Effect of a hyperbranched polymer over the thermal curing and the photocuring of an epoxy resin

J. M. Morancho · A. Cadenato · X. Ramis · X. Fernández-Francos · M. Flores · J. M. Salla

Abstract In this study, the authors study by calorimetry the influence of hyperbranched polyester Boltron®H40 on the thermal curing and the photocuring of a diglycidyl ether of bisphenol epoxy resin (DGEBA) using ytterbium (III) trifluoromethanesulfonate and triarylsulfonium hexafluorantimonate as thermal and photo cationic initiators, respectively. In the dynamic thermal curing at different heating rates, the authors have seen a decelerating effect when H40 is added to DGEBA, the system with 10% of H40 being the slowest. An isoconversional method has been used to determine the apparent activation energy of the thermal curing. In the isothermal photocuring at low temperatures, the authors have also appreciated a decelerating effect on adding H40, obtaining a minimum conversion when the H40 proportion is 15%. However, at high temperatures, the photocuring process can be accelerated at the first part of this process. This behavior is a consequence of the temperature dependence of H40 solubility in DGEBA, the viscosity of the system, and the hydroxyl-induced chain-transfer reaction. The values found of the maximum glass transition temperature in the thermal curing and in the photocuring, show that H40 is not completely solubilized in the reacted system.

Keywords Epoxy networks · Hyperbranched · Photocuring · Thermal curing · Kinetics · Toughness

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Introduction

Hyperbranched polymers (HBPs) are a kind of polymeric modifiers that can be used to increase the toughness of epoxy resins. Their main advantages are their lower viscosity compared with their linear counterparts, the possibility of tailoring their core and branches structure, and functionalization of the end groups so that they can be made compatible with the surrounding matrix material [1]. HBPs can solve the problems related to processability and compatibility which are found using other modifiers [2, 3] like glass particles, rubber, and thermoplastic [4–9]. During the curing process, HBPs also reduce the shrinkage [3] and the internal stress [2]. Reaction-induced phase separation can produce a beneficial increase in the toughness of the resulting material [2]. The moment in which this phase separation happens can be controlled by selecting their solubility, reactivity, and processing conditions [10]. The glass transition of the epoxy resin can decrease [3] or may not be affected [2].

The use of the epoxy resins includes several applications: adhesives, castings, coatings, electric laminates, encapsulation of semiconductor devices, matrix material for composites, structural components [1, 11–15], and cryogenic engineering [16–19]. In many of these studies, the epoxy resin was cured with a hardener and modified with a HBP, but very few articles have been published studying the influence of the addition of the HBP in an epoxy resin without adding a hardener [20–23]. The authors have previously studied the influence of some HBPs in the thermal curing and in the photocuring of Diglycidyl ether of bisphenol A (DGEBA). Concretely, in [22], the authors have analyzed the thermal curing of DGEBA modified with Boltorn®H30 and in [24], the thermal curing and the photocuring of DGEBA modified with Boltorn®H20 have

been analyzed. In these studies, the authors have observed the influence of the viscosity, solubility, and number of hydroxyl groups over the kinetics reaction.

In this article, the authors study the influence of Boltorn®H40 over the thermal curing and the photocuring of DGEBA and compare the results obtained with that obtained when the modifier is Boltorn®H20 [24]. H40 has a greater molecular weight than H20 and increases more the viscosity of the reacting system. In the analyzed mixtures, H40 always decelerates the thermal curing and more than H20. In the photocuring, H40 only accelerates it at high temperatures.
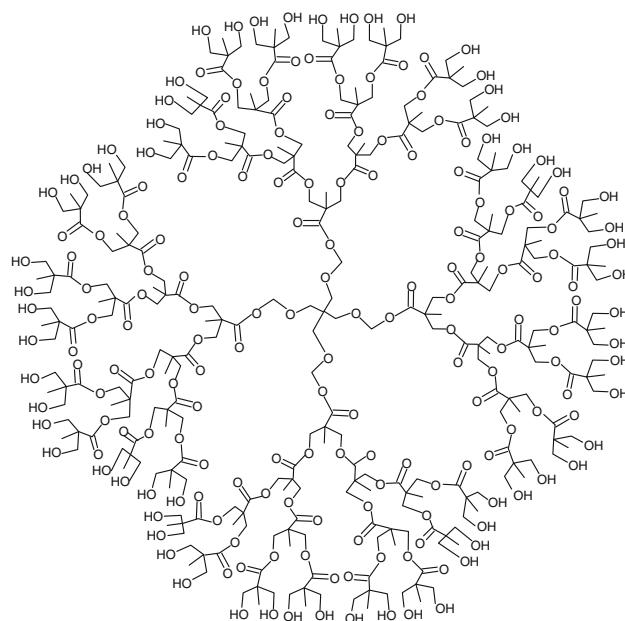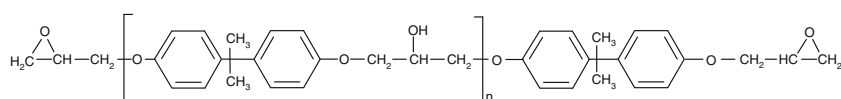
Experimental

Materials

Diglycidyl ether of bisphenol A with an epoxy equivalent of 182 g ee^{-1} (EPIKOTE 827, Shell Chemicals) has been cured with BOLTORN®H40, a hydroxyl-terminated hyperbranched polyester with a molecular weight of 5100 g mol^{-1} (Perstorp Specialty Chemicals) and 64 terminal groups. Schemes 1 and 2 show the formulae of DGEBA and BOLTORN®H40. Ytterbium triflate (Yb(OTf)$_3$) (Aldrich) was used as thermal cationic initiator. Triarylsulfonium hexafluoroantimonate (TAS-Sb) (50% w/w in propylene carbonate, Aldrich) was used as cationic photoinitiator.

Preparation of curing systems

The mixtures of liquid DGEBA and solid H40 were prepared by mixing and heating the desired quantities of these substances using a hot air blower and vigorously stirred. In the thermally curable samples, 1% of the thermal initiator was added to the mixtures at room temperature and then they were stirred and kept at −18 °C to prevent polymerization. In the photocurable samples, 2% of the photoinitiator was added (because the concentration of photoinitiator was 50% in weight in the photoinitiator solution, 2% of this solution was needed for a concentration of 1% of photoinitiator in the reactive mixture), and then they were stirred and kept in the dark at −18 °C to prevent photoactivation and polymerization. Table 1 shows the number of hydroxyl equivalents per epoxy equivalent for the different samples analyzed.

Scheme 2 Idealized chemical structure of the hyperbranched polymer BOLTORN®H40

Table 1 Hydroxyl equivalents per epoxy equivalent (eq OH ee^{-1}) of DGEBA with different proportions of H40

%H40	eq OH/ee^{-1}
0	0.042
5	0.162
10	0.296
15	0.445
20	0.613

Thermal curing

The thermally curable samples were cured at different heating rates (2, 5, 7.5, 10, and 15 °C min^{-1}) with a Mettler DSC-822e calorimeter from 0 °C to 250 °C. The ultimate glass transition temperature of the cured materials ($T_{g\infty}$) was determined on the basis of a second dynamic run from −100 °C to 250 °C at 10 °C min^{-1}.

Photocuring

The photocurable samples were photocured at different temperatures, with a Mettler DSC-821e calorimeter appropriately modified with a Hamamatsu Lightningcure LC5 (Hg–Xe lamp) with two beams, one for the sample

Scheme 1 Chemical structure of DGEBA epoxy monomer

side and the other for the reference side. Samples of ca 5 mg were cured in open aluminum pans in a nitrogen atmosphere. Two scans were performed on each sample to subtract the thermal effect of UV irradiation from the photocuring experiment, each one consisting of 4 min of temperature conditioning, 30 min of irradiation, and finally 4 more minutes without UV light. The light intensity used was 21 mW cm^{-2} and was calculated by irradiation of graphite-filled pans on only the sample side.

Dynamic postcuring experiments were carried out in the same DSC, without UV irradiation, from 30 °C to 250 °C at 10 °C min^{-1} to determine the residual heat. After this, a second dynamic run was carried out to determine $T_{g\infty}$.

Theory

In the thermal curing processes the degree of conversion (α) was calculated as:

$$\alpha = \frac{\Delta H_T}{\Delta H_{dyn}} \tag{1}$$

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 of the experience, which is associated with complete conversion of all reactive groups (the authors have confirmed by FTIR that the polymerization is complete in the systems studied). In Table 2, there are listed average values (ΔH_{ave}) of ΔH_{dyn} for each of the studied mixtures, calculated as the average total reaction heat of the experiments at different heating rates.

Accepting that rate of conversion ($d\alpha/dt$) depends on the temperature and the conversion degree of the reaction and the Arrhenius equation is met, the non-isothermal kinetics analysis may start with the kinetic equation:

$$\frac{d\alpha}{dt} = k_o \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{2}$$

Table 2 Average total reaction heat (ΔH_{ave}), maximum glass transition temperature ($T_{g\infty}$), and glass transition temperature calculated using Fox equation (T_{gFox}) (Eq. 10) for the thermal curing of DGEBA with different proportions of H40 (the values of $T_{g\infty}$ are average values of the different samples analyzed)

%H40	ΔH_{ave}/kJ ee^{-1}	$T_{g\infty}$/°C	T_{gFox}/°C
0	96.7	130.0	130.0
5	102.1	122.1	122.4
10	106.4	118.6	115.0
15	116.0	119.3	108.0
20	116.1	112.6	101.1

where k_o is the preexponential factor, E activation energy, R universal gas constant, T temperature, and $f(\alpha)$ is a function of degree of conversion which depends on the mechanism governing the reactive process.

By reordering, the so-called temperature integral can be written as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_o}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) \cdot dT \tag{3}$$

where β is the heating rate (dT/dt) and $g(\alpha)$ an integral function of the degree of conversion. Equation 3 may be integrated employing Doyle's approach [25] and rewritten in logarithm form as:

$$\ln\beta = \ln\left[\frac{k_o E}{g(\alpha)R}\right] - 5.330 - \frac{1.0516E}{RT} = A_{int} - \frac{1.0516E}{RT} \tag{4}$$

This equation applied to constant conversion, enables us to determine E and the kinetic parameter A_{int} (Ozawa method [26]) for each degree of conversion.

In isothermal photocuring experiments, the degree of conversion was calculated as:

$$\alpha = \frac{\Delta H_t}{\Delta H_{ave}} \tag{5}$$

where ΔH_t is the heat released up to a time t. The values used of ΔH_{ave}, obtained dynamically when the material reacts completely, are shown in Table 2. The kinetic study of the photocuring was carried out following the approach used by Tryson and Shultz [27]. In the experiments using light, the rate of disappearance of the monomer ($-d[M]/dt$, which is proportional to the calorimetric signal) can be written as:

$$-\frac{d[M]}{dt} = k_p \left(\frac{\phi I_{abs}}{k_t}\right)^{1/2} [M] \tag{6}$$

where k_p and k_t are the rate constants of propagation and termination, respectively and the formation of free radicals is the result of the product of the quantum yields and the photon absorption rate (ϕI_{abs}). Equation 6 can be deduced based on the following hypotheses: (a) the reaction rate of any free radical with a monomer does not depend on the type of radical; (b) the termination reactions are bimolecular; (c) transfer reactions are disregarded; (d) there is a steady-state concentration of free radicals; and (e) due to theoretical considerations, it is assumed that the rate depends on the first power of monomer concentration.

Equation 6 can be expressed depending on the degree of conversion as [28]:

$$\frac{d\alpha}{dt} = k_p \left(\frac{\phi I_{abs}}{k_t}\right)^{1/2} (1 - \alpha) \tag{7}$$

If we define the apparent kinetic constant (k_{ap}) as

$$k_{ap} = k_p \left(\frac{\phi I_{abs}}{k_t} \right)^{1/2} \qquad (8)$$

then, the Eq. 7 is

$$\frac{d\alpha}{dt} = k_{ap}(1 - \alpha) \qquad (9)$$

This equation allows to find the values of k_{ap} during the photocuring process from the degree of conversion and the rate of conversion, and it is a general and simplified expression that can be applied even though the system under study is different. Moreover, k_{ap} can be used as a comparative parameter equivalent to reaction rate. A similar approach has been used by other authors to study photopolymerization processes [29–31].

When two polymers are mixed and only one phase is formed the glass transition of the blend can be found using the Fox equation [32]:

$$\frac{1}{T_g} = \frac{w}{T_{g1}} + \frac{1 - w}{T_{g2}} \qquad (10)$$

where T_g is the glass transition of the blend, T_{g1} and T_{g2} are the glass transition temperatures of the neat compounds 1 and 2, respectively and w is the weight fraction of compound 1 in the blend.

Results and discussion

Thermal curing

In the thermal curing process, the degree of conversion (α) was calculated following Eq. 1. Figure 1 shows the degree of conversion versus the temperature of the thermal curing at 10 °C min^{-1} of DGEBA with different proportions of

H40. The addition of this hyperbranched polymer decelerates the reaction, the system with a 10% of H40 being the slowest. As it can be seen in Tables 1 and 2, the addition of H40 increases the number of hydroxyl groups and the total reaction heat, but it also increases the viscosity, which makes the formation of active species difficult through the interaction between the epoxy groups and the initiator and slow down the propagation reaction. The increase of the total reaction heat can be related with the participation of the hydroxyl groups in the curing. Upon addition of lower amounts of H40, the process is decelerated, which means that the factor of viscosity has more influence in the reaction rate than the increase of hydroxyl groups that would accelerate the curing. At proportions higher than 10%, the hydroxyl groups begins to have more influence and then these proportions are faster than the system with 10% of H40. In [24], the authors studied the influence of another HBP, H20, over the thermal curing of the same epoxy resin. Although both HBPs increase the viscosity of the reaction medium, in H20 the acceleration caused by hydroxyl groups was more important and therefore the formulation with 20% H20 was even faster than neat DGEBA. On the contrary, the effect of hydroxyl groups in H40 formulations is not as important, probably due to lower solubility and availability of hydroxyl groups, and therefore the viscosity is the dominant factor, making all H40 formulations significantly slower than neat DGEBA.

Figure 2 shows the degree of conversion versus temperature of the thermal curing of DGEBA with 10% of H40 at different heating rates. As expected, this figure shows how a decrease in the heating rate displaces the curing curves down to lower temperatures. Applying the Ozawa isoconversional method to the thermal curing of the different formulations, a good lineal dependence between the logarithm of the heating rate and the reciprocal temperature was observed, as it is predicted by Eq. 4. From the slope of

Fig. 1 Degree of conversion of the thermal curing at 10 °C min^{-1} of DGEBA with different proportions of H40
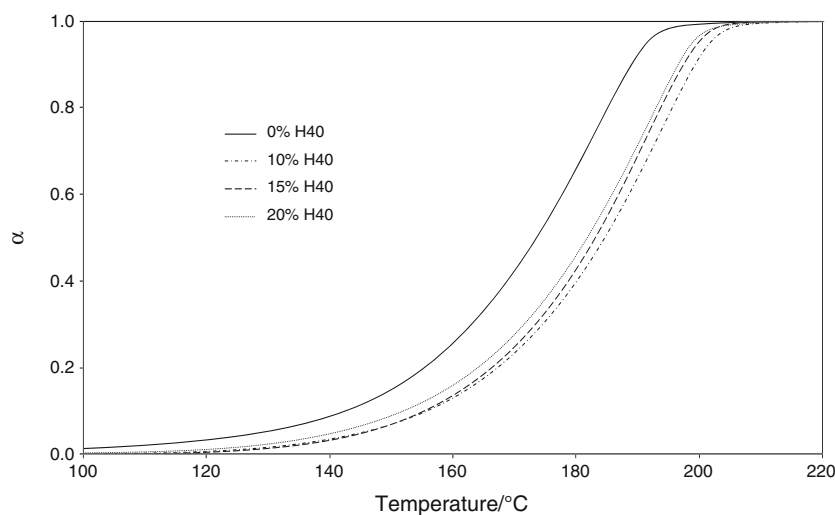
Fig. 2 Degree of conversion of the thermal curing of DGEBA with 10% of H40 at different heating rates
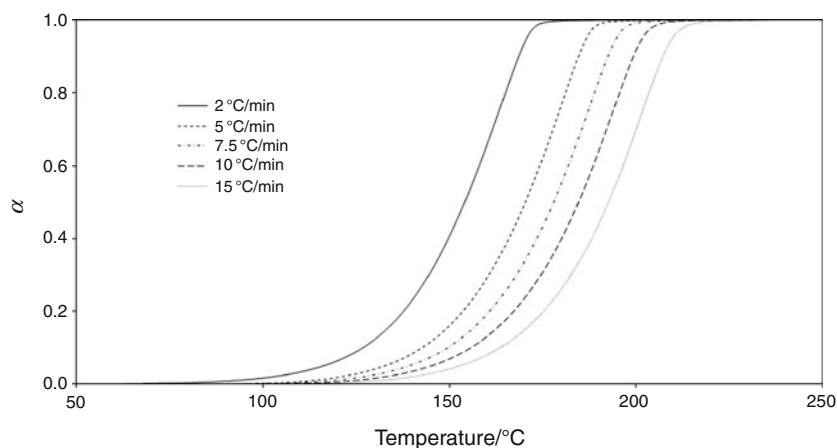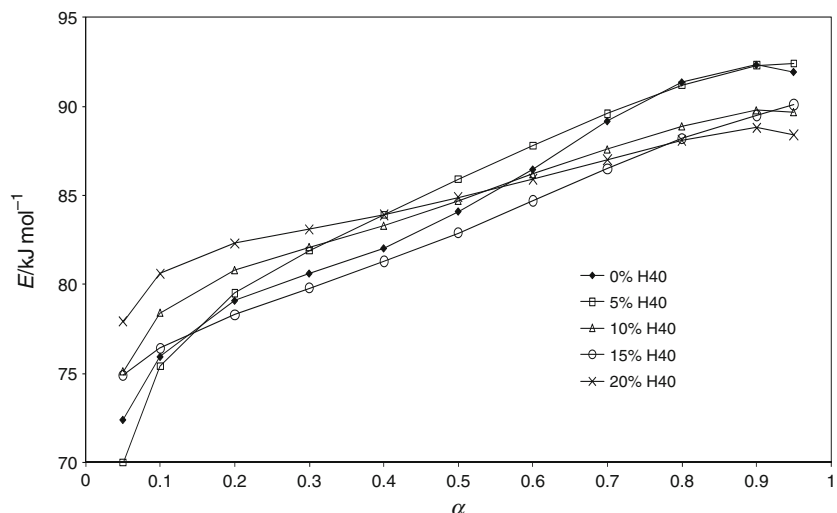

Fig. 3 Activation energy versus the degree of conversion for the thermal curing of DGEBA with different proportions of H40

these lineal dependences, the values of the activation energy can be found for every degree of conversion. These values have been represented for all the formulations in Fig. 3. The activation energy slightly increases during the curing process because of the thermal activation of the reaction, although the variation of this magnitude decreases when the proportion of H40 is increased. This trend is similar when H20 is used as a modifier [24]. The standard deviations of the values of the activation energy vary between 0.3 and 4.0 kJ mol^{-1}, being 1.5 kJ mol^{-1} as the mean value.

Table 2 presents the values of the maximum glass transition temperature ($T_{g\infty}$) of the different systems studied after thermal curing. It can be seen that the addition of H40 reduces the value of $T_{g\infty}$ because it acts as an internal plasticizer, reducing the cross-linking density, although there is not a well defined trend within the experimental composition range. In this table, the values of the theoretical glass transition temperature calculated using the Fox equation (T_{gFox}) (Eq. 10) can also be seen. A significant difference between the experimental and calculated values (with

the exception of the system with 5% of H40) indicating that H40 is not completely solubilized in the thermally cured systems can be appreciated.

Photocuring

Figure 4 shows the heat flow and the degree of conversion (see inset) versus the photocuring time of DGEBA with 10% of H40 at different temperatures. As usually reported for other photocuring systems [33], at the beginning of the process the heat flow and the degree of conversion increase with temperature. Table 3 shows the values of the isothermal curing heat (ΔH_{iso}) for the different systems and temperatures analyzed. For all the systems, this heat increases with temperature as expected, since photocuring takes place up to vitrification at temperatures lower than the ultimate glass transition [33, 34] and so conversion increases with photocuring temperature. For the same temperature, this heat increases with H40 proportion, although some values (mainly in the systems with 10 and 15% of H40) do not follow this trend. The amount of

Fig. 4 Photocuring of DGEBA with 10% of H40 at different temperatures and as an *inset* the degree of conversion for the same system and processes
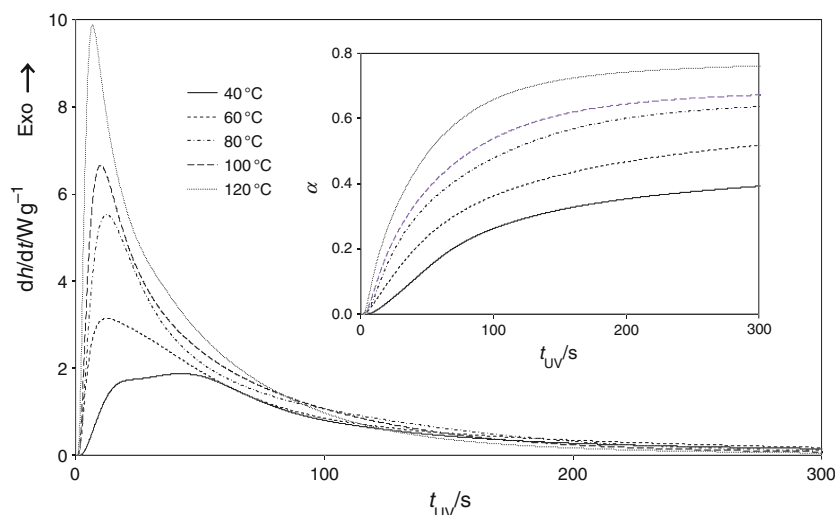

Table 3 Values of ΔH_{iso} in kJ ee^{-1} for the photocuring of DGEBA with different proportions of H40 and temperatures

%H40	40 °C	60 °C	80 °C	100 °C	120 °C
0	49.1	63.3	71.0	78.0	84.4
5	50.1	63.1	75.1	80.7	86.7
10	51.1	63.3	71.3	75.9	82.7
15	51.0	63.9	71.0	76.1	81.5
20	57.4	65.9	82.3	88.4	93.1

Table 4 Values of α_{iso} for the photocuring of DGEBA with different proportions of H40 and temperatures

%H40	40 °C	60 °C	80 °C	100 °C	120 °C
0	0.504	0.648	0.727	0.799	0.864
5	0.486	0.611	0.728	0.783	0.840
10	0.476	0.589	0.664	0.706	0.770
15	0.436	0.545	0.606	0.650	0.696
20	0.489	0.562	0.702	0.754	0.794

hydroxyl groups which participate in the curing process can explain this behavior. In [24], the isothermal curing heat always increased with H20 proportion at the same temperature, probably due to the higher availability of hydroxyl groups that led to a higher participation of H20 in the curing process.

Table 4 shows the values of α_{iso}, the degree of conversion attained at the end of the isothermal photocuring process for the different systems and temperatures analyzed, calculated using Eq. 5. The general trend is to decrease the degree of conversion with the increase in the amount of H40, but there is not a well defined behavior within the experimental composition range. These results differ from that obtained with H20 [24], where it was

observed that α_{iso} increased with the amount of H20, although at 120 °C the trend was reversed.

Figures 5 and 6 show the heat flow and the degree of conversion (see inset) versus the photocuring time of DGEBA with different proportions of H40 at 40 and 120 °C, respectively. In the inset of Fig. 5 the degree of conversion of 10% of H40 has not been represented because it is very similar to the curve corresponding to 20% of H40. Figure 5 clearly shows that the addition of H40 decelerates the photocuring process especially at the beginning, the system with 15% of H40 being the slowest.

At 60 °C, the situation is similar than at 40 °C, but at the beginning of the process the system with 10% of H40 presents the minimum values of the heat flow. At 80 °C and at low times, the systems with 5 and 20% of H40 are slightly faster than the neat DGEBA and the system with 15% of H40 is the slowest. At 100 °C, the modified systems are faster than neat DGEBA at the beginning, with the exception of 10% of H40 that is the slowest.

In Fig. 6 (120 °C), at the beginning of photocuring only the system with 15% of H40 presents lower curing rates than neat DGEBA. Indeed, the inset does not show noticeable differences between neat DGEBA and H40 formulations, except the system with 15%.

In the previous study [24], the situation was clearer. At 40 °C, the heat flow and the degree of conversion decrease when H20 proportion increases at the beginning of the process and increase at higher times. However, at 120 °C, the heat flow and the degree of conversion always increase with H20 proportion.

In Figs. 7 and 8, the logarithm of the apparent kinetic constant (Eq. 9) is represented versus the degree of conversion for different proportions of H40 at 40 and 120 °C, respectively. As it has been seen in Fig. 5, the addition of H40 decelerates the photocuring process at 40 °C, presenting the system with 15% of H40 the minimum values

Fig. 5 Photocuring at 40 °C of DGEBA with different proportions of H40 and as an *inset* the degree of conversion for the same systems and process
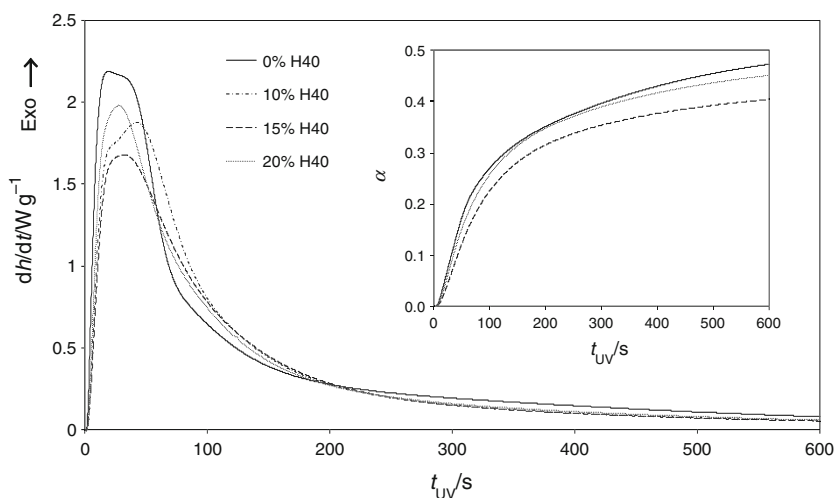

Fig. 6 Photocuring at 120 °C of DGEBA with different proportions of H40 and as an *inset* the degree of conversion for the same systems and process
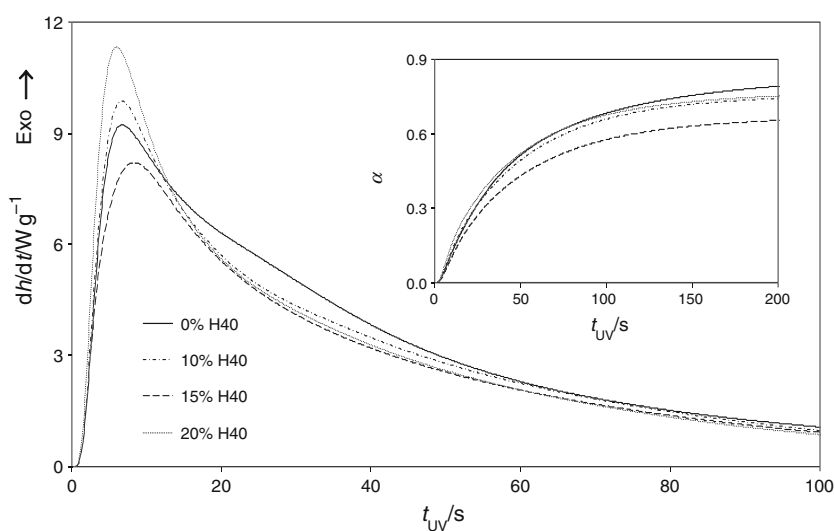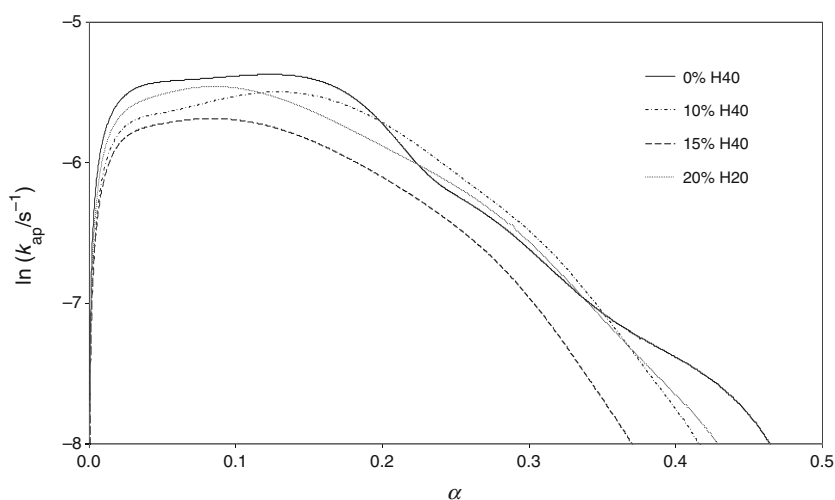

Fig. 7 Logarithm of the apparent kinetic constant versus the degree of conversion for the photocuring at 40 °C of DGEBA with different proportions of H40

of this kinetic parameter. At 120 °C, as in Fig. 6, at lower photocuring times the systems with 10 and 20% of H40 present greater values of k_{ap} than the neat DGEBA. The system with 15% of H40 always presents the minimum values of k_{ap} too. The maxima and the shoulder shown in Figs. 5 and 7 for the system with 10% of H40 can be

Fig. 8 Logarithm of the apparent kinetic constant versus the degree of conversion for the photocuring at 120 °C of DGEBA with different proportions of H40
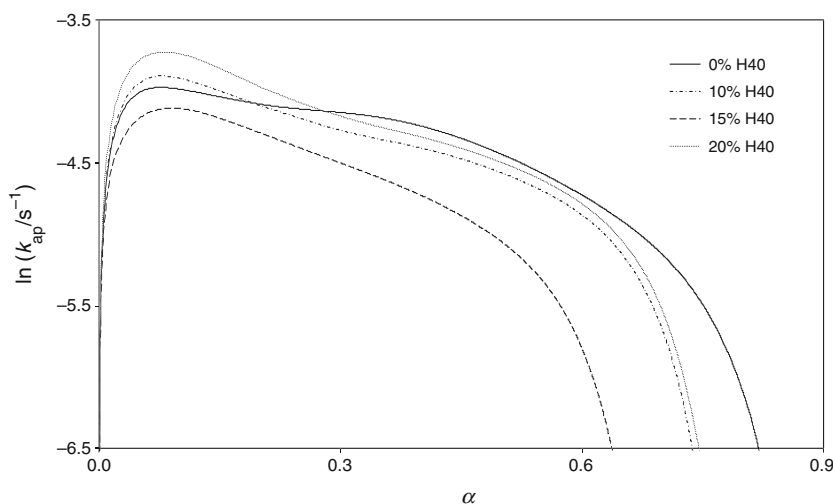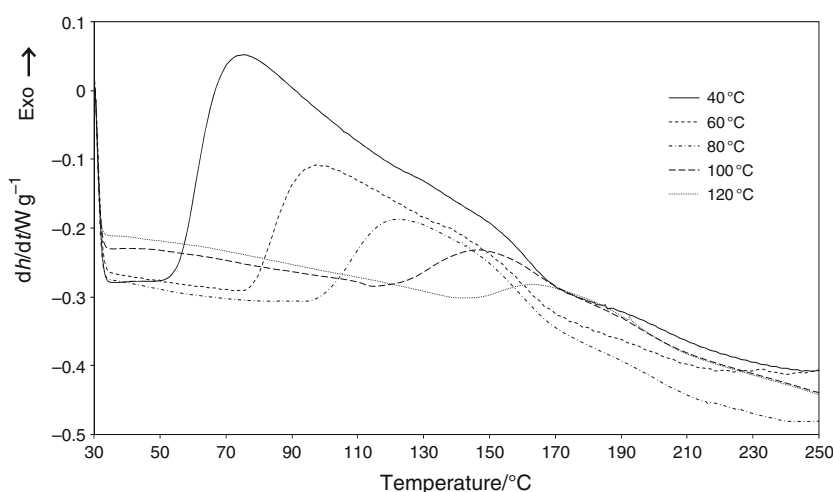

Fig. 9 Dynamic postcuring experiments at 10 °C min^{-1} of DGEBA with 20% of H40 after photocuring at different temperatures

related to a change on the kinetics of curing. Probably, the reaction rate is also affected by the competition between the propagation mechanisms, active monomer (AM), and active chain-end (ACE) [22]. In the absence of hydroxyl groups, the curing only takes place via ACE mechanism whereas in the presence of hydroxyl groups, the curing can also take place via AM mechanism trough proton-transfer reactions.

From the data shown in Figs. 5, 6, 7 and 8, it can be hypothesized that at lower curing temperatures the low solubility of H40 in DGEBA results in a delay of the curing process due to an increase in the viscosity of the system. At higher temperatures, especially at 120 °C the greater solubility of H40 in the epoxy system can explain that the systems with 10 and 20% of H40 are faster than the neat one because of the higher availability of hydroxyl groups which accelerate the curing process, making up for the viscosity increase. However, this effect is not as noticeable as with H20 as modifier [24] because of the lower availability of surface hydroxyl groups in H40.

Figure 9 shows the dynamic experiences made after the photocuring at different temperatures of DGEBA with 20% of H40. The postcuring begins when the system reaches its photocuring temperature and devitrifies. The heat released decreases when the photocuring temperature increases, because in the photocuring experience the heat of reaction increase with temperature [24, 33].

The ultimate glass transition temperatures of the photocured samples are indicated in Table 5. As in the thermal curing, this temperature decreases when the H40 proportion is increased, indicating a plasticizer effect of H40 [24]. However, this decrease is very small. Moreover, it can be noticed that a strong disagreement between the experimental and theoretical values obtained using the Fox equation (Eq. 10) indicated limited participation of H40 in the photocuring process, because of the low solubility of H40 in DGEBA and the low availability of hydroxyl groups. If these values are compared with the thermal curing results, it can be seen that the $T_{g\infty}$ after photocuring is much higher, because ytterbium triflates are able to

Table 5 Maximum glass transition temperature ($T_{g\infty}$) and glass transition temperature calculated using Fox equation (T_{gFox}) (Eq. 10) for the photocuring of DGEBA with different proportions of H40 (the values of $T_{g\infty}$ are average values of the different samples analyzed)

%H40	$T_{g\infty}$/°C	T_{gFox}/°C
0	161.9	161.9
5	161.4	151.4
10	157.2	141.4
15	154.4	131.8
20	154.0	122.7

induce reorganization, cyclization, and/or degradation reactions when the curing reaches much too high temperatures, which results in a network structure with a lower degree of cross-linking and consequently with lower $T_{g\infty}$ [35, 36].

Conclusions

In thermal curing, the addition of H40 always decelerates the process. The lower amount of available hydroxyl groups of H40, which cannot make up for the increase in viscosity upon addition of H40, seems to explain this behavior.

The effect of H40 on the photocuring of DGEBA formulations depends on the process temperature. At low temperatures (40 °C), the reaction is decelerated due to the low solubility of the hyperbranched polymer in DGEBA. At high temperatures (120 °C), the photocuring process can be accelerated due to greater solubility of H40. The competition between AM and ACE propagation mechanisms can also affect curing kinetics.

According to the glass transition temperatures, after thermal curing and photocuring, it can be concluded that H40 is not well solubilized in DGEBA, implying that there is a two-phase morphology in the fully cured materials.

References

1. Sörensen K, Pettersson BO, Boogh L, Månson JAE. Dendritic polyester macromolecule in thermosetting resin matrix. PCT Pat./SE94/04440, 1994.
2. Mezzenga R, Boogh L, Månson JAE. A review of dendritic hyperbranched polymer as modifiers in epoxy composites. Compos Sci Technol. 2001;61:787–95.
3. Zhang Y, Zhang D, Qin C, Xu J. Physical and mechanical properties of dental nanocomposites composed of aliphatic epoxy resin and epoxidized aromatic hyperbranched polymers. Polym Compos. 2009;30:176–81.
4. Riew CK, Siebert AR, Smith RW, Fernando M, Kinloch AJ. Toughened epoxy resins: preformed particles as tougheners for adhesives and matrices. In: Riew CK, Kinloch AJ, editors. Toughened plastics II novel approaches in science and engineering. Advances in chemical series, vol 252. Washington: American Chemical Society; 1996. p. 33–44.
5. Wu SH. Phase structure and adhesion in polymer blends: a criterion for rubber technology. Polymer. 1985;26:1855–63.
6. Pearson RA, Yee AF. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide). Polymer. 1993;34:3658–70.
7. Hedrick JL, Yilgor I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulphone) modified epoxy networks. Polymer. 1991;32:2020–32.
8. Wilkinson SP, Ward TC, McGrath JE. Effect of thermoplastic modifier variables on toughening a bismaleimide matrix resin for high-performance composite materials. Polymer. 1993;34:870–84.
9. Kunz SC, Sayre JA, Assink RA. Morphology and toughness characterization of epoxy resins modified with amine and carboxyl terminated rubbers. Polymer. 1982;23:1897–906.
10. Mezzenga R, Plummer CJG, Boogh L, Månson JAE. Morphology build-up in dendritic hyperbranched polymer modified epoxy resins: modelling and characterization. Polymer. 2001;42:305–17.
11. Kinloch AJ, Shaw SJ, Tod DA, Hunston DL. Deformation and fracture behaviour of a rubber-toughened epoxy: 1. Microstructure and fracture studies. Polymer. 1983;24:1341–54.
12. Ho T-H, Wang C-S. Toughening of epoxy resins by modification with dispersed acrylate rubber for electronic packaging. J Appl Polym Sci. 1993;50:477–83.
13. Guo QP, Habrard A, Park Y, Halley PJ, Simon GP. Phase separation, porous structure, and cure kinetics in aliphatic epoxy resin containing hyperbranched polyester. J Polym Sci B. 2006;44:889–99.
14. Ratna D, Varley R, Simon GP. Toughening of trifunctional epoxy using an epoxy-functionalized hyperbranched polymer. J Appl Polym Sci. 2003;89:2339–45.
15. He S, Shi K, Bai J, Zhang Z, Li L, Du Z, Zhang B. Studies on the properties of epoxy resins modified with chain-extended ureas. Polymer. 2001;42:9641–7.
16. Evans D, Canfer SJ. Radiation stable, low viscosity impregnating resin systems for cryogenic applications. Adv Cryog Eng. 2000;46:361–8.
17. Ueki T, Nishijima S, Izumi Y. Designing of epoxy resin systems for cryogenic use. Cryogenics. 2005;45:141–8.
18. Nishijima S, Honda Y, Okada T. Application of the positron annihilation method for evaluation of organic materials for cryogenic use. Cryogenics. 1995;35:779–81.
19. Yang J-P, Chen Z-K, Yang G, Fu S-Y, Ye L. Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer. Polymer. 2008;49:3168–75.
20. Sangermano M, Malucelli G, Bongiovanni R, Priola A, Harden A, Rehnberg N. Hyperbranched polymers in cationic photopolymerization of epoxy systems. Polym Eng Sci. 2003;43:1460–5.
21. Esposito Corcione C, Malucelli G, Frigione M, Maffezzoli A. UV-curable epoxy systems containing hyperbranched polymers: kinetics investigation by photo-DSC and real-time FT–IR experiments. Polym Test. 2009;28:157–64.
22. Fernández-Francos X, Salla JM, Cadenato A, Morancho JM, Serra A, Mantecón A, Ramis X. A new strategy for controlling

shrinkage of DGEBA resins cured by cationic copolymerization with hydroxyl-terminated hyperbranched polymers and ytterbium triflate as an initiator. J Appl Polym Sci. 2009;111:2822–9.

23. Sangermano M, Malucelli G, Bongiovanni R, Priola A, Harden A. Investigation on the effect of the presence of hyperbranched polymers on thermal and mechanical properties of an epoxy UV-cured system. Polym Int. 2005;54:917–21.

24. Morancho JM, Cadenato A, Ramis X, Fernández-Francos X, Salla JM. Thermal curing and photocuring of an epoxy resin modified with a hyperbranched polymer. Thermochim Acta. 2010;510:1–8.

25. Doyle CD. Series approximations to the equation of thermogravimetric data. Nature. 1965;207:290–1.

26. Ozawa T. New method of analyzing thermogravimetric data. Bull Chem Soc Jpn. 1965;38:1881–6.

27. Tryson GR, Shultz AR. A calorimetric study of acrylate photopolymerization. J Polym Sci. 1979;17:2059–75.

28. Morancho JM, Cadenato A, Fernández-Francos X, Salla JM, Ramis X. Isothermal kinetics of photopolymerization and thermal polymerization of bis-GMA/TEGDMA resins. J Therm Anal Calorim. 2008;92:513–22.

29. Lecamp L, Youssef B, Bunel C, Labaudy P. Photoinitiated polymerization of a dimethacrylate oligomer: 2. Kinetic studies. Polymer. 1999;40:1403–9.

30. Watts DC. Reaction kinetics and mechanics in photo-polymerised networks. Dent Mater. 2005;21:27–35.

31. Cook WD. Thermal aspects of the kinetics of dimethacrylate photopolymerization. Polymer. 1992;33:2152–61.

32. Fox TG. Influence of diluent and of copolymer composition on the glass temperature of a polymer system. Bull Am Phys Soc. 1956;1:123.

33. Scott TT, Cook WD, Forsythe JS. Photo-DSC cure kinetics of vinyl ester resins. I. Influence of temperature. Polymer. 2002;43:5839–45.

34. Fernández-Francos X, Salla JM, Cadenato A, Morancho JM, Mantecón A, Serra A, Ramis X. Influence of the initiating mechanism on the cationic photopolymerization of a cycloaliphatic epoxy resin with arylsulfonium salts. J Polym Sci A. 2007;45:16–25.

35. Fernández-Francos X, Salla JM, Pérez G, Mantecón A, Serra A, Ramis X. New thermosets obtained by thermal and UV-induced cationic copolymerization of DGEBA with 4-phenyl-γ-butyrolactone. Macromol Chem Phys. 2009;210:1450–60.

36. Aspinall HC, Dwyer JLM, Greeves W, McIver EG, Woolley JC. Solubilized lanthanide triflates: Lewis acid catalysis by polyether and poly(ethylene glycol) complexes of Ln(OTf)$_3$. Organometallics. 1998;17:1884–8.