. In the measurement of viscosity, the gel point is associated with the state in which viscosity tends to infinity [16,17]. By means of dynamic mechanical tests, gelation can be detected: (a) as the point where the shear storage modulus and the shear loss modulus are of equal value and tan $\delta = 1$ [18] (this is not necessarily true of all thermoset polymers) [19]; (b) as the point at which tan δ becomes independent of the frequency [9,19]; (c) as the maximum in the tan δ curve [10,11,20,21]; (d) after the onset of decrease in the rate of growth of the shear loss modulus during the cure [22], and (e) as the crossing point between the tangent line at G' curve (shear storage modulus) and the base line ($G' = 0$) [20,23]. In TMA, gelation is associated with the moment when the material changes from liquid to solid and gains mechanical stability [5,24]. Gelation can also be detected by means of other techniques, such as torsional braid analysis [25] and electron spin resonance [26]. All these techniques allow us to determine the time taken by the material to gel at a specific temperature, but not the conversion level attained. This conversion level is often determined in DSC on the basis of the gel times obtained through some of the aforementioned techniques. This procedure can be erroneous, since the material does not take the same time to gel in the different techniques, particularly if a support is used for the sample in some of those techniques [6]. In this work we determine gelation by means of DMTA and TMA (using a new methodology) and we observe that it coincides with gelation as determined on the basis of solubility tests and is close to gelation as calculated theoretically. The conversion level in gelation is determined by means of DSC on the basis of residual heat in the gelled samples.

As a rule, the study of curing by means of DSC is complex for powder coatings, since exothermal heats are low. During isothermal curing at high temperatures, part of the heat is lost during stabilisation of the apparatus. At low temperatures the heat is released slowly but falls below the sensitivity level of the apparatus. One possibility is to work with dynamic cures in DSC; here, although the reactive process can be followed, the kinetic data obtained can show the lack of precision characteristic of the method, and in many instances the experimental reaction interval is very different from the isothermal interval. Curing may also be followed indirectly, by means of temperature scans of partially cured samples [6,27].

As an alternative to calorimetric cures, there is the possibility of curing the material in DMTA or TMA. The measurement of dynamic mechanical properties of a coating is complex, since samples generally need to be applied to a support. Accurate analysis requires the use of supports that do not significantly influence the peak loss temperature or the values of dynamic mechanical data (e.g. E', E'' and tan δ). Quantitative analysis requires uniform and reproducible samples and supports with high rigidity in comparison with that of the coating [3,10,28,29]. Two of the objectives of this work, aspects that are not widely dealt with in the literature, were to determine the relationship between the degree of mechanical conversion determined in DMTA and the degree of chemical curing, and to establish the curing kinetics in DMTA [20,28].

Some authors have used dilatometric techniques to measure shrinkage in thermosets during curing and related it to conversion and morphological changes [30,31]. Follensbee et al. [32] used TMA to measure shrinkage during curing and observed that it lags behind chemical conversion. Skrovanek and Shoff [33], using thermal mechanical analysis for organic coatings, have shown how softening points, the degree of conversion, indentation hardness, the modulus and creep behaviour can be determined. In the work presented here, we measure shrinkage of the coating during curing in TMA in order to determine the extent of the reaction and the curing kinetics.

Determination of the glass transition temperature, T_g, involves measurement of the temperature at which a property undergoes a significant change when the material converts from a glassy to a rubbery state. The techniques generally used are those set out for determination of vitrification. As a rule, the values for T_g obtained by means of different techniques are not directly comparable. Knowledge of the relationship between the T_g and the degree of conversion, α, is required for the accurate description of the curing process and for construction of the time–temperature–transformation (TTT) diagram [3,5,6]. The experimental technique normally used to establish the $T_g - \alpha$ relationship consists of stopping the reaction at different times and performing a dynamic scan in DSC to obtain the T_g and the residual heat. Where the T_g is determined by a technique other than calorimetry, chemical conversion is difficult to establish. One possibility, although it involves a certain degree of experimental difficulty, is to remove the material from the apparatus when the latter

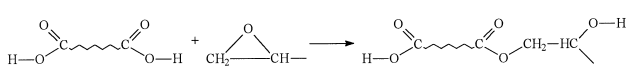
reaches a certain glass transition temperature, to carry out a dynamic scan by DSC [28,29]. Although various equations have been used in the literature to describe the $T_g-\alpha$ data, systems with a high crosslinking density might fail to be described correctly [34–37]. In our work we combine the use of the DiBenedetto equation [34] with experimental determination of the T_g by DMTA, TMA and DSC, and we establish the relationship between the T_g and the degree of conversion for the three techniques used. This relationship serves as a point of connection between the data for curing obtained by means of the different techniques.

As already mentioned, the objective of this work was to study the curing of a powder coating by means of DMTA, TMA and DSC. Both the physical and chemical processes taking place during the reactive process are determined. Mechanical conversion is related to chemical conversion and the curing kinetics is established on the basis of these conversions by means of isoconversional analysis. The technique and the support used are seen to influence curing. Consequently, the times for the processes in the different techniques are not interchangeable. Lastly, the TTT diagram for the curing of the coating is constructed on the basis of calorimetric data.

2. Experimental

2.1. Materials

The powder coating studied is a physical blend of a lightly branched carboxyl-terminated polyester and triglycidylisocyanurate (TGIC), with a polyester/TGIC weight proportion of 93/7 (Cray Valley, 4704). The polyester has a functionality of $f = 2.3$, an acid number of 33 and an $M_n = 3910$, while the TGIC has $f = 3$ and $M_n = 297$. The molar ratio of COOH groups/epoxy groups is 0.774. The chemical reaction that takes place during the curing process, assuming that no secondary reactions occur, may be represented schematically as follows:



The coating used has a $T_{go} = 60$ °C, a $T_{g\infty} = 75$ °C and a fusion temperature of 100 °C. These three data were obtained by means of dynamic scans by DSC at 10 °C/min. During the first heating, glass transition accompanied by an ageing peak, endothermic fusion and exothermic curing were observed (Fig. 6). The fusion temperature was taken as the minimum of the second endothermic peak. The T_{go} was determined by means of a second scan after heating to 110 °C to eliminate the thermal history. The $T_{g\infty}$ was determined after complete curing of the material by means of a second scan. In general, these coatings were cured at temperatures approaching those of industrial curing, higher than $T_{g\infty}$.

2.2. Techniques

Calorimetric analysis was carried out using a Mettler-Toledo DSC30 calorimeter. The weight of the samples was approximately 10 mg. All of the samples were cured in a nitrogen atmosphere. Dynamic curing was carried out at rates of 0.5, 2, 3, 4, 5, 6, 7.5, 9, 10, 12, 15 and 20 °C/min from −50 to 250 °C. In the dynamic curing processes the degree of chemical conversion was calculated as:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}} \quad (1)$$

where ΔH_T is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to that temperature, and ΔH_{dyn} is the total reaction heat associated with complete conversion of all reactive groups. A value of 37.5 J/g was taken for ΔH_{dyn}, calculated as the average value for heat reaction obtained dynamically at the different rates of heating. In order to establish the relations $T_g-\alpha$ and α–time, isothermal curing was carried out for different times at temperatures of 110, 120, 130, 140 and 150 °C. After curing, the sample was cooled and by means of a dynamic scan at 10 °C/min, the glass transition temperature and the residual heat were determined. All the T_gs were calculated as the temperature of the half-way point of the jump in heat capacity when the material changed from the glassy state to the rubbery state. With isothermal curing the degree of chemical conversion was calculated on the basis of residual heat as:

$$\alpha_{DSC} = 1 - \frac{\Delta H_{t,\,res}}{\Delta H_{dyn}} \quad (2)$$

where $\Delta H_{t,\,res}$ is the residual heat obtained after isothermal curing up to a time t.

In order to determine experimentally the vitrification line of the TTT diagram, isothermal curing was carried out at below $T_{g\infty}$, in thermostatically controlled baths at temperatures of 60–75 °C. Prior to the curing process, the samples were heated in the DSC at 10 °C/min until fusion, then cooled to an amorphous state and subjected to curing. The samples were removed at different times, and by means of a dynamic scan at 10 °C/min the T_g and the residual heat were determined. The residual heat was used to calculate the degree of conversion (Eq. (2)). The material was considered to be vitrified when its T_g coincided with the curing temperature and no ageing peak was observed. Thermostatically controlled baths were used instead of DSC, since vitrification times can be very long (for example, approximately 1000 h at a temperature of 72 °C).

Dynamic mechanical analysis was carried out in a nitrogen atmosphere with a Rheometrics PL-DMTA MKIII analyser. Measurement of the shear storage modulus (E') and loss tangent (tan δ) during curing and of partially and fully cured samples was carried out at a frequency of 1 Hz and working in single cantilever with rectangular samples

($25 \times 12 \times 0.5\ mm^3$) with a free length of 2 mm. Solid coatings were applied to a fibreglass support and brought to fusion to attain complete impregnation of the support. Isothermal curing for different times was carried out at temperatures between 110 and 150 °C. Isothermal temperature was attained by heating at 2 °C/min from 35 to 105 °C, followed by a second heating at 10 °C/min to the curing temperature. After isothermal curing, a dynamic scan was carried out at 2 °C/min to determine the T_g of the partially and fully cured materials. The T_g was taken in DMTA as the maximum temperature of tan δ. The degree of mechanical conversion in DMTA is calculated as [20]:

$$\alpha_{DMTA} = \frac{E'_t - E'_o}{E'_\infty - E'_o} \tag{3}$$

where E'_t, E'_o and E'_∞ are, respectively, the shear storage modulus at a time t, at the onset (uncured coating), and upon completion of the reactive process (fully cured coating). For the purposes of comparison only, we also determined the mechanical conversion by DMTA on the basis of the area under the tan δ curve as [28]:

$$\alpha_{\tan\,\delta} = \frac{\Delta \tan\,\delta_t}{\Delta \tan\,\delta_\infty} \tag{4}$$

where $\Delta \tan\,\delta_t$ and $\Delta \tan\,\delta_\infty$ are, respectively, the areas under the tan δ curve at a time t and a time at which the sample is fully cured. These areas were obtained by integrating the tan δ curve versus time. The comparison between the two mechanical conversions is of interest as the fibre content can influence $\alpha_{\tan\,\delta}$. This is due to the fact that the contribution of the fibre cannot be eliminated from $\alpha_{\tan\,\delta}$ because it contributes as much to the loss modulus as it does to the storage modulus. Within certain samples cured isothermally for different times by DMTA, the samples were removed from the support and a dynamic scan was carried out by DSC at 10 °C/min to determine the T_g and the residual heat. This residual heat was used as a measure of chemical curing (Eq. (2)). These tests enable us to establish the relationship between the degree of chemical conversion and the degree of mechanical conversion, and the relationship between the T_g determined by DSC and DMTA.

Thermal mechanical analysis was carried out in a nitrogen atmosphere using a Mettler-Toledo TMA40 analyser. Measurement of shrinkage, $\Delta L = L_t - L_o$, undergone by coatings during curing and the shrinkage rate, dL/dt, was carried out with application of a force of 0.01 N. In this case, the coatings taken to fusion impregnated a cellulose support and this was placed between two discs of Al_2O_3. Isothermal curing for different times was carried out at 110, 120, 130, 140 and 150 °C. The isothermal curing temperature was attained by heating at 2 °C/min from 35 to 105 °C, followed by a second rapid heating to the curing temperature. Determination of the T_g by TMA was carried out by means of a dynamic scan at 10 °C/min applying a periodic force (cycle time = 12 s) of 0.25 ± 0.25 N. The T_g was taken in TMA as the temperature at which an increase in the amplitude of oscillations was observed [38] (Fig. 10). Assuming that there is a relationship between shrinkage and conversion during curing [31], the degree of mechanical conversion in TMA is calculated as:

$$\alpha_{TMA} = \frac{L_t - L_o}{L_\infty - L_o} \tag{5}$$

where L_t, L_o and L_∞ are, respectively, the values for the thickness of the sample at a time t, at the onset and upon completion of the reactive process when the material is fully cured.

In order to determine the α_{gel} on the basis of solubility tests, we performed the following procedure. The coating was cured in thermostatically-controlled baths and two fragments of the sample were removed at different curing times. One of them was subjected to DSC to determine the conversion level attained and the other was subjected to a solubility test to determine the fraction of the material soluble in dimethylformamide.

3. Theoretical

Kinetic study may start with the rate equation, $d\alpha/dt = k(T)f(\alpha)$, where $d\alpha/dt$ is the reaction rate, $k(T)$ is the rate constant that depends on temperature and $f(\alpha)$ is function of the degree of conversion associated with the reaction mechanism.

The kinetic analysis of the curing of coatings was carried out using an isoconversional method. The hypothesis used by this methodology is that dependence of the rate constant on temperature follows the Arrhenius law and that at each degree of conversion the reaction mechanism is the same, regardless of the temperature [39].

Integrating the reaction rate in isothermal experiments and substituting the Arrhenius equation we can obtain:

$$\ln t = \ln\left[\frac{g(\alpha)}{k_o}\right] + \frac{E}{RT} = A + \frac{E}{RT} \tag{6}$$

where E is the activation energy, k_o is the frequency factor, R is the universal gas constant, T is temperature, t is time, $A = \ln[g(\alpha)/k_o]$ is a constant for each degree of conversion, and $g(\alpha)$ the following function of the degree of conversion:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{7}$$

For isothermal curing, we used the integral method (Eq. (6)) to determine the kinetic parameters. For each degree of conversion, Eq. (6) is a linear relationship between the logarithm of the time to reach that conversion level and the inverse of the curing temperature. By applying Eq. (6) to a series of temperatures, we can determine the activation energy and the constant A as the slope and the intercept, respectively, of the linear relationship $\ln t$ versus $1/T$ for

each degree of conversion. Eq. (6) has been used in this work to carry out isothermal kinetic analysis of curing by DMTA and TMA.

For dynamic curing, the following integral method was used [40]:

$$\log \phi = \log\left[\frac{k_o E}{g(\alpha)R}\right] - 2.315 - 0.4567\frac{E}{RT}$$

$$= A' - 0.4567\frac{E}{RT} \quad (8)$$

where ϕ is the rate of heating and $A' = \log[k_o E/g(\alpha)R] - 2.315$ is a constant for each degree of conversion. In this procedure, at a constant degree of conversion, the linear relationship $\log \phi$ versus $1/T$ allows us to determine the constant A' and E on the basis of the intercept and the slope, respectively. This method has been used in this work to determine the dynamic kinetic parameters of the curing of the coating by DSC.

The constant A' is observed to be directly related by E/R to the constant A of isothermal adjustment (Eq. (6)). Thus, taking the dynamic data A' and E and applying Eq. (8), we can determine the constant A for the isothermal isoconversional lines (Eq. (6)) and simulate isothermal curing. Specifically, in this work, on the basis of the dynamic parameters obtained by means of DSC, we determine the isothermal parameters corresponding to curing by DSC and compare them with the isothermal data obtained by means of DMTA and TMA. Details on the methodology used and the deduction of the kinetic equations set out above can be found in previous works [5,41].

To analyse the effect of crosslinking on T_g and estimate the one-to-one relationship between the degree of conversion and the glass transition temperature, we use the DiBenedetto equation [34]:

$$\frac{T_g - T_{go}}{T_{go}} = \frac{\left(\frac{\epsilon_X}{\epsilon_M} - \frac{F_X}{F_M}\right)\alpha}{1 - \left(1 - \frac{F_X}{F_M}\right)\alpha} \quad (9)$$

where ϵ_X/ϵ_M is the relationship between the lattice energy of the crosslinked and non-crosslinked polymers and F_X/F_M is the relationship between the segmental mobilities of the same polymers. These two relationships are generally treated as two empirical constants characteristic of each thermoset system.

4. Results and discussions

4.1. Curing kinetics

Fig. 1 depicts isothermal curing of the coating by DMTA. The shear storage modulus is observed to increase during the curing process and tends to stabilise when curing is completed. While the absolute value of the modulus does not represent the actual modulus of the resin, but rather of a composite, observed behaviour suggests the existence of a proportional relationship between progress of the reaction and increase of the modulus. The degree of mechanical conversion is determined on the basis of this increase by means of Eq. (3). Fig. 2 shows the curves mechanical conversion, α_{DMTA}, versus time, t, during isothermal curing of the coating by DMTA at different temperatures. For each degree of conversion, using Eq. (6), we determine the isoconversional lines and their associated kinetic parameters (Table 1). The reliability of the isoconversional procedure is evident in Fig. 2, where comparison is made of the $\alpha_{DMTA}-t$ experimental curves and the curves predicted on the basis of the data from Table 1. This table also shows that the activation energy decreases as the reaction progresses, reaching a minimum value and then increasing slightly. This behaviour, also observed by means of calorimetry in other materials [27,42,43], can be explained by the physical and chemical changes that occur during the curing process. It can also be explained by the existence of the so-called compensation effect between the activation energy and the frequency factor (included in the kinetic parameter A) [41,44].

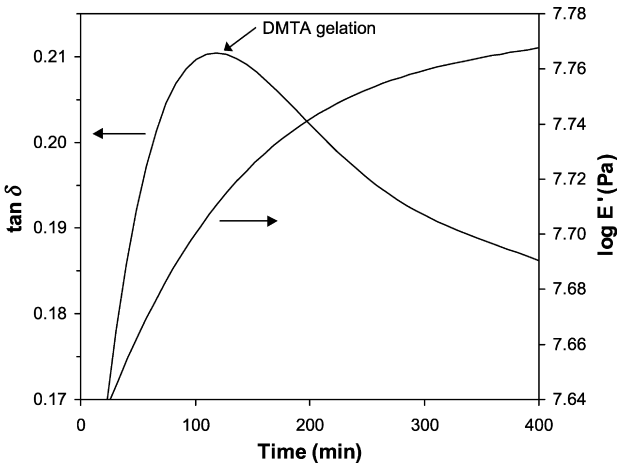


Fig. 1. Storage modulus, E', and loss tangent, tan δ, versus time for the powder coating cured isothermally at 125 °C by DMTA.

Fig. 1 shows that the curve tan δ versus time reaches a maximum attributable to gelation of the material (as will be discussed below). No vitrification peak is observed, since curing temperatures are higher than $T_{g\infty}$. Using the area under the tan δ curve in isothermal curing, we evaluated the degree of mechanical curing by application of Eq. (4) and calculated the curves for $\alpha_{\tan\delta}$ versus time (figure not shown). Using Eq. (6), we determine the kinetic parameters of curing for each degree of conversion. Table 1 shows that these parameters are relatively similar to those obtained on the basis of the modulus, although regressions are slightly worse. The inset in Fig. 2 compares the $\alpha_{DMTA}-t$ and $\alpha_{\tan\delta}-t$ curves at temperatures of 120 and 150 °C. We note that the two curves, indicating the mechanical degree of conversion, are similar, and therefore that the corresponding

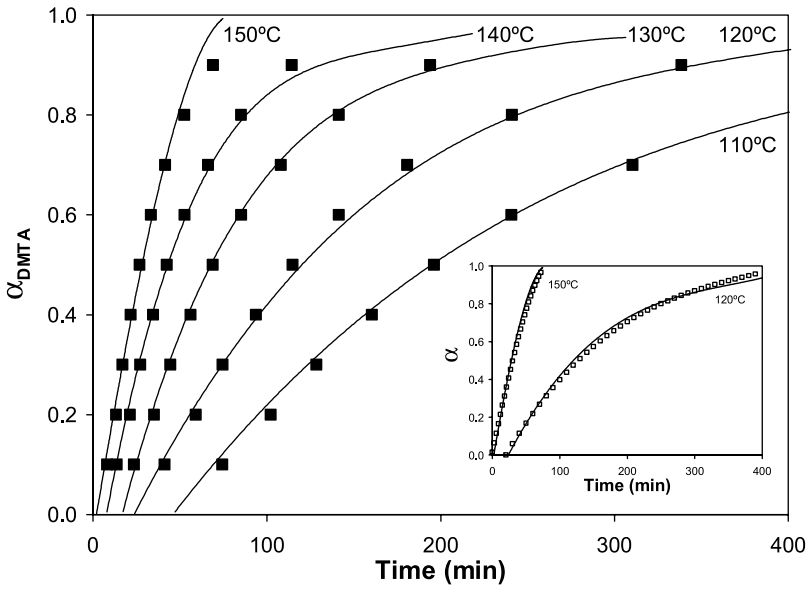


Fig. 2. α_{DMTA} versus curing time at different temperatures. The solid lines are the experimental curves and the symbols are the predicted data. Inset: Degree of mechanical conversion versus curing time. The solid lines and symbols correspond to the conversions determined on the basis of the modulus and on the basis of tan δ, respectively.

methods are practically equivalent. The minor differences observed between these curves and between the kinetic parameters calculated on the basis of α_{DMTA} and $\alpha_{\tan\,\delta}$ can be attributed to the different calculation of the degree of conversion and not to kinetic changes. In general, integration of the area under tan δ shows greater imprecision owing to the difficulty in correctly establishing the limits of integration.

Fig. 3 shows isothermal curing of the coating by TMA. Note that the material shrinks considerably during this process and then tends not to show any observable dimensional changes in the sample when curing is complete. The same figure shows the derivative of the signal. There is an abrupt change in the rate of shrinkage, which, as discussed below, is associated with gelation of the coating. It is reasonable to assume that there is a relationship between the shrinkage undergone by the coating during curing and the degree of progress of the reaction. The degree of mechanical conversion by TMA is calculated on the basis of shrinkage using Eq. (5). Fig. 4 shows the experimental curves for α_{TMA} versus time, t, during isothermal curing of the coating by TMA at different temperatures. For each degree of conversion, using Eq. (6) we determine, as with DMTA, the kinetic parameters of curing (Table 1). Fig. 4 also shows the $\alpha_{TMA}-t$ curves predicted on the basis of the kinetic data shown in Table 1. Owing both to the good fits obtained (Table 1) and to the accuracy of the simulation, we once again note the reliability of the kinetic method used.

As mentioned above, monitoring of isothermal curing is not feasible with DSC. Therefore, in order to compare the

Table 1
Kinetic parameters of curing of a coating by DMTA, TMA and DSC

	DMTA (E')			DMTA (tan δ)			TMA			DSC			
α	E (kJ/mol)	A (min)	r	E (kJ/mol)	A (min)	r	E (kJ/mol)	A (min)	r	E (kJ/mol)	A' (K min^{-1})	A (min)	r
0.1	74.0	−18.94	0.999	79.1	−20.55	0.998	57.8	−17.81	0.995	120.3	16.94	−34.76	0.983
0.2	68.7	−16.94	0.999	74.1	−18.61	0.997	58.1	−17.14	0.998	110.5	15.25	−30.94	0.990
0.3	68.0	−16.51	0.999	70.7	−17.28	0.999	60.7	−17.47	0.999	106.0	14.40	−29.03	0.991
0.4	67.4	−16.07	0.999	66.1	−15.65	0.999	62.5	−17.64	0.999	103.3	13.85	−27,80	0.992
0.5	67.1	−15.79	0.999	64.2	−14.87	0.997	64.9	−18.03	0.999	102.4	13.56	−27.13	0.993
0.6	66.6	−15.42	0.999	62.4	−14.12	0.991	69.1	−18.97	0.997	103.0	13.46	−26.90	0.993
0.7	67.7	−15.52	0.999	61.0	−13.51	0.990	73.5	−19.96	0.995	104.2	13.42	−26.80	0.992
0.8	70.2	−16.00	0.999	60.3	−13.13	0.981	78.4	−20.96	0.995	106.4	13.47	−26.88	0.990
0.9	73.3	−16.60	0.995	60.8	−13.06	0.982	85.2	−22.22	0.998	107.8	13.33	−26.55	0.985

A and E have been calculated on the basis of isothermal experiments with DMTA and TMA, as the intercept and the slope of the isoconversional relationship $\ln t = A + E/RT$, with $A = \ln[g(\alpha)/k_o]$. A' and E have been obtained, on the basis of dynamic experiments with DSC, as the intercept and the slope of the isoconversional relationship $\log \phi = A' - 0.4567E/RT$, with $A' = [\log(k_o E/g(\alpha)R) - 2.315]$. The value of A in DSC has been calculated on the basis of the values A' and E. α refers to α_{DMTA}, $\alpha_{\tan\,\delta}$, α_{TMA} and α_{DSC} depending on the technique and variable used. The kinetic data obtained by DMTA are duplicated, depending on the use of E' or tan δ for calculating the degree of conversion.

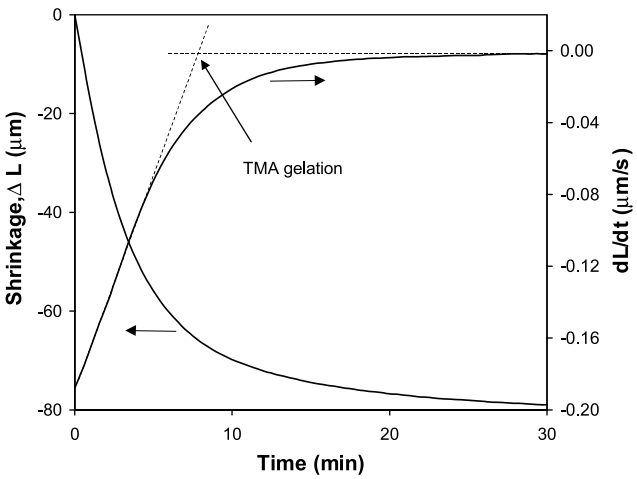


Fig. 3. Shrinkage and shrinkage rate versus time for the coating cured isothermally at 130 °C by TMA.

curing process by DSC with curing by TMA and DMTA, we study the dynamic curing by DSC and on the basis of the dynamic kinetic parameters we obtain the isothermal parameters. By means of dynamic curing at different rates (figure not shown) and application of Eq. (1), we obtain the curves for α_{DSC} versus temperature (figure not shown). On the basis of these curves and at a constant rate of conversion, we use Eq. (8) to determine the isoconversional lines and their associated dynamic parameters (Table 1). Assuming that the dynamic and isothermal kinetics are the same, on the basis of the dynamic parameters E and A' we use the intercept of Eq. (8) to calculate the isothermal parameter A of Eq. (6). The reliability of this procedure is observed in the inset in Fig. 12, where the experimental isothermal α–t curve (determined on the basis of the residual heats of partially cured samples) and the curve predicted on the basis of the kinetic data, E and A, given in Table 1, are compared.

We now have the same kinetic data, E and A, for all the techniques used. It is difficult to deduce from direct

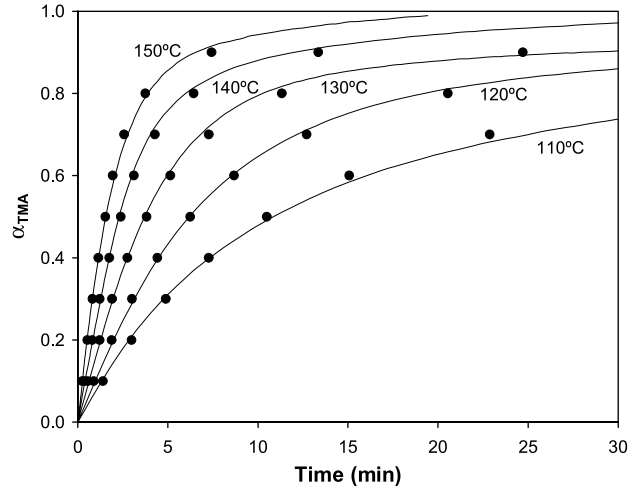


Fig. 4. α_{TMA} versus curing time at different temperatures. The solid lines are the experimental curves and the symbols are the predicted data.

examination of these parameters how the support and technique used influence the curing kinetics. We observe that the kinetic parameters of DMTA and TMA are of the same order of magnitude, which would appear to indicate that they correspond to similar kinetics. On the other hand, the DMTA and DSC data are dissimilar in respect of their numerical value, but show a similar trend, while the TMA data show a different trend, since the activation energy increases constantly. This last comparison would lead to a conclusion diametrically opposed to the first one, i.e. that the kinetics of DSC and DMTA are similar, while the kinetics of TMA is different.

In order to make a correct comparison of the kinetic data, we must take into account that the activation energy and the frequency factor are two non-independent parameters, linked by the Arrhenius equation, and that therefore they cannot be discussed separately.

On the basis of the two parameters, E and A, and using the isoconversional lines of Eq. (6), the temperature and curing time for a single conversion can be compared. For example, at a conversion of 70% and a temperature of 120 °C, using the data given in Table 1 we can calculate the following curing times: $t_{DMTA} = 181.2$ min, $t_{TMA} = 12.6$ min and $t_{DSC} = 162.5$ min. It is evident that the kinetics of DMTA and DSC are similar, while it is clearly different in TMA. This result may already be deduced from the experimental α–t curves (Figs. 2, 4 and 12 (inset)), where the DMTA and DSC data show similar curing times. This can be explained, as shown below, by a compensation effect between the activation energy, E, and the frequency factor k_o. Thus, high activation energies with low frequency factors can describe the same kinetics as low activation energies with high frequency factors.

In order to calculate the frequency factor on the basis of the parameter A, we must establish the function $g(\alpha)$ describing the process. For this coating, as shown in a previous work [41], the function $f(\alpha)$ associated with the reaction that correctly describes the curing is:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{10}$$

with $n + m = 2$ and $n = 1.9$. The function $g(\alpha)$ associated with this $f(\alpha)$ has a value of:

$$g(\alpha) = \frac{z^{1-n}}{n-1}; \qquad z = \frac{1-\alpha}{\alpha} \tag{11}$$

For each degree of conversion, we calculate the function $g(\alpha)$ and, on the basis of this function and the parameter A, the frequency factor. Fig. 5 shows the curves for $\ln k_o$ versus E for the four kinetics of Table 1. We clearly observe that all of the kinetic data are grouped into compensation curves of the type:

$$\ln k_{o,\alpha} = aE_\alpha + b \tag{12}$$

where $k_{o,\alpha}$ and E_α represent the Arrhenius parameters subject to change with changes in α. The slope a is related to the isokinetic temperature [42] and the intercept b, which is

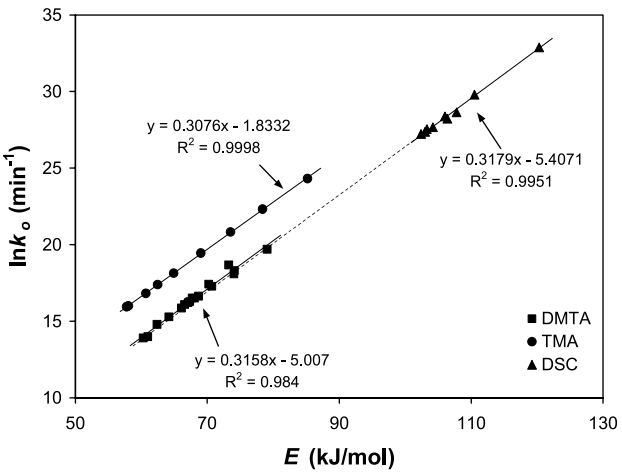


Fig. 5. Compensation curves $\ln k_{o,\alpha} = aE_\alpha + b$ associated with each technique used. The kinetic data for DMTA obtained on the basis of the modulus and tan δ have been grouped on one straight line. The broken line corresponds to extrapolation of the straight line for DSC to the area of the data for DMTA.

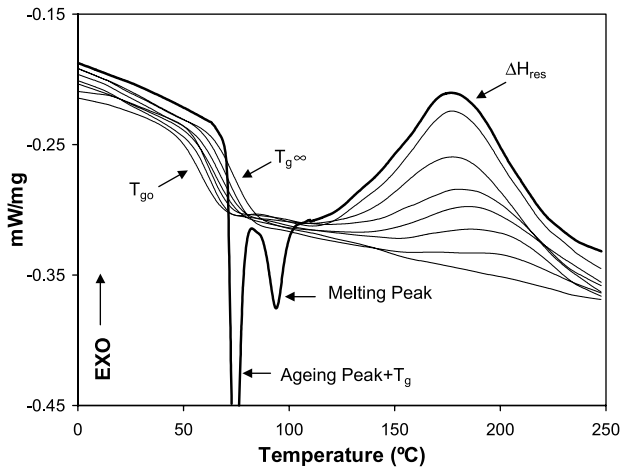


Fig. 6. DSC thermograms at 10 °C/min of coatings with different degrees of conversion. In general, ΔH_{res} is the residual heat of the partially cured samples, except for uncured coatings where it represents the total reaction heat. The dark line corresponds to the DSC thermogram of the coating with no prior heat treatment.

independent of temperature, with the reaction rate and the function $f(\alpha)$. Fig. 5 shows that all the regressions of the compensation curves are correct, thereby supporting the procedure used. It is interesting to note that the DMTA and DSC data fall roughly on the same compensation curve, indicating that they have similar kinetics, although their activation energies and frequencies are very different. The TMA data are very distant from the DSC and DMTA data, showing a clearly different kinetics. The kinetics study allows us to conclude that the support and the technique can influence the curing kinetics. In the case of TMA, the kinetics is faster, possibly owing to an increase in the contact support. DSC and DMTA show similar kinetics, since much of the coating, in DMTA, is free in the fibreglass mesh and reacts in a similar way to the pure resin in DSC. We can also conclude, generally, that the activation energy cannot be used on its own as a comparative kinetic parameter. If we wish to compare kinetic data, this must be done using pairs of $[E, A]$ or the kinetic triplet $[E, k_o, g(\alpha)$ or $f(\alpha)]$.

4.2. $T_g - \alpha$ relationship

By means of DSC, DMTA and TMA, the relationship between the degree of conversion and the glass transition temperature was determined. The T_g and the residual heat were determined by means of DSC, using partially cured samples and a second dynamic scan. The degrees of conversion were calculated using Eq. (2). Fig. 6 shows the DSC thermograms for the uncured, partially cured, and fully cured coating. We observe that as the material is more crosslinked, its T_g increases and its residual heat decreases. Fig. 7 shows the $T_g - \alpha$ relationship determined on the basis of the curves shown in Fig. 6 and other similar curves. We observe, as in many thermosets, that there is a one-to-one relationship between the degree of conversion and the glass transition temperature. This relationship is independent of curing conditions (temperature, heating rate, mass). This means that for a certain degree of conversion the molecular structure is always the same, or that any variation will not significantly affect the T_g. The experimental data are fitted using the DiBenedetto equation (Eq. (9)) and the best fit obtained for the values $\epsilon_X/\epsilon_M = 0.489$ and $F_X/F_M = 0.468$.

Samples were cured isothermally by DMTA for different times. To calculate the glass transition temperature, chemical conversion and mechanical conversion of these partially cured samples, we used the procedure set out below. Two samples were prepared for each curing time in DMTA. The first sample was removed from DMTA and its chemical conversion was determined by means of a

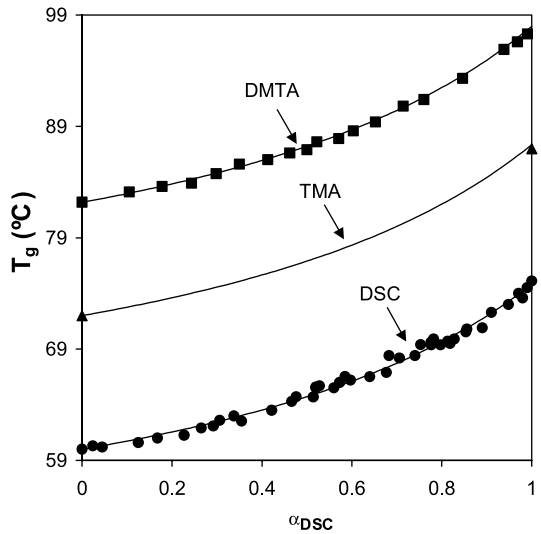


Fig. 7. $T_g - \alpha$ relationship determined by DSC, TMA and DMTA. The symbols correspond to the experimental data and the lines correspond to the fits according to the DiBenedetto equation.

dynamic scan by DSC. The second sample was subjected to a second dynamic scan by DMTA to determine its T_g as the maximum of tan δ. The mechanical conversion of these samples was determined on the basis of the curing time and the $\alpha_{DMTA}-t$ curves (Fig. 2). Fig. 8 shows the increase in T_g (maximum tan δ) with the increase in the degree of conversion (curing time). In general, the T_g determined for DMTA is approximately 22 °C higher than that determined by DSC. Fig. 7 also shows the relationship between the T_g determined by DMTA and the degree of chemical conversion. Experimental data fit reasonably well with the DiBenedetto equation using the values of $\epsilon_X/\epsilon_M = 0.489$ and $F_X/F_M = 0.468$ obtained from the calorimetric $T_g-\alpha$ relationship and the T_{go} obtained by DMTA ($T_{go} = 82$ °C).

Fig. 9 compares the mechanical conversion associated with modulus change with the chemical or calorimetric conversion obtained by direct measurements of chemical conversion on the DMTA samples. We observe that the latter is higher than α_{DMTA} until reaching $\alpha_{DSC} \approx 75\%$ (gelation of the material), after which the two conversions are similar up until the completion of curing.

With TMA the T_g was determined by means of a dynamic scan with a periodic force. T_g is defined as the onset temperature value of the amplitude change. Fig. 10 shows the determination by TMA of the T_g for a completely cured coating. Since the coating completely saturates the cellulose support, it is not possible simply to remove the coating to determine the chemical conversion on the basis of residual heat. Therefore, only the T_g of the uncured and fully cured material was determined. We have seen that the T_g determined by TMA is 12 °C higher than that determined by DSC. Using the DiBenedetto equation with the values $\epsilon_X/\epsilon_M = 0.489$ and $F_X/F_M = 0.468$, estimated on the basis of the calorimetric data, and the T_{go} determined by TMA ($T_{go} = 72$ °C), we have established the relationship between T_g determined by TMA and the degree of chemical

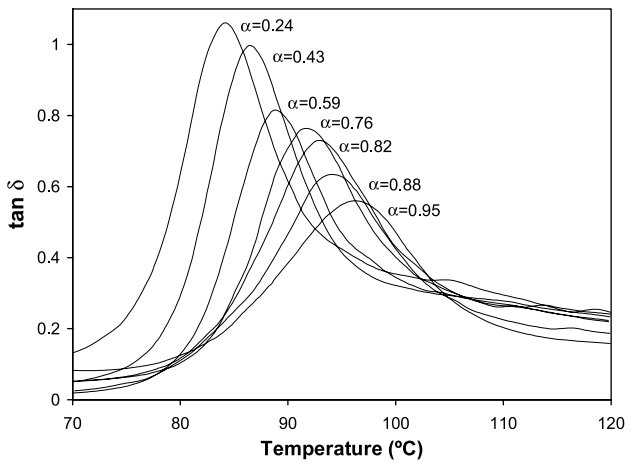


Fig. 8. Loss factor versus temperature for coatings with different degrees of chemical conversion obtained by direct measurements on the DMTA samples cured at 120 °C.

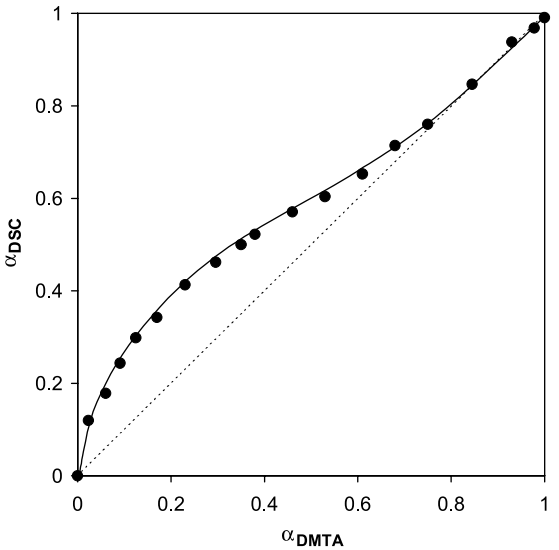


Fig. 9. Chemical conversion determined by DSC versus mechanical conversion determined by DMTA (E').

conversion. Fig. 7 shows that relationship and we observe how the value of the $T_{g\infty}$ fits correctly.

While it has not been possible to determine systematically the chemical conversion of the samples cured by TMA, there are experimental dates suggesting that α_{DSC} is similar to α_{TMA}. Furthermore, the proportion of shrinkage undergone by the material to the increase in chemical conversion (decrease in the number of moles) is known [31].

As a general rule, if we know the relationship between the T_g and the degree of chemical conversion, the relationship between mechanical and chemical conversion and the isoconversional lines of Table 1 for the three techniques used, the DMTA, DSC and TMA data are interconvertible. We can calculate the data of a technique on the basis of the data of another technique. For example, we can calculate the chemical conversion, which is not directly measurable, of samples cured by DMTA and TMA by measuring their T_g with either of these two techniques and determining the corresponding chemical conversion in the $T_g-\alpha_{DSC}$.

We have seen that there is a one-to-one relationship between T_g and α regardless of the technique used. The technique only affects the value of the T_g, and not that relationship. If we know the relationship between the T_g and the chemical conversion, and the latter can fit the DiBenedetto equation correctly, we can determine the $T_g-\alpha$ relationship for any other technique. To do so, all we need are the fitting parameters ϵ_X/ϵ_M and F_X/F_M and the T_{go} obtained by the technique for which we wish to establish the $T_g-\alpha$ relationship.

The different value obtained for the T_g depending on the technique used (Fig. 7) can be explained by the different frequency, ν, applied to the sample. At higher frequencies (shorter relaxation time), the T_g appears at a higher temperature. In approximate terms, we can establish the

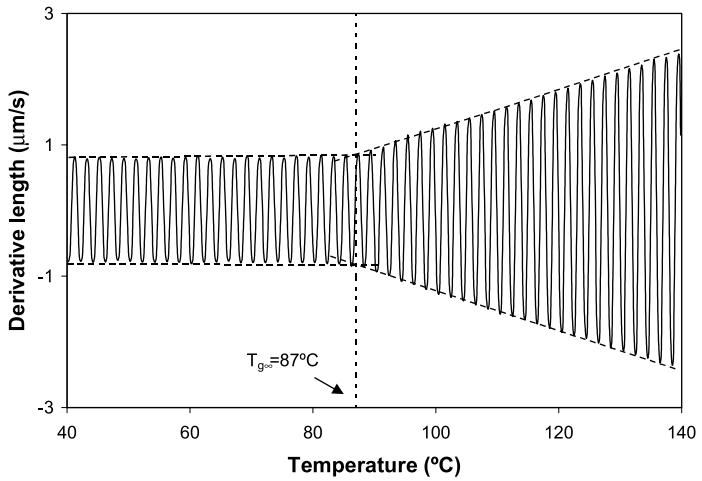


Fig. 10. TMA thermogram of a fully cured coating with application of a periodic force.

following frequencies: $\nu_{DMTA} = 1$ Hz, $\nu_{TMA} = 0.083$ Hz and $\nu_{DSC} = 1.32 \times 10^{-3} - 1.77 \times 10^{-2}$ Hz. These frequency values are consistent with the experimental T_gs, $T_{gDMTA} > T_{gTMA} > T_{gDSC}$. The frequency with DMTA is the frequency applied in the experiment and the frequency with TMA is calculated as the inverse of the applied period, $\nu_{TMA} = 1/12$ Hz. To estimate the equivalent frequency for DSC, we apply the rule for transformation of cooling rate to frequency deduced by Donth [45]:

$$\nu = \frac{\beta}{2\pi a \delta T} \tag{13}$$

where β is the cooling rate, δT is the mean temperature fluctuation of the cooperatively rearranging regions and a an experimental constant. δT can be determined, by TMDSC, as half of the width of the glass transition interval of the real part of the complex heat capacity. On a logarithmic scale, the term $a\delta T$ is the shift factor between frequency and rate. The experimental term $a\delta T$ is given widely differing values in the literature, varying between 1.5 and 20 for amorphous polymers [46–48]. Taking these two values, we establish a minimum and maximum value for frequency as a reference. Preliminary results shows that for the coating studied the term $a\delta T$ has an approximate value of 2 ($\nu = 0.013$ Hz).

4.3. Gelation

Gelation is determined by DMTA as the point at which tan δ reaches a maximum value during isothermal curing (Fig. 1). When the material approaches gelation, viscosity tends to infinity. This involves an increase in dissipated energy and therefore in the shear loss modulus, E'', associated with the viscous portion. It has been shown experimentally that gelation determined as the maximum of tan δ coincides with the criterion of taking gelation as the point at which the rate of increase in E'' drops off during curing (figure not shown). In the experiments carried out, the maximum of tan δ cannot be confused with vitrification, since the material does not vitrify because the curing temperature is higher than the $T_{g\infty}$ of the material. Samples were removed from DMTA when they reached the maximum and a dynamic scan revealed chemical conversion in gelation of $\alpha_{gel} = 0.76$.

With TMA, gelation is determined on the basis of experiments measuring the shrinkage of the material during curing (Fig. 3). While the material is liquid it shrinks proportionally to the progress of curing; when the material gels and gains mechanical stability, there is an abrupt change in shrinkage and tends to zero when the material is fully cured. This is also clearly observed in the derivative of the signal (rate of shrinkage). The gel point is defined as the intersection between the tangent to the rate curve where this rate tends to zero and the tangent to the region of linear behaviour. Conversion in gelation is determined on the basis of the gel time and the $\alpha_{TMA} - t$ curves. Depending on the experiment, this conversion varies between 0.71 and 0.78, and we have taken a mean value of $\alpha_{gel} = 0.74$.

By solubility tests we have determinated that the material is completely soluble prior to gelation and that solubility begins to decrease at a conversion level of around 0.75. This result is consistent with results obtained by DMTA and TMA and confirms the reliability of the two methodologies proposed.

Although it is difficult to define the gel point exactly, since this is a complex process possibly involving a certain range of conversions, the results discussed allow us to consider gelation an isoconversional phenomenon. For the purposes of calculation and comparison, we have taken a α_{gel} of 0.75, calculated as the mean value of different experimental determinations.

As a rule, gel times determined by different techniques do not agree, since the curing kinetics is affected by the technique and support used. The point of connection between the different techniques used to determine gelation is the constant value of α_{gel} and not the gel time.

Lastly, we have made theoretical calculations of conversion in gelation and changes in molecular weights

on the basis of the stoichiometry of the reactive process. The relationship between the weight average molecular weight and conversion and between the number average molecular weight and conversion is established using the Macosko and Miller approximation for non-linear step growth non-linear polymers for cases of equal reactivity [49]. Using the Macosko and Miller notation, we can write:

$$\bar{M}_W = \frac{M_{Af}^2 \frac{rg}{f}[1+(g-1)r\alpha_A^2] + 2M_{Af}M_{Bg}rg\alpha_A + M_{Bg}^2[1+(f-1)r\alpha_A^2]}{\left(M_{Af}\frac{rg}{f}+M_{Bg}\right)[1-(f-1)(g-1)r\alpha_A^2]} \tag{14}$$

M_{Af} and M_{Bg} are, respectively, the molecular weights of the component A with functionality f and of the component B with functionality g. For the coating studied here, A is the carboxyl-terminated polyester and B is the TGIC. α_A is the fraction of component A that is polymerised and coincides with the conversion of the reaction. r is the stoichiometric ratio and can be calculated on the basis of the initial moles of each component, A_{fo} and B_{go}, and of their functionality, as:

$$r = \frac{fA_{fo}}{gB_{go}} \tag{15}$$

For our reactive system, $r = 0.774$.

At extent α_A, the number average molecular weight is calculated as the quotient of the total mass and the number of moles present:

$$\bar{M}_n = \frac{M_{Af}A_f + M_{Bg}B_g}{A_{fo} + B_{go} - \alpha_A f_A A_{fo}} \tag{16}$$

where the number of moles present is the initial number of moles less the bonds formed.

Theoretical conversion in gelation can be determined by making $\bar{M}_W$ tend to infinity in Eq. (14) or on the basis of Flory's works [50], as:

$$(\alpha_A\alpha_B)_{gel} = r\alpha_{gel}^2 = \frac{1}{(f-1)(g-1)} \tag{17}$$

For our reactive system, by means of Eq. (17), we calculate a theoretical conversion in gelation of $\alpha_{gel} = 0.7$, slightly lower than the theoretical conversion of 0.75 determined experimentally. As a rule, Eq. (17) underestimates α_{gel}, since it does not take into account intramolecular cyclisations or the differing reactivity of the functional groups [51].

Introducing the degrees of conversion in the $\alpha_{TMA}-t$ curves in Eq. (14) and Eq. (16), we can determine the changes in molecular weights over time. Fig. 11 shows these changes for a curing temperature of 130 °C. The $\bar{M}_W$ is proportional to viscosity [25], and therefore the $\bar{M}_W-t$ curve allows us to predict the increase in viscosity until an infinite value is reached when the material gels. This same figure also shows the shrinkage rate versus curing time, on the basis of which we can determine the gel time. We observe the existence of a certain correlation between the increase in weight average molecular weight and the decrease in the shrinkage rate. Specifically, there is a shift of under one minute between the time at which the $\bar{M}_W$ tends to infinity and the time when the material gels in TMA. Therefore, it would appear reasonable to assume that both criteria express approximately the same phenomenon of gelation. We also observe that gelation in TMA follows, as mentioned above, a conversion that is slightly higher than theoretical conversion. In respect of powder coatings, the literature gives the criterion that the material gels when $\bar{M}_n$ becomes equal to 20000 [1]. Applying this criterion, our system would gel at $\alpha_{gel} = 0.77$. This value is similar to the one determined experimentally and slightly higher than the theoretical gelation value.

4.4. TTT diagram

The TTT diagram for calorimetric curing of the coating has been constructed using the experimental data determined in the foregoing sections, following the methodology set out below. The isoconversional lines were drawn using Eq. (6) and the parameters A and E obtained by DSC (Table 1). The T_{go} and the $T_{g\infty}$ were determined by calorimetry of uncured and fully cured samples. The gelation line was drawn using Eq. (6) applied to the conversion of $\alpha_{gel} = 0.75$. The vitrification times were taken as the time required for the material to reach a conversion in which T_g is equal to the curing temperature of T_c. These times were calculated on the basis of the isoconversional lines as the time required for a given conversion, for T_c to be equal to the calorimetric T_g corresponding to this conversion in the $T_g-\alpha$ diagram (Fig. 7). The temperature at which the material gels and vitrifies simultaneously, ${}_{gel}T_g$, was determined as the temperature at which the material vitrifies with a conversion equal to $\alpha_{gel} = 0.75$ (Fig. 7). The time required for the material to gel and vitrify simultaneously was determined by extrapolating the isoconversional line of $\alpha_{gel} = 0.75$ to a curing temperature equal to ${}_{gel}T_g$.

Fig. 12 shows the TTT diagram for the powder coating constructed using the methodology set out above. We observe that the vitrification line does not show the typical sigmoidal profile with a minimum vitrification time. This profile normally reflects the opposing influence exercised by the temperature and the decrease in the concentration of reactive groups as the T_g approaches the value of $T_{g\infty}$ over the reaction rate. The coating studied has a very low reactivity ($\Delta H_{dyn} = 37.5$ J/g) and a T_g very close to $T_{g\infty}$, meaning that the effect of the decrease in reactive groups will always prevail over the effect of the increase in temperature, with the vitrification line showing a profile corresponding to the upper portion of the sigmoid.

The inset in Fig. 12 shows the comparison, at 120 °C, of the experimental and predicted curves degree of conversion versus curing time. The results show that, within the experimental range of temperatures, the methodology used to determine the isothermal kinetic parameters, E and A, on

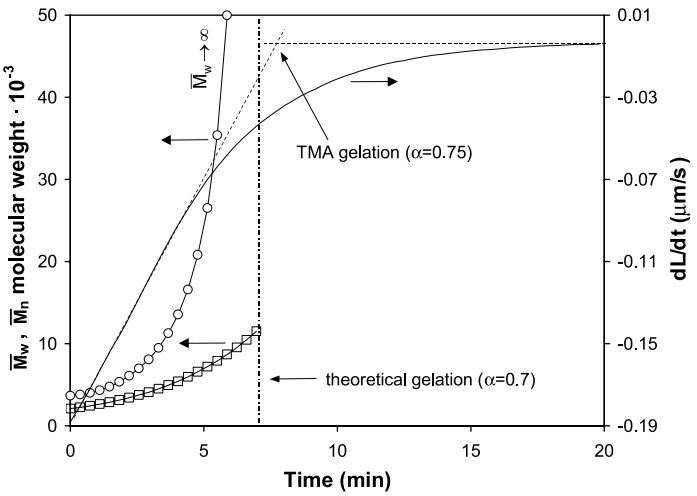


Fig. 11. Average molecular weights, $\bar{M}_w$ (○), $\bar{M}_n$ (□), and rate of shrinkage versus time for a coating cured at 130 °C.

the basis of dynamic experiments, is correct. Most of the TTT diagram has been constructed by extrapolation of the isoconversional lines from high temperatures to low temperatures (vitrification line). To verify the reliability of this procedure, we determined the vitrification line experimentally. This involves curing the material at unconventional temperatures of between 60 and 75 °C. The material was considered to have vitrified when its T_g was equal to the curing temperature and no ageing peak was detected. We observe that the experimental vitrification line and the predicted vitrification line show the same profile. This result once again supports the kinetic methodology used and the reliability extrapolation of kinetic data.

With the proposed methodology, the only experimental parameters required for construction of the TTT diagram are isoconversional kinetics, the $T_g - \alpha$ relationship and conversion in gelation.

5. Conclusions

The curing of thermosetting coatings can be examined by DMTA and TMA, as an alternative to curing in DSC.

Isoconversional kinetic analysis is a reliable method for studying the curing kinetics of coatings by DMTA, TMA and DSC. Isothermal kinetic parameters calculated on the basis of dynamic data are equivalent to those determined on the basis of isothermal experiments.

Activation energy cannot be used as the sole comparative kinetic parameter. Correct comparison of kinetic data

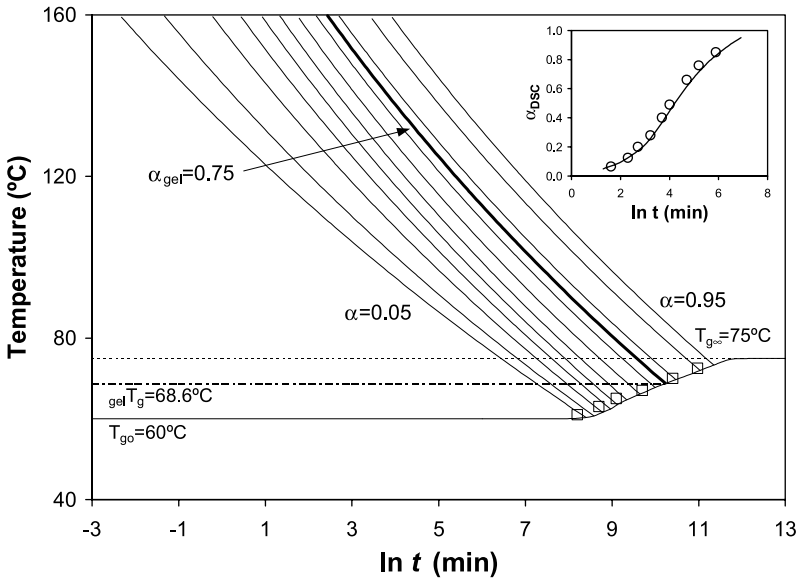


Fig. 12. TTT diagram of calorimetric curing of a powder coating. Conversion levels of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.75, 0.8, 0.9, 0.95 are shown. The symbols (□) represent experimental vitrification times. Inset: degree of conversion versus the logarithm of curing time for a sample cured at 120 °C. The circles represent the experimental data determined on the basis of residual heat of cured samples at different times. The solid line represents the prediction carried out using the isoconversional lines (Eq. (6), Table 1).

requires the use of pairs of $[E, A]$ or the kinetic triplet $[E, k_o, g(\alpha)$ or $f(\alpha)]$.

The curing kinetics are modified by the technique and support used. Specifically, curing by DSC and by DMTA show similar kinetics, while kinetics in curing by TMA is clearly different.

Chemical conversion is higher than mechanical conversion determined in DMTA (E') up until gelation, and after this point the two conversions are the same.

The $T_g - \alpha$ relationship obtained by DMTA, TMA and DSC shows the same profile with a temperature shift associated with the different frequency applied to the sample in each technique.

If we know the isoconversional lines, the $T_g - \alpha$ relationships and the relationship between chemical conversion and mechanical conversion, we can transform the data obtained for one technique into those obtained by another.

Gelation is an isoconversional phenomenon. The conversion attained when the material gels in DMTA and in TMA is similar to the conversion detected by solubility tests and does not differ greatly from theoretical predictions.

The TTT diagram for the coating, which shows a non-sigmoidal vitrification line, can be constructed simply using as experimental information only the isoconversional kinetics, the $T_g - \alpha$ relationship and the conversion attained in gelation.

Acknowledgements

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