Thermochimica Acta 510 (2010) 1–8

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal curing and photocuring of an epoxy resin modified with a hyperbranched polymer

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ARTICLE INFO

Article history:
Received 11 January 2010
Received in revised form 5 May 2010
Accepted 24 May 2010
Available online 1 June 2010

Keywords:
Epoxy networks
Hyperbranched
Toughness
Photocuring
Kinetics

ABSTRACT

In this work we study the influence of a hyperbranched polymer (BOLTORN® H20) on the thermal curing and photocuring of DGEBA. Addition of low amounts of H20 slowed down dynamic thermal curing but further addition accelerated the process. During isothermal photocuring, H20 decelerated the process at low temperatures and accelerated it at high temperatures. The temperature dependence of H20 solubility, its viscosity and the hydroxyl-induced chain-transfer reaction, are responsible for this behaviour. The addition of H20 resulted in a decrease in the glass transition temperature using both curing techniques but in a different way.

1. Introduction

Epoxy resins are widely used in several applications: adhesives, coatings, castings, electric laminates, encapsulation of semiconductor devices, matrix material for composites, structural components [1–6] and cryogenic engineering [7–9] because of their mechanical properties, adhesion and chemical resistance. However, due to their high cross-link density they are inherently brittle, which limits their applicability. To increase their toughness, different modifiers have been added like rubber, thermoplastic and glass particles, but they always limit the processability of the resin systems [10–15]. Another type of modifiers are the hyperbranched polymers (HBPs), which can solve the problems related to processability, property compromises and compatibility which are found with the other modifiers [3,16]. The main advantages of HBPs 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 [17]. HBPs can increase the toughness of the epoxy resins and they can also reduce the shrinkage of the resin during the curing process [16] and the internal stress [3]. The glass transition temperature of the epoxy resin can decrease [16] or may not be affected [3]. The increase in toughness can be caused by phase separation [3], which can be controlled by selecting their solubility, reactivity and processing conditions [18].

Ratna et al. [19] have found that the improvement in toughness by adding HBP to an epoxy resin is higher than that of conventional toughening agents like CTBN (carboxyl-terminated copolymer of butadiene and acrylonitrile). Yang et al. [20] have employed a HBP to improve the mechanical properties of an epoxy resin at liquid nitrogen temperature (77 K). They found that, by adding a proper content of this modifier, ductility and impact strength were simultaneously improved without reducing the glass transition temperature. In these works an epoxy resin was cured with a hardener and modified with a HBP. But very few papers have been published on the modification of the epoxy resin with a HBP without adding a hardener [21–24]. Previously we studied the cationic thermal curing of DGEBA with H30 using ytterbium triflate as initiator [23]. A complex effect on reaction kinetics was observed, influenced by the viscosity, solubility and role of hydroxyl groups in the cationic homopolymerization of epoxides. Sangermano et al. have successfully photocured a cycloaliphatic diepoxide with different generation hydroxyl-terminated hyperbranched polyesters (Boltorn series) [24] with a positive effect on kinetics and mechanical properties. UV curing is used in different fields, as the coating industry, graphic arts and microelectronics, owing to its high efficiency, environmental protection and energy saving [21,25]. Cationic UV curing of epoxy resins also benefits from the lack of oxygen inhibition in comparison with radical systems, which makes them attractive in some applications [26].

In the present paper we analyze the effect of a hydroxyl-terminated hyperbranched polyester, H20 (Boltorn series), on the thermal curing and photocuring of a DGEBA epoxy resin. An accelerating effect in the cure kinetics has been found in thermal curing

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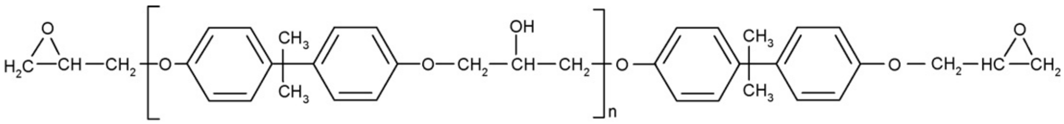
doi:10.1016/j.tca.2010.05.008



Scheme 1. Chemical structure of DGEBA epoxy monomer.

only at high proportions of H20. In photocuring the accelerating effect has been found at high temperatures for all the tested formulations.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent of 182 g/ee (EPIKOTE 827, Shell) has been cured with BOLTORN® H20, a hydroxyl-terminated hyperbranched polyester with a molecular weight of 2100 g/mol (Perstorp Specialty Chemicals). Schemes 1 and 2 show the formulae of DGEBA and BOLTORN® H20. 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.

2.2. Preparation of curing systems

The mixtures of liquid DGEBA and solid H20 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.

Table 1
Hydroxyl equivalents per epoxy equivalent (eq OH/ee) of DGEBA with different proportions of H20.

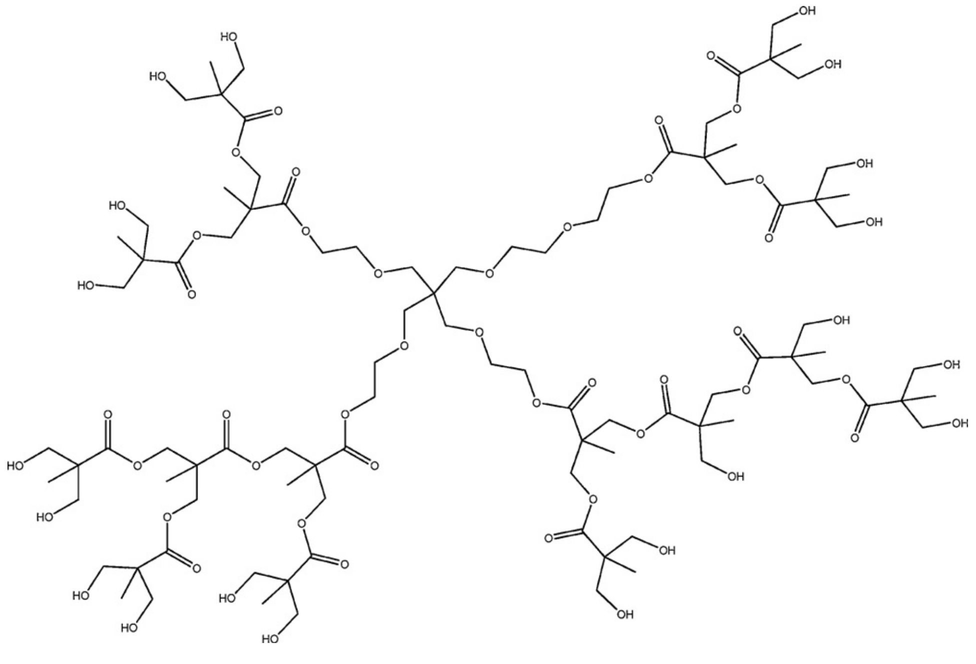
% H20	eq OH/ee
0	0.042
5	0.115
10	0.196
15	0.287
20	0.389

2.3. Thermal curing

The thermally curable samples were cured at different heating rates 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.

2.4. 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 side and the other for the reference side. Samples of ca. 5 mg were cured in open aluminium 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, 20 min of irradiation and finally 4 min more without UV



Scheme 2. Idealized chemical structure of the hyperbranched polymer BOLTORN® H20.

Table 2
Average total reaction heat (ΔH_{ave}) and maximum glass transition temperature ($T_{g\infty}$) for the thermal curing of DGEBA with different proportions of H20.

% H20	ΔH_{ave} (kJ/ee)	$T_{g\infty}$ (°C)
0	96.7	130.0
5	97.6	115.9
10	102.2	114.2
15	104.7	114.1
20	108.0	98.0

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 to determine the residual heat. After this, a second dynamic run was carried out to determine $T_{g\infty}$.

3. Theory

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

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

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 (we 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:

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

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

By reordering, we can write the so-called temperature integral:

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

where β is the heating rate (dT/dt) and $g(\alpha)$ an integral function of the degree of conversion. Eq. (3) may be integrated employing Doyle's approach [27] and rewritten in logarithm form as

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

This equation applied to constant conversion, enables us to determine E and the kinetic parameter A_{int} (Ozawa method [28]) for each degree of conversion.

In isothermal photocuring experiments the degree of conversion was calculated as

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

where ΔH_t is the heat released up to a time t. The values used of ΔH_{ave} are shown in Table 2. The kinetic study of the photocuring was carried out following the approach used by Tryson and Shultz [29]. 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

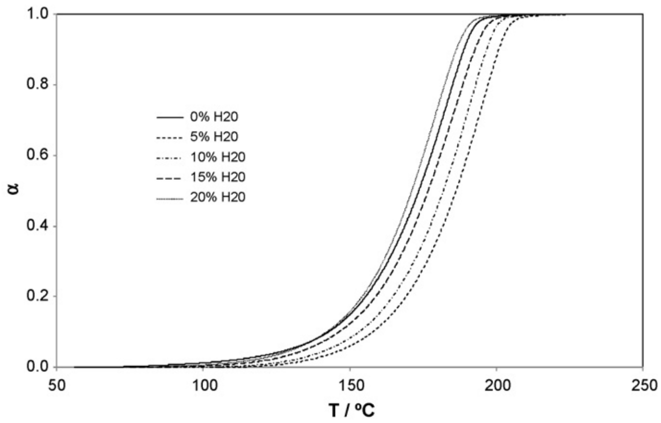


Fig. 1. Degree of conversion of the thermal curing at 10 °C/min of DGEBA with different proportions of H20.

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

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}). Eq. (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; (e) due to theoretical considerations, it is assumed that the rate depends on the first power of monomer concentration.

Eq. (6) can be expressed depending on the degree of conversion as [30]:

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

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

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

then, the Eq. (7) is

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

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 [31–33].

4. Results and discussion

4.1. Thermal curing

First, we will analyze the thermal curing, where the degree of conversion has been calculated using Eq. (1). Fig. 1 shows the degree of conversion versus temperature of the thermal curing at 10 °C/min of DGEBA with different proportions of H20. It can be seen that the addition of a 5% of this HBP decelerates the reaction, but a further increase in the H20 proportion accelerates the process, becoming faster than that of the neat epoxy resin when the H20

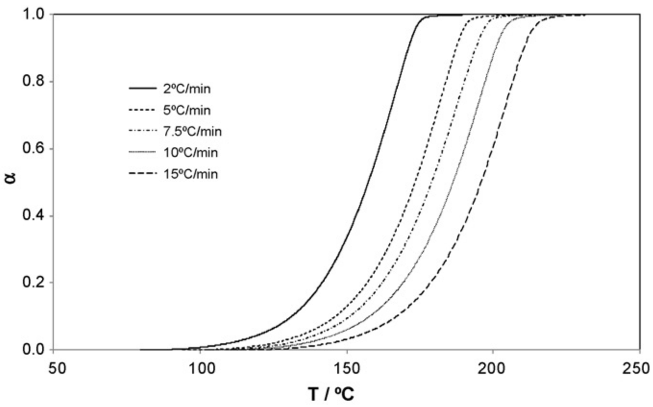


Fig. 2. Degree of conversion of the thermal curing of DGEBA with 5% of H20 at different heating rates.

proportion is 20%. The addition of H20 increases the viscosity and makes difficult the formation of active species through the interaction between the epoxy groups and the initiator. Consequently, the rate of chain propagation is reduced. But the addition of this HBP increases the number of hydroxyl groups, which could accelerate the curing reaction. The low solubility of H20 in DGEBA at low temperatures may also play a role in the curing kinetics because of the low availability of hydroxyl groups at lower temperatures. The different effects of these factors explain the different influence of the H20 proportion during the process [23]. In Table 2, the values of the total reaction heat have been calculated per epoxy equivalent. Increasing the H20 proportion, ΔH_{ave} slightly increases. Therefore, hydroxyl groups of H20 seem to play an active role in the curing, as deduced by both the increase in the heat released and the curing kinetics.

Fig. 2 shows the degree of conversion versus temperature of the thermal curing of DGEBA with 5% of H20 at different heating rates. As expected, this figure shows how a decrease in the heating rate displaces the curing curves down to lower temperatures. If the Ozawa isoconversional method is applied to the thermal curing of the different formulations, it is observed a good lineal dependence between the logarithm of the heating rate and the reciprocal temperature, as it is predicted by Eq. (4). From the slope of these lineal dependences we can find the values of the activation energy for every degree of conversion. These values have been represented for all formulations in Fig. 3, where it can be noticed that activation energy is not constant throughout the curing process, as reported for the curing of other thermosets [34–36]. In general, it can be appreciated that the activation energy slightly increases with the degree of conversion, due to the thermal activation of the reaction. In neat DGEBA the increase in activation energy throughout the process is higher than in the other formulations. Neat DGEBA is the faster at low conversions and then it has smaller activation energy. The systems with proportions of H20 higher than 5% present very similar values of activation energy and they are smaller than the values of the system with 5% of H20. This system is the slowest and then it presents higher average activation energy than the others. The system with 20% of H20 is the fastest at the middle and in the end of the process and then it presents the smallest activation energies in these parts. This trend is similar to the observed in systems with H30 and can be caused by the complex interplay of the factors determining the curing kinetics, as stated above [23].

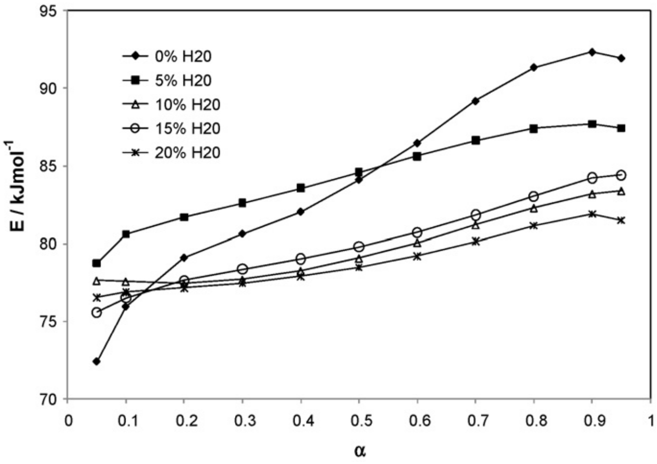


Fig. 3. Activation energy versus the degree of conversion for the thermal curing of DGEBA with different proportions of H20.

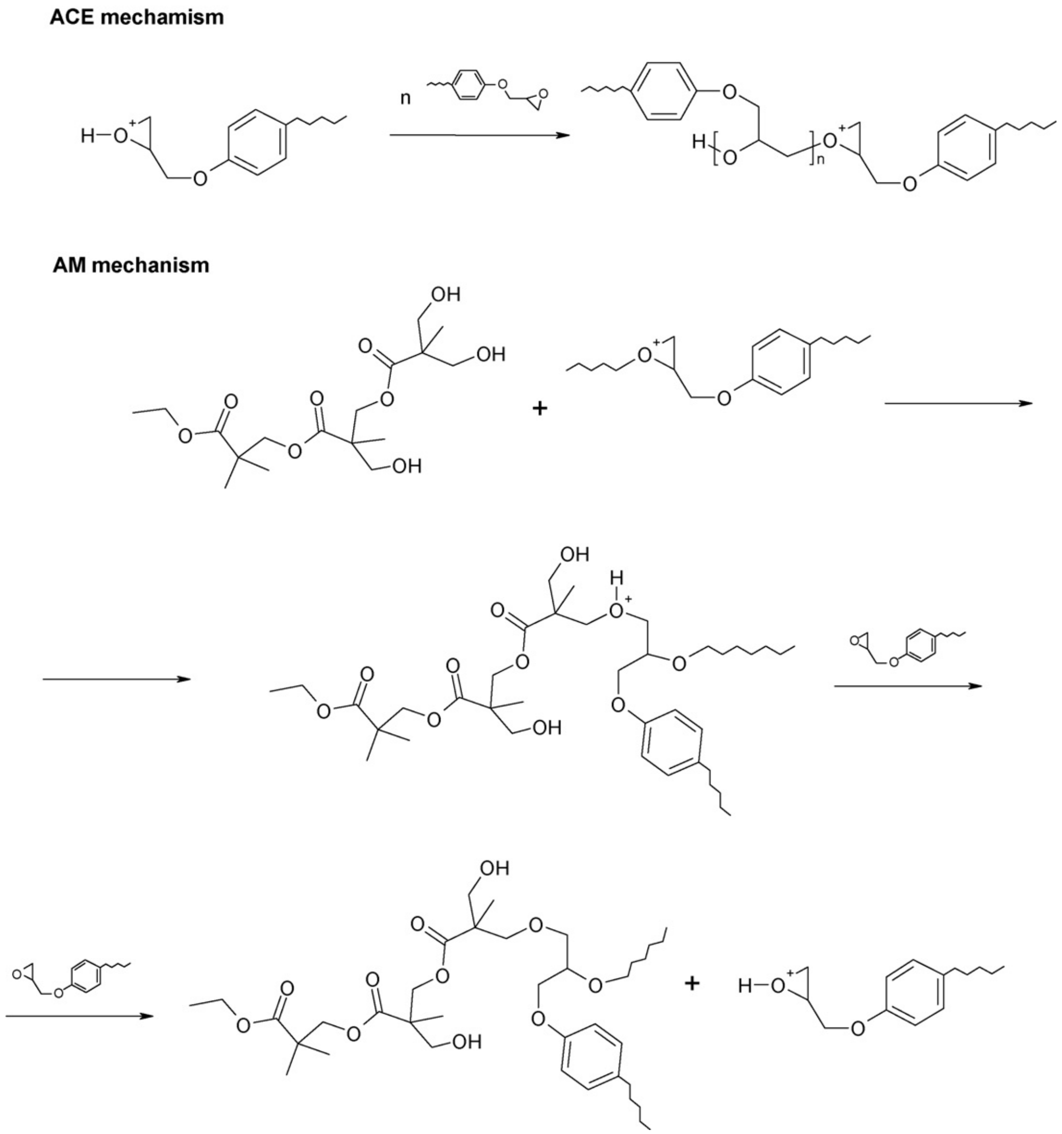
Table 3
Values of ΔH_{iso} in kJ/ee for the photocuring of DGEBA with different proportions of H20 and temperatures.

% H20	40 °C	60 °C	80 °C	100 °C	120 °C
0	48.7	62.7	70.3	77.3	83.6
5	49.0	63.4	70.9	79.0	84.5
10	52.6	65.6	75.8	84.5	87.6
15	53.4	69.0	77.0	86.6	89.5
20	57.6	72.7	81.8	88.5	90.6

Table 2 shows the values of the ultimate glass transition temperature ($T_{g\infty}$) obtained in a second dynamic run at 10 °C/min (the results shown in this table are average values of the different samples analyzed). The addition of H20 leads to a decrease in $T_{g\infty}$ but with 5, 10 and 15% proportions the values are very similar. Up to 5% of H20, this modifier is well solubilised in the epoxy resin. H20 reduces the cross-linking density and acts as an internal plasticizer in these systems, reducing their $T_{g\infty}$. H20 can participate in the curing process via hydroxyl-induced chain-transfer reactions, the so-called activated monomer (AM) mechanism which takes place during cationic polymerization of epoxides in the presence of hydroxylic compounds, in addition to the epoxy propagation via the active chain-end (ACE) (see Scheme 3) [23,26,37–39]. For every chain-transfer event, the growing of a chain is stopped and it becomes attached to a H20 hydroxyl group. As a result, a new hydroxyl-terminated growing chain is formed, thus reducing the cross-linking density. The presence of a bulky molecule such as H20, which might be just loosely attached to the network structure by few of its hydroxyl groups, can account for an internal plasticization. Taking into account the similar $T_{g\infty}$ of formulations with higher H20 content, one can hypothesize that the degree of incorporation of H20 hydroxyl groups is not complete and the effective degree of modification of the network structure may be similar to that of the formulation with low H20 content.

4.2. Photocuring

Fig. 4 shows the heat flow and the degree of conversion (see inset) versus the photocuring time of DGEBA with 5% of H20 at different temperatures. It can be seen that at the beginning of the process the heat flow, which is proportional to the rate of conversion ($d\alpha/dt$), and the degree of conversion increase with temperature, as usually reported for other photocuring systems [40]. The area of the isothermal cure is the isothermal curing heat (ΔH_{iso}). Table 3 shows how the isothermal reaction heat increases with temperature, as expected, since photocuring takes place up to vitrification at temperatures lower than the ultimate glass transition [40,41] and so conversion increases with photocuring temperature. This table also shows the same tendency for the other systems under study. If we compare the values of this magnitude for a determined temperature, we can appreciate that ΔH_{iso}



Scheme 3. Active chain-end mechanism (ACE) for the cationic homopolymerization of epoxy monomers and active monomer mechanism (AM) for the reaction between the hydroxyl and epoxy groups.

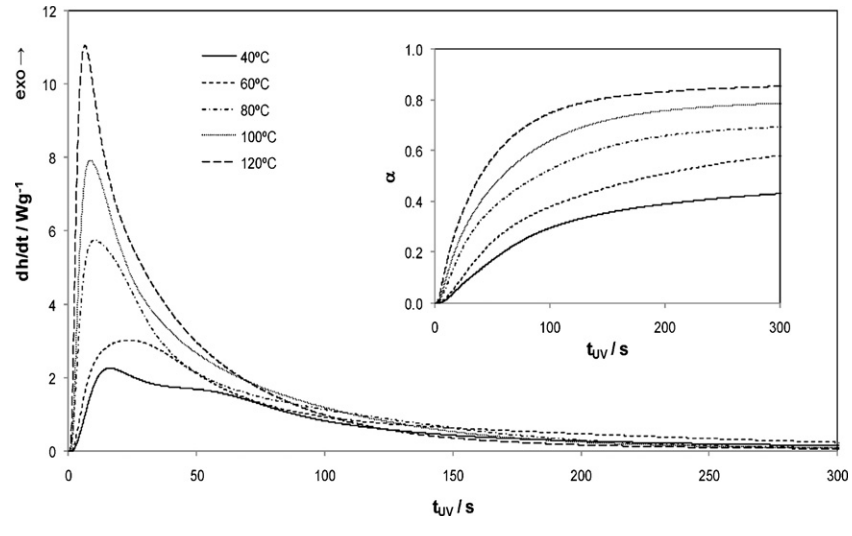


Fig. 4. Photocuring of DGEBA with 5% of H20 at different temperatures and as an inset, the degree of conversion for the same system and processes.

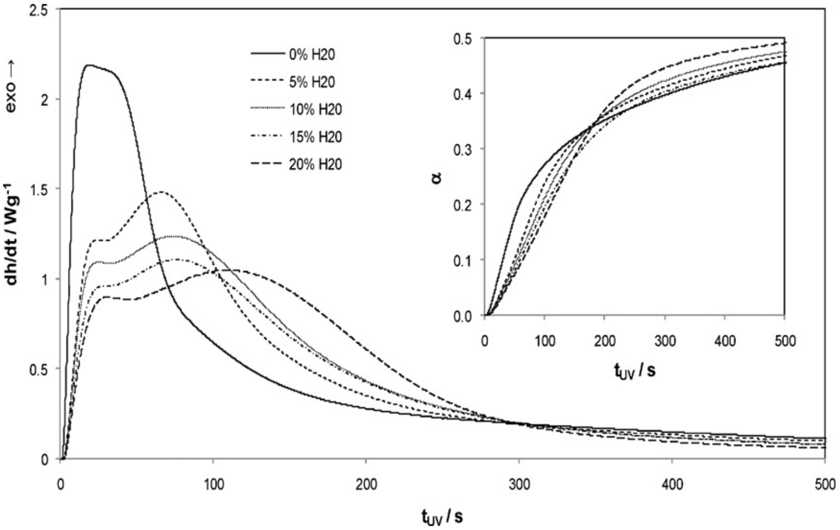


Fig. 5. Photocuring at 40 °C of DGEBA with different proportions of H20 and as an inset, the degree of conversion for the same systems and process.

Table 4
Values of α_{iso} for the photocuring of DGEBA with different proportions of H20 and temperatures.

% H20	40 °C	60 °C	80 °C	100 °C	120 °C
0	0.504	0.648	0.727	0.799	0.864
5	0.502	0.650	0.727	0.809	0.866
10	0.514	0.642	0.741	0.826	0.857
15	0.510	0.659	0.735	0.828	0.855
20	0.534	0.674	0.758	0.820	0.839

increases with H20 proportion, indicating that H20 may participate in the curing process via the AM mechanism, thus decreasing the density of cross-linking and allowing a greater conversion of epoxy groups at vitrification.

Table 4 shows the degree of curing after the photocuring experience, α_{iso}, calculated for the different formulations and photocuring temperatures using Eq. (5). As seen above with reaction heat, it can be seen that it increases with photocuring temperature. It is also observed, as deduced from the reaction heat values, that the addition of H20 increases α_{iso} except at the highest temperature. Some authors have reported a maximum achievable degree of conversion in radical photocurable systems [33] due to entrapment of active species. However, in this case all systems showed an exotherm during dynamic postcuring, so that reaction could proceed to completion. It is hypothesized that some of the reaction heat might not be adequately detected during the process because the increasing reaction rate with the addition of H20 at high photocuring temperatures could result in some loss of reaction heat.

Fig. 5 shows the dependence of the heat flow and the degree of conversion (see inset) versus the photocuring time at 40 °C for DGEBA with different proportions of H20. When the H20 proportion is small, the reaction rate and the degree of conversion at the beginning of the process are higher, but later on during curing the situation is reversed and α_{iso} increases with H20 proportion, as shown in Table 4. The same occurs at 60 °C, but at 80 °C the system with 5% of H20 is the fastest at the beginning and the system with 20% of H20 is the slowest. At 100 °C, the systems with 20% and 10% of H20 are the fastest and the slowest, respectively. At 120 °C, as can be seen in Fig. 6 (plots of heat flow and the degree of conversion versus the photocuring time at 120 °C for the different systems studied) the tendency is completely inverted. At the beginning of the process, the heat flow, the degree of conversion and the rate of conversion increase with the content in H20 but eventually α_{iso} decreases when the H20 proportion increases as it is shown in Table 4. At the lowest temperatures H20 is not completely solubilised in the epoxy resin, hindering the photocuring.

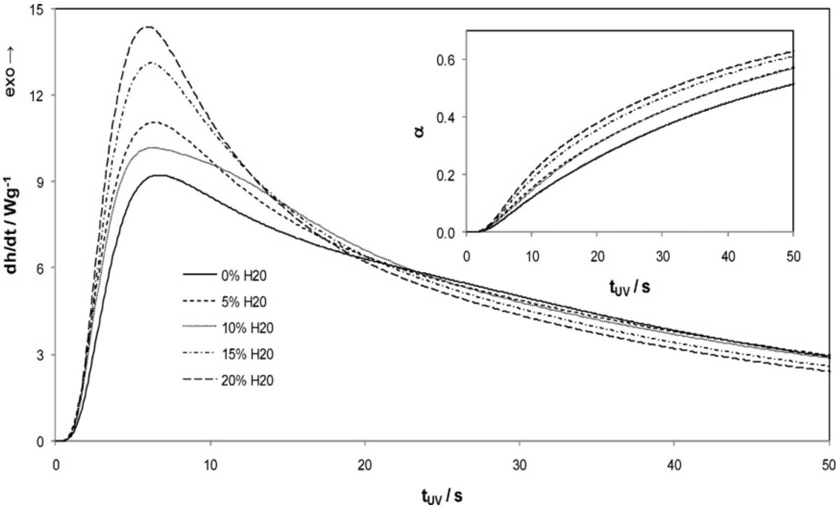


Fig. 6. Photocuring at 120 °C of DGEBA with different proportions of H20 and as an inset, the degree of conversion for the same systems and process.

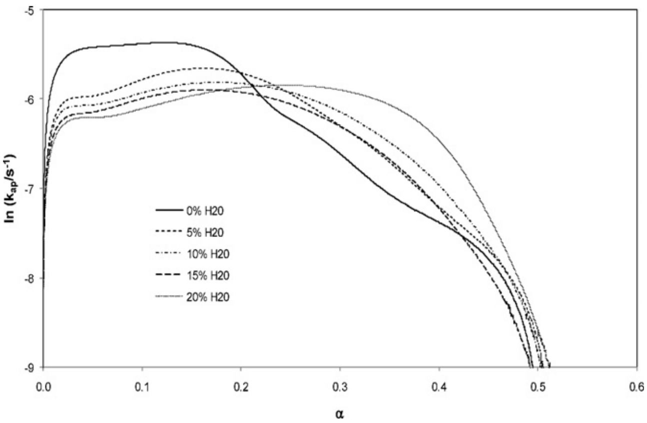


Fig. 7. Logarithm of the apparent kinetic constant versus the degree of conversion for the photocuring at 40 °C of DGEBA with different proportions of H20.

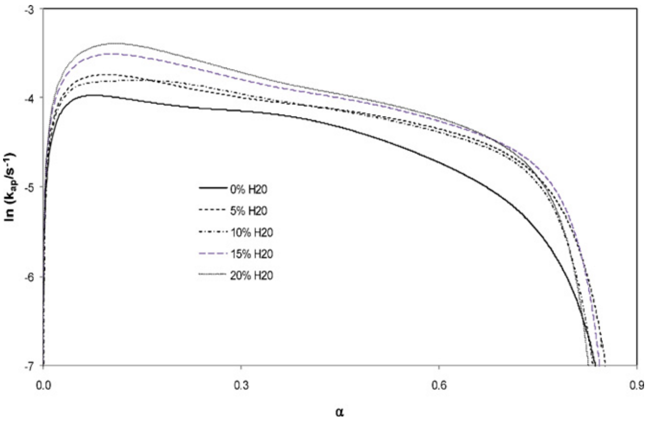


Fig. 8. Logarithm of the apparent kinetic constant versus the degree of conversion for the photocuring at 120 °C of DGEBA with different proportions of H20.

The same trend can be observed in Figs. 7 and 8, which plot the logarithm of the apparent kinetic constant (calculated from Eq. (9)) at 40 °C and 120 °C, respectively, versus the degree of conversion for DGEBA with different proportions of H20. The two maxima shown in Figs. 5 and 7 can be related to a change on the kinetics of curing. At short reaction time or low degree of conversion the process is controlled by hydroxyl-chain-transfer reaction and the activated initiator species and seems to be affected by the low solubility of H20 in the medium, that is, the availability of hydroxyl groups. Keeping in mind that H20 might participate as chain-transfer agent, as depicted in Scheme 3, it might trap the active species due to its low solubility. As the reaction goes on, some H20 might become solubilised and become incorporated into the network structure, thus making possible an increase in the reaction rate. At the highest temperature H20 is solubilised in the epoxy resin, its hydroxyl groups are available from the beginning of the process and can thus accelerate the process. Hence the increase in reaction rate, as seen in Figs. 6 and 8.

Sangermano et al. [24] added different HBPs (Boltorn H20, H30 and H40) to a bis-cycloaliphatic diepoxy resin and photocured it. They always found an increase in the reaction rate increasing the HBP proportion, due to the solubility of the HBPs in the epoxy resin at any proportion. In our system only at high temperatures the reaction rate increases with H20 proportion, as mentioned before, because H20 is only completely solubilised in DGEBA at these temperatures. Sangermano et al. [24] also found an increase in α_{iso} for the same reasons commented before.

As mentioned in the experimental part, a dynamic postcuring was made after the photocuring process. Fig. 9 plots the dynamic postcuring of DGEBA with 5% of H20 after photocuring the system at the indicated temperatures. The postcuring process begins after the sample has reached its photocuring temperature confirming the hypothesis above that the materials cure up to vitrification [40], because only once the system regains mobility, that is, devitrifies, it is able to resume the curing process. Accordingly, the heat released decreases when the photocuring temperature increases, in agreement with the higher heat released during photocuring, as seen in Table 3.

The ultimate glass transition temperatures determined in the second dynamic scan after photocuring are listed in Table 5 for all formulations (the results shown in this table are average values of the different samples analyzed). We can see that this magnitude decreases when H20 proportion increases. As in thermally cured systems, this is motivated by the chain-transfer mechanism: when the cationic polymerization of epoxies is carried out in the presence of hydroxylic compounds, it results in a decrease of the cross-link density and then the network structure becomes more flexible and $T_{g\infty}$ decreases [22,24,42]. These values are higher than in the case of the thermal curing (see Table 2), as observed for other epoxy cationic systems [43]. It is hypothesized that

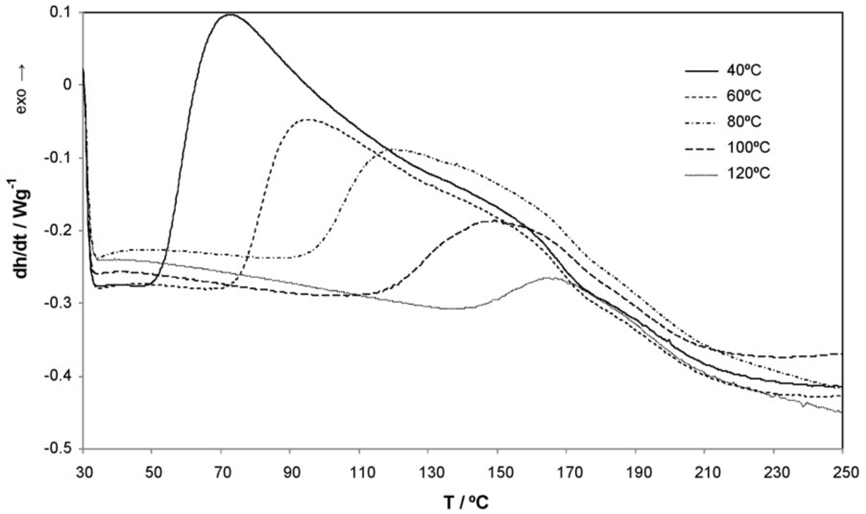


Fig. 9. Dynamic postcuring experiments at 10 °C/min of DGEBA with 5% of H20 after photocuring at different temperatures.

Table 5
Maximum glass transition temperature determined in the second dynamic scan after photocuring of DGEBA with different proportions of H20.

% H20	$T_{g\infty}$ (°C)
0	161.9
5	156.0
10	149.2
15	144.6
20	141.4

ytterbium triflates are able to 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 $T_{g\infty}$ [42,44].

5. Conclusions

The effect of H20 over the thermal curing of DGEBA depends on the proportion added of this modifier. This influence is due to the hydroxyl groups of H20, the proportion of initiator per epoxy group, the solubility of H20 in the epoxy resin and the viscosity. These factors influence in different manner, because at low proportions of H20 the process is decelerated but at high proportions (20% H20) it is accelerated.

However, in the photocuring the major factor that influences the reaction rate when the H20 proportion is modified is the temperature. At high temperatures (120 °C) the reaction rate increases with H20 proportion because the modifier is solubilised in the epoxy resin, but at low temperatures (40 °C and 60 °C) the reaction decreases at the beginning of the process increasing the H20 proportion, because H20 is not completely solubilised in the epoxy resin.

Due to the participation of H20 in the cationic curing of DGEBA via the AM mechanism the materials obtained either by thermal curing or thermal curing have lower $T_{g\infty}$ with the addition of H20. The loosening of the network structure is caused by both the termination and reinitiation of growing chains as a consequence of the chain-transfer but also to the presence of H20 loosely connected to the network which might act as an internal plasticizer.

Acknowledgements

The authors would like to thank CICYT and FEDER for their financial support (grant MAT2008-06284-C03-02) and “Generalitat de Catalunya” (2009-SGR-1512) for their financial support.

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