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Abstract In the present work, we report the preparation and characterization of a new family of thermosets based on off-stoichiometric anhydride–epoxy formulations in the presence of an anionic initiator. Diglycidyl ether of bisphenol A (DGEBA) and hexahydro-4-methylphthalic anhydride (HHMPA) have been used as epoxy and anhydride comonomers, respectively, and 1-methylimidazole (IMI) has been used as anionic initiator. The isothermal curing kinetics and the thermal properties of the stoichiometric and the off-stoichiometric

systems have been compared. The kinetics of the isothermal curing has been analyzed by differential scanning calorimetry (DSC) using an isoconversional method and the Šesták–Berggren equation to determine the activation energy, the frequency factor and the reaction orders. The materials obtained were characterized by DSC and dynamic mechanical analysis. Gelation during epoxy–anhydride condensation was determined by thermomechanical analysis. At the same curing temperature, the reaction is faster in the system with excess of epoxy groups. However, the glass transition temperatures of the partially cured stoichiometric system are greater. The gelation time of the off-stoichiometric system is shorter than that of the stoichiometric one. The results indicate that the dual-curing character of off-stoichiometric DGEBA/HHMPA thermosets with IMI as anionic initiator makes them suitable for multistage curing processes with easy control of degree of cure and material properties in the intermediate stage and enhanced final material properties.

Keywords (separated by '-') Epoxy networks - Isothermal cure - Kinetics - Gelation

Footnote Information



Curing and thermomechanical properties of off-stoichiometric anhydride–epoxy thermosets

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Abstract

In the present work, we report the preparation and characterization of a new family of thermosets based on off-stoichiometric anhydride–epoxy formulations in the presence of an anionic initiator. Diglycidyl ether of bisphenol A (DGEBA) and hexahydro-4-methylphthalic anhydride (HHMPA) have been used as epoxy and anhydride comonomers, respectively, and 1-methylimidazole (IMI) has been used as anionic initiator. The isothermal curing kinetics and the thermal properties of the stoichiometric and the off-stoichiometric systems have been compared. The kinetics of the isothermal curing has been analyzed by differential scanning calorimetry (DSC) using an isoconversional method and the Šesták–Berggren equation to determine the activation energy, the frequency factor and the reaction orders. The materials obtained were characterized by DSC and dynamic mechanical analysis. Gelation during epoxy–anhydride condensation was determined by thermomechanical analysis. At the same curing temperature, the reaction is faster in the system with excess of epoxy groups. However, the glass transition temperatures of the partially cured stoichiometric system are greater. The gelation time of the off-stoichiometric system is shorter than that of the stoichiometric one. The results indicate that the dual-curing character of off-stoichiometric DGEBA/HHMPA thermosets with IMI as anionic initiator makes them suitable for multistage curing processes with easy control of degree of cure and material properties in the intermediate stage and enhanced final material properties.

Keywords Epoxy networks · Isothermal cure · Kinetics · Gelation

Introduction

Epoxy resins are widely used as adhesives, coatings, castings, electrical and electronic materials, encapsulation of semiconductor devices, matrix material for components, structural components [1–12], flame retardants [13, 14] and in cryogenic engineering [15–17] thanks to their mechanical and chemical properties, superior adhesion to various substrates, thermal stability and electrical characteristics. One of the most common curing agents for epoxy resins are

anhydrides [4, 18, 19]. The reaction of epoxides with anhydrides can proceed through an anionic (catalyzed) or a non-catalyzed mechanism. Details of both mechanisms are provided in previous manuscripts [20, 21]. During the curing, there may also be a competition between two processes: The first and the most important one is the condensation reaction between the epoxy and anhydride groups [18]. The second one is epoxy homopolymerization that can only take place at higher temperatures [22, 23].

Dual curing is a methodology that can be applied in multi-step fabrication procedures, which have enormous advantages, such as flexibility in the fabrication and the possibility to create complex structures for advanced applications [24]. This dual-curing methodology consists in the combination of two different and independent curing reactions, each one for each curing stage. The first step of the dual-curing system and the characteristics of the intermediate material are controlled by the stoichiometry of the formulation. Thus, it is necessary that the curing

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reactions of the first step be completely controlled, allowing to select the intermediate material properties. The second step must only be initiated by increasing the temperature, by irradiation, etc., so that it does not overlap with the first curing stage. In previous studies of our group, click-type reactions were combined with homopolymerization processes of the monomer in excess. For example, a first thiol-epoxy reaction or a first epoxy-amine reaction was combined with a second anionic epoxy homopolymerization [24, 25]. The intermediate materials were stable for several times and processable, and the final thermosets obtained had good characteristics, which depend on the composition of the initial formulation.

Although the anhydride-epoxy reaction cannot be classified as click reaction, this process has been demonstrated to reach completion. According to that in the present work, we studied the possibility of obtaining a dual-curing system by adding an excess of the epoxy resin to epoxy-anhydride formulations in the presence of a tertiary amine, which catalyze both processes [24]. In the first step of this process, a stoichiometric epoxy-anhydride reaction takes place at low temperature. In the second step, at higher temperatures, the homopolymerization of the epoxy excess will occur. In this way, the intermediate properties of the system can be controlled to facilitate the preparation of easily handled and storage stable materials after the initial curing stage. Upon application of a second stimulus (heating), these materials attain their ultimate properties [24, 26].

In the present work, we report the preparation and characterization of a new family of thermosets based on off-stoichiometric anhydride-epoxy formulations in the presence of 1-methylimidazole. The kinetics of the isothermal curing stage have been analyzed by differential scanning calorimetry using an isoconversional method and the Šesták-Berggren equation to determine the activation energy, the frequency factor and the reaction orders [27]. The materials obtained were characterized by calorimetry and dynamic mechanical analysis. Gelation during epoxy-anhydride condensation was determined by thermomechanical analysis.

Experimental

Materials

Diglycidyl ether of bisphenol A (DGEBA, Epikote 828, Hexion Specialty Chemicals B. V.) and hexahydro-4-methylphthalic anhydride (HHMPA, Sigma-Aldrich) have been used as epoxy and anhydride comonomers, respectively. 1-methylimidazole (IMI, Sigma-Aldrich) was used as anionic initiator.

Preparation of curing formulations

Two systems have been studied: a stoichiometric DGEBA/HHMPA formulation with 2% by weight of IMI (E828-HHMPA 100-IMI) and a DGEBA/HHMPA formulation with a 50% of excess of epoxy groups and 2% by weight of IMI (E828-HHMPA 50-IMI). The different components have been mixed at room temperature and vigorously stirred.

Differential scanning calorimetry

The kinetics of the curing was evaluated by DSC analysis (Mettler DSC-822e calorimeter). First, the two systems have been cured isothermally at different temperatures (65, 70, 75, 80, 85 and 90 °C in the case of the system E828-HHMPA 100-IMI and 50, 55, 60, 65, 70, 75 and 80 °C in the case of the system E828-HHMPA 50-IMI). After that a dynamic scan has been performed from 0 to 250 °C at 10 °C min⁻¹ to determine the glass transition temperature (T_g) and the residual heat (Δh_{res}). In the case of the system E828-HHMPA 100-IMI, the use of ADSC (alternate differential scanning calorimetry) has been necessary for the determination of the T_g after isothermal curing in some cases, because of the overlapping between the relaxation and residual peaks. In the ADSC experiments, the samples were heated from 0 to 250 °C at a heating rate of 2 °C min⁻¹, an amplitude of 0.5 °C and a modulation period of 1 min. The value of the T_g has been taken as the middle point of the heat capacity step in the reversing heat flow curve.

A dynamic scan from 0 to 250 °C at 10 °C min⁻¹ was also performed on samples without isothermal treatment to determine the total heat of curing (Δh_{dyn}) and the ultimate T_g ($T_{g\infty}$).

Thermomechanical analysis

A Mettler thermomechanical analyzer SDTA840 was used to determine the gel point during epoxy-anhydride polycondensation (isothermal curing). A silanized glass fiber disk about 5 mm in diameter was impregnated with the liquid (uncured) formulation and sandwiched between two aluminum disks. The sample was placed at a determined temperature (65, 70 and 75 °C in the case of the system E828-HHMPA 100-IMI and 55, 65 and 80 °C in the case of the system E828-HHMPA 50-IMI) and subjected to an oscillatory force from 0.005 to 0.1 N with an oscillation frequency of 0.083 Hz. The gel time, t_{gel} , was taken as the onset in the decrease of the oscillation amplitude measured by the probe. The conversion of epoxy groups at the gel point, α_{gel} , was determined as the conversion reached in the DSC at the gel time.

148 Dynamic mechanical analysis

149 To prepare the specimens, the mixtures were cured in a
150 rectangular mold, with different thermal treatments. The
151 dimensions of the specimens were $20 \times 10 \times 2 \text{ mm}^3$,
152 approximately. The samples were tested in a DMA (dy-
153 namic mechanical analysis, TA instruments Q800) at $3 \text{ }^\circ\text{C}$
154 min^{-1} using the single cantilever mode, with an amplitude
155 of $10 \text{ }\mu\text{m}$ and a frequency of 1 Hz .

156 Theory

157 In the isothermal curing studied, the relative degree of
158 conversion is defined as:

$$\alpha = \frac{\Delta h_t}{\Delta h_{\text{iso}}} \quad (1)$$

160 where Δh_t is the heat released up to a time t and Δh_{iso} is the
161 total reaction heat released during the isothermal cure. The
162 kinetics of this curing has been analyzed by means of an
163 integral isoconversional method, using the following
164 equation [27]:

$$\ln t_\alpha = \ln \left[\frac{g(\alpha)}{A_\alpha} \right] + \frac{E_\alpha}{RT_\alpha} \quad (2)$$

166 where R is the gas constant. At a determined relative
167 degree of conversion, t_α is the time attained, A_α is the
168 frequency factor, E_α is the activation energy, and $g(\alpha)$ is
169 the following integral obtained from a function of the rela-
170 tive degree of conversion $f(\alpha)$:

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

172 The activation energy at a given relative conversion can
173 be obtained from the slope of the representation of $\ln t_\alpha$
174 versus the reciprocal of the temperature (see Eq. 2). Pro-
175 vided that the kinetic model is known, the natural loga-
176 rithm of the frequency factor can be determined from the
177 intercept at the origin. This analysis can be repeated at
178 different relative degrees of conversion throughout the
179 curing process.

180 Results and discussion

181 Differential scanning calorimetry

182 Figure 1 shows the isothermal curing curves at different
183 temperatures of the system E827-HHMPA 50-1MI, corre-
184 sponding to the first stage, epoxy-anhydride reaction, in
185 the curing process. In the inset of this figure, the relative

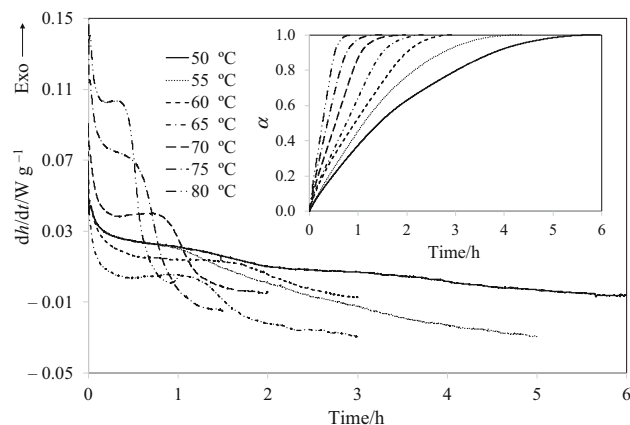


Fig. 1 Heat flow of the isothermal curing of E828-HHMPA 50-1MI at different temperatures. In the inset, relative degree of conversion versus curing time

186 degree of conversion (Eq. 1) has been represented against
187 reaction time. In this equation, the horizontal right baseline
188 has been used to determine Δh_t . Figure 2 shows similar
189 results for the stoichiometric E827-HHMPA 100-1MI
190 system. As expected, reaction rate increases with tempera-
191 ture. The temperatures analyzed are different in both
192 systems, due to their different reactivity, especially taking
193 into consideration that in the case of the off-stoichiometric
194 system, the homopolymerization of excess epoxy groups is
195 activated at higher temperatures. Figures 1 and 2 also show
196 two exothermic peaks that can be attributed to (1) the
197 initiation of the reaction by nucleophilic attack of 1MI to
198 the epoxy ring [28] followed by (2) the anionic alternating
199 copolymerization of epoxy and anhydride groups. The
200 mechanism of this reaction is shown in references [20, 21].
201 Epoxy homopolymerization should not be considered since
202 the range of the temperature selected is too low. In previ-
203 ous manuscripts, it has been proved that in the presence of
204 1-MI, homopolymerization reaction does not start until

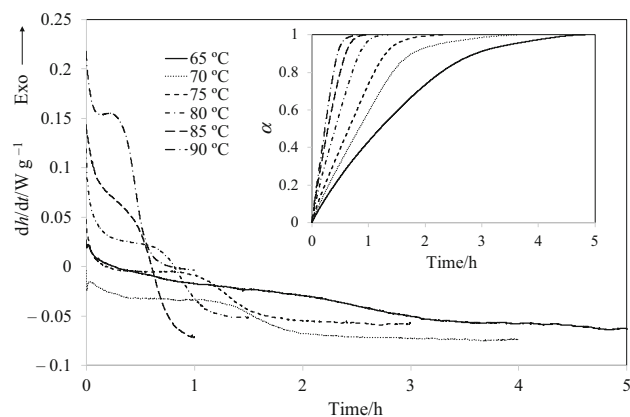


Fig. 2 Heat flow of the isothermal curing of E828-HHMPA 100-1MI at different temperatures. In the inset, relative degree of conversion versus curing time



100–110 °C in off-stoichiometric amine–epoxy thermosets [26] and in off-stoichiometric thiol–epoxy thermosets [25]. Moreover, the vitrification of anhydride–epoxy system during isothermal curing can also prevent the activation of the polyetherification process and stabilize the intermediate material. Figure 3 compares the isothermal curing at 70 °C of both systems. In the inset of this Figure, the relative degree of conversion found using Eq. (1) has also been plotted versus time. In the off-stoichiometric formulation, the reaction is faster, due to the higher amount of hydroxyl groups coming from DGEBA that promotes the esterification of hydroxyl groups and the subsequent opening of the epoxy groups in an uncatalyzed mechanism [20, 21]. The higher amount of epoxy groups in the off-stoichiometric formulation also increases the reaction rate above that of the stoichiometric one, because the rate-limiting step in the anionic epoxy–anhydride copolymerization is the attack of the highly stable carboxylate anion to the epoxy ring [20, 21].

Figure 4 shows the dynamic scans performed after the isothermal curing at different temperatures of the off-stoichiometric formulation. In every dynamic scan, it can be observed that at temperatures higher than the T_g of the partially cured material, the materials devitrify, producing a shoulder and an exothermic peak associated with the first stage of the post-curing (ending of the epoxy–anhydride polycondensation) and with the homopolymerization of the excess of epoxy resin, respectively. It can also be observed, as previously stated, that the homopolymerization of the epoxy groups takes place at high temperatures. A suitable selection of the curing temperatures of both curing processes makes it possible to obtain a sequential curing. It is expected that off-stoichiometric intermediate materials, after the isothermal curing, will be stable and can be stored at room temperature (below T_g of intermediate materials) for a long time. The stability of these materials is

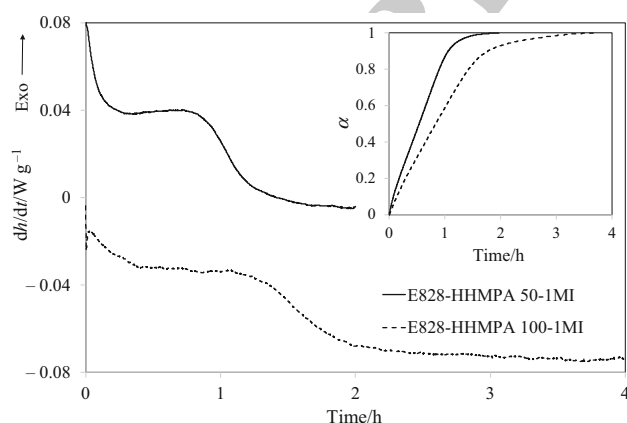


Fig. 3 Heat flow of the isothermal curing at 70 °C of the two studied systems. In the inset, relative degree of conversion versus curing time

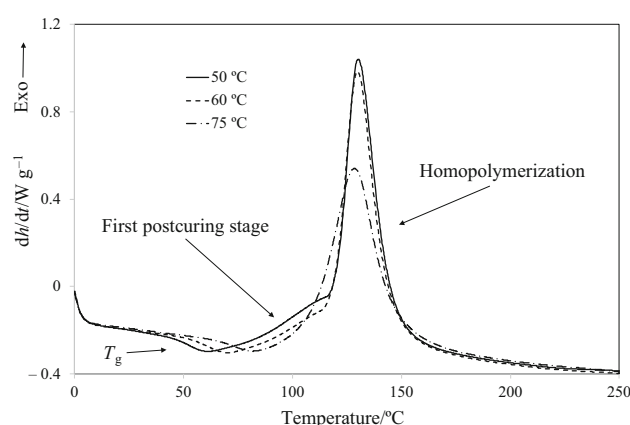


Fig. 4 Dynamic scans made after the isothermal curing at different temperatures of the system E828-HHMPA 50-1MI. In the legend, the temperatures of the isothermal curing are indicated

established not only by the deactivation of the homopolymerization at low temperatures, but also by the vitrification of the intermediate formulations.

Table 1 shows the activation energy and the natural logarithm of the frequency factor of the isothermal epoxy–anhydride condensation of the two studied systems at different relative degrees of conversion, found using Eq. (2). The average regression coefficient on applying this equation is 0.996. The average error of the activation energy and the natural logarithm of the frequency factor values listed in Table 1 are 7.1 kJ mol⁻¹ and 2.5, respectively, determined using a confidence interval of 95%. To determine the orders of the reaction, a model-fitting method and the Šesták–Berggren equation $f(\alpha) = \alpha^m(1 - \alpha)^n$ [27] were used with $m + n = 2$ [29]. With this condition, the following expression for $g(\alpha)$ is obtained:

$$g(\alpha) = \frac{1}{1-m} \left(\frac{\alpha}{1-\alpha} \right)^{1-m} \quad (4)$$

The off-stoichiometric system always has activation energies and frequency factors smaller than the stoichiometric one. For the off-stoichiometric system, the activation energy always increases, although at the beginning of the process hardly changes. The frequency factor always increases, but at relative degrees of conversion between 0.1 and 0.3, it decreases slightly. Lower activation energies in the off-stoichiometric formulation agree with the higher reaction rate observed for this formulation (see Fig. 3 inset). The slight increase observed in activation energies values on increasing conversion can be explained by the competition between catalyzed and uncatalyzed mechanisms [21], which becomes more evident at high conversion.

The activation energy of the stoichiometric system slightly increases initially but the increase is rather high at the end of the process. The frequency factor slightly

Table 1 Activation energies and natural logarithms of the frequency factor at different relative degrees of conversion of the isothermal curing for all the studied systems

System	$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$	$\alpha = 0.95$
E828-HHMPA 50-1MI											
$E_a/\text{kJ mol}^{-1}$	48.5	50.3	50.6	50.8	51.4	52.4	54.3	57.1	59.6	61.8	61.9
$\ln(A/\text{s}^{-1})$	10.9	11.2	11.0	10.9	11.0	11.4	12.1	13.1	14.2	15.3	15.6
E828-HHMPA 100-1MI											
$E_a/\text{kJ mol}^{-1}$	66.2	66.7	67.0	67.8	68.8	70.0	71.1	72.0	73.1	75.8	80.0
$\ln(A/\text{s}^{-1})$	16.6	16.4	16.3	16.4	16.7	17.0	17.4	17.8	18.4	19.6	21.3

decreases at the beginning of the process, but it increases after a relative degree of conversion of 0.3. The high increase of activation energy at the end of the process could be related to diffusion phenomena, which does not exist in the first stage of the curing for off-stoichiometric formulations.

The values of the parameters m and n of both systems are shown in Table 2. They are similar indicating that the underlying reaction mechanism of the isothermal curing hardly changes. This could be expected if one assumes that for the off-stoichiometric E827-HHMPA 50-1MI formulation, only the epoxy-anhydride alternating copolymerization takes place during the isothermal experiments in the DSC in the range of temperatures selected.

Table 2 also shows the values of $T_{g\infty}$ and the total heat of curing for both systems. The value of $T_{g\infty}$ for both systems is the same. In previous studies of our group in dual-cured materials, an excess of epoxide leads to increase the $T_{g\infty}$ of the material [25, 26], since the homopolymerization of epoxide always leads to a more compact network structure. Then, the higher the excess of epoxide, the higher the $T_{g\infty}$ of the material. In the present case, this effect is not observed, since the values of $T_{g\infty}$ of both systems are the same. The similarity between the total reaction heats and those reported for equivalent epoxy systems indicates that epoxides reacted almost completely [30, 31].

Tables 3 and 4 show the glass transition temperatures (T_g) of both systems after the isothermal curing. In the off-stoichiometric system (Table 3), they are similar to the

corresponding curing temperature, indicating that at the end of the isothermal curing, the system indeed vitrifies and that the mobility of the system becomes severely restricted when the glass transition temperature approaches curing temperature. However, in the stoichiometric system (Table 4), the T_g s are always greater than the corresponding curing temperature, indicating that vitrification takes place before the end of the isothermal curing. This indicates that the reaction can continue so that the T_g can exceed the curing temperature [32, 33]. The presence of unreacted anhydride monomers in the stoichiometric system at the end of the isothermal curing may explain the higher mobility of the system near vitrification, and therefore, the higher T_g achieved at the end of the isothermal curing process.

The degree of conversion attained at the end of the isothermal curing (α_{iso}) is defined as [33]:

$$\alpha_{\text{iso}} = \frac{\Delta h_{\text{iso}}}{\Delta h_{\text{dyn}}} \quad (5)$$

Assuming that the addition of the residual heat and the heat of the isothermal cure is equal to the total heat of curing ($\Delta h_{\text{iso}} + \Delta h_{\text{res}} = \Delta h_{\text{dyn}}$), Eq. (5) becomes [34]

$$\alpha_{\text{iso}} = \frac{\Delta h_{\text{iso}}}{\Delta h_{\text{dyn}}} = \frac{\Delta h_{\text{dyn}} - \Delta h_{\text{res}}}{\Delta h_{\text{dyn}}} = 1 - \frac{\Delta h_{\text{res}}}{\Delta h_{\text{dyn}}} \quad (6)$$

In this work, α_{iso} was calculated by using Eq. (6) instead of Eq. (5), since in some isothermal experiments, it was difficult to establish a baseline to determine the heat of reaction by integration of the calorimetric signal. Tables 3 and 4 show the values of α_{iso} for the two studied systems.

Table 2 Ultimate glass transition temperature ($T_{g\infty}$), dynamic curing heat (Δh_{dyn}) and the parameters m and n of the Sesták-Berggren equation of the isothermal curing for all the studied systems

System	E828-HHMPA 50-1MI	E827-HHMPA 100-1MI
$T_{g\infty}/^\circ\text{C}$	126	126
$\Delta h_{\text{dyn}}/\text{kJec}^{-1}$	110	120
m	0.388	0.410
n	1.612	1.590

Table 3 Glass transition temperatures after the isothermal curing (T_g) and degree of conversion attained at the end of the isothermal curing (α_{iso}) at different curing temperatures (T_c) for the system E828-HHMPA 50-1MI

$T_c/^\circ\text{C}$	$T_g/^\circ\text{C}$	α_{iso}
50	52	0.497
55	56	0.537
60	60	0.549
65	64	0.590
70	72	0.601
75	72	0.629
80	77	0.632



Table 4 Glass transition temperatures after the isothermal curing (T_g) and degree of conversion attained at the end of the isothermal curing (α_{iso}) at different curing temperatures (T_c) for the system E828-HHMPA 100-1MI

$T_c/^\circ\text{C}$	$T_g/^\circ\text{C}$	α_{iso}
65	84	0.779
70	90	0.804
75	92	0.813
80	95	0.825
85	97	0.863
90	105	0.875

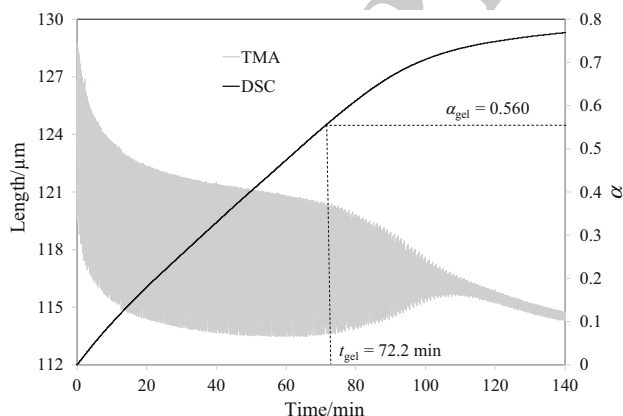
332 In both systems, α_{iso} increases with temperature similar to
 333 T_g as it is shown in the same tables. The off-stoichiometric
 334 system (Table 3) presents smaller values of α_{iso} than the
 335 stoichiometric one (Table 4), since within the experimental
 336 range of temperatures, the excess of epoxides remains
 337 unreacted. As it was shown, the homopolymerization of
 338 epoxy groups takes place at higher temperatures than the
 339 epoxy-anhydride polycondensation (see Fig. 4).

340 Thermomechanical analysis

341 Figure 5 shows the TMA and DSC analysis of the
 342 isothermal curing of the system E828-HHMPA 100-1MI at
 343 70 °C. By the combined use of TMA and DSC, the gelation
 344 time (t_{gel}) and the conversion at gel point (α_{gel}), respec-
 345 tively, can be obtained. These parameters were determined
 346 for this system at different temperatures (Table 5) and for
 347 the system with an excess of epoxide (Table 6).

348 By increasing the curing temperature, the reaction rate is
 349 increased and the time to reach gelation becomes shorter.
 350 At 65 °C, the gelation time corresponding to E828-
 351 HHMPA 50-1MI is shorter than that of E828-HHMPA
 352 100-1MI, in agreement with the higher reaction rate
 353 observed in off-stoichiometric formulations (see Fig. 3).

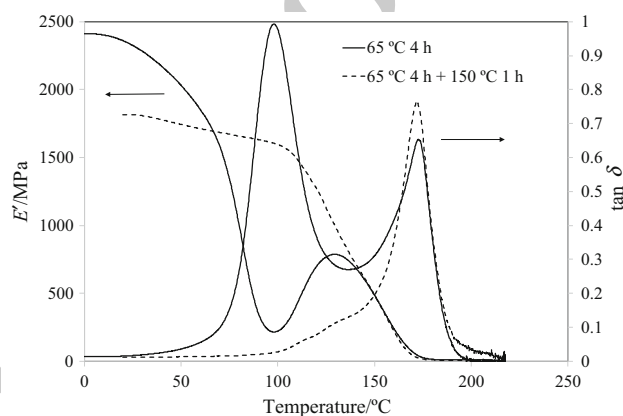
354 The values corresponding to α_{gel} for the system E828-
 355 HHMPA 100-1MI (Table 5) are similar to the values found
 356 for other stoichiometric anhydride-epoxy thermosets [35].

**Fig. 5** DSC and TMA experiments of E828-HHMPA 100-1MI at 70 °C**Table 5** Gelation time (t_{gel}) and conversion at the gel point (α_{gel}) for the system E828-HHMPA 100-1MI

$T_c/^\circ\text{C}$	t_{gel}/min	α_{gel}
65	88.0	0.455
70	72.2	0.560
75	52.4	0.511

Table 6 Gelation time (t_{gel}) and conversion at the gel point (α_{gel}) for the system E828-HHMPA 50-1MI

$T_c/^\circ\text{C}$	t_{gel}/min	α_{gel}
55	89.2	0.361
65	73.4	0.482
80	27.2	0.438

**Fig. 6** Storage modulus (E') and loss tangent ($\tan \delta$) of E828-HHMPA 100-1MI partially (65 °C for 4 h) and completely cured (65 °C for 4 h and 150 °C for 1 h)

The values of α_{gel} for the system E828-HHMPA 50-1MI (Table 6) are smaller than those of E828-HHMPA 100-1MI. Probably, the differences observed in α_{gel} values between both formulations can be due to the different hydroxyl contents and the effect of the excess of the DGEBA that inhibit the intramolecular cyclization responsible for the increase of α_{gel} [36]. In any case, the values of α_{gel} for the system E828-HHMPA 50-1MI (Table 6) are relatively close to those reported for other similar systems [35, 37].

Dynamic mechanical analysis

Figure 6 shows, for E828-HHMPA 100-1MI formulation, the DMA traces after isothermal curing at 65 °C with and without isothermal post-curing at 150 °C. In the specimen without isothermal post-curing it can be seen the α -relaxation (related with T_g) and the post-curing process. The post-curing results in an increase of the storage modulus and the apparition of the new maximum of $\tan \delta$ (related with T_g) at higher temperatures. The completely cured

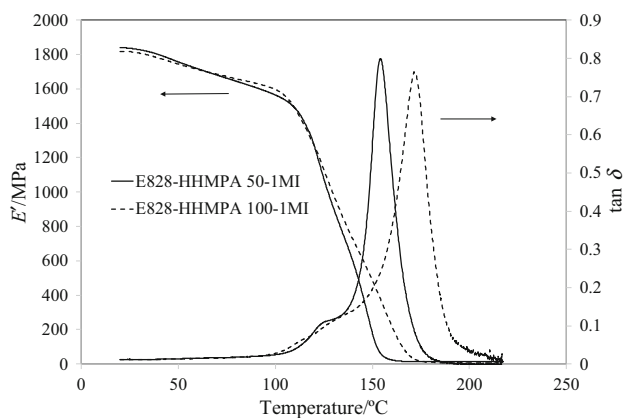


Fig. 7 Storage modulus (E') and loss tangent ($\tan \delta$) of the two systems completely cured (65 °C for 4 h and 150 °C for 1 h)

sample (post-cured 1 h at 150 °C) has a higher temperature of α -relaxation than the partially one. The maximum of $\tan \delta$ of the fully cured sample has a value comparable to that of the second maximum of the partially cured sample, indicating that the post-curing of this system in the DMA equipment produces a material with similar properties to that of the system cured in the oven following a different temperature schedule.

Figure 7 compares stoichiometric and off-stoichiometric fully cured formulations. E828-HHMPA 50-1MI has a lower maximum of $\tan \delta$ temperature due to the less compact network structure. This result is in agreement with the T_g values obtained with DSC (Table 2). The DMA scan of the partially cured sample of E828-HHMPA 50-1MI could not be performed, because the specimen of this sample was too brittle for analysis.

Conclusions

A new dual-curing system based on off-stoichiometric anhydride–epoxy formulations was developed. A base-catalyzed anhydride–epoxy condensation takes place at low temperatures in the first curing stage, while the excess of epoxy mostly homopolymerizes in the second curing stage at higher temperatures.

The dual-curing process is quasi-sequential with stable intermediate materials that can be stored and further processed. This stability is ensured by the vitrification of the materials during the first curing stage and by deactivation of epoxy homopolymerization at low temperatures.

In the off-stoichiometric system, the isothermal reaction between anhydride and epoxy groups ends earlier than in the stoichiometric system. Although reaction kinetics is modified, the reaction mechanism has not changed since the values of the parameters of both model reactions are similar.

The catalytic effect of the hydroxyl groups present in the epoxy monomer on the anhydride–epoxy condensation was demonstrated by the decrease in the activation energy upon an increase in epoxy content.

Gelation time and conversion at gel point are influenced by the excess of epoxy groups. These results are in agreement with earlier studies of reaction kinetics using differential scanning calorimetry.

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