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Unexpected differences between thermal and photoinitiated cationic curing of a diglycidyl ether of bisphenol A modified with a multiarm star poly(styrene)-*b*-poly(ϵ -caprolactone) polymer

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Abstract. The effect of adding a multiarm star poly(styrene)-*b*-poly(ϵ -caprolactone) polymer on the cationic thermal and photoinitiated curing of diglycidyl ether of bisphenol A was studied. This star-polymer decelerated the thermal curing of diglycidyl ether of bisphenol A and modified the final structure of the epoxy matrix. The photocuring was influenced significantly by the addition of the multiarm star. When the proportion of this modifier added was 5%, much more time was necessary for complete photocuring (160 min at 40°C). In the presence of 10% of modifier, the degree of photocuring reached was very low (0.196 at 120°C). A subsequent thermal post-curing was necessary to cure completely the system. During photocuring in presence of poly(styrene)-*b*-poly(ϵ -caprolactone), the formation of dormant species, which are reactivated when the temperature increases, takes place. The kinetics of the thermal curing and the photocuring was analyzed using an isoconversional method due to the complexity of the reactive process. Applying this method, it has been confirmed the dependence of activation energy on the degree of conversion. The fracture morphology analyzed by scanning electron microscopy exhibited a second phase originated during photocuring by the presence of the modifier.

Keywords: thermosetting resins, multiarm star polymer, thermal curing, photocuring, kinetics

1. Introduction

Epoxy resins are used in a wide range of applications, such as adhesives, coatings, castings, electrical and electronic materials, encapsulation of semiconductor devices, matrix material for composites, structural components [1–9] and cryogenic engineering [10–12]. Epoxy resins have good mechanical and chemical properties, adhesion, thermal stability and electrical characteristics. However, they are inherently brittle due to their relatively rigid

molecular structure, which limits their use. In coatings, the curing shrinkage can cause serious problems due to the generation of microvoids and microcracks, deformation and loss of adhesion. Then the protection capability and durability of the coating are reduced, which allows corrosion of the substrate as a result of the penetration of moisture [13]. In order to increase the toughness of the epoxy resins different modifiers can be added to them, like rubber and thermoplastic, but they always limit the processability of the resin systems [14–19].

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Hyperbranched polymers (HBP) are a new family of polymeric modifiers that can be added to epoxy resins to increase their toughness without compromising the processability due to their highly branched dendritic structure [20]. The main advantages of HBPs are their low viscosity compared with their linear counterparts, the possibility of tailoring their core and branches structure and the functionalization of the end groups so that they can be compatible with the surrounding matrix [21]. HBPs can also reduce the shrinkage of the resin during the curing process [22] and the internal stresses [6]. The glass transition of the epoxy resin can be reduced by HBPs [21] or left unaltered [6], depending on different factors, such as the formation of a second phase during curing, the glass transition temperature of HBP and the interactions between modifier and epoxy matrix. In previous works, the influence of some HBPs in the thermal curing and the photocuring cationically initiated of a diglycidyl ether of bisphenol A (DGEBA) has been studied [23–25].

In addition to HBPs, multiarm star polymers can also be considered as a new class of reactive modifiers for epoxy resins. In this paper, the influence of a multiarm star polymer based on hyperbranched poly(styrene)-*b*-poly(ϵ -caprolactone) on the cationic thermal curing and on the cationic photocuring of an epoxy resin is reported. This polymer was previously synthesized and used as a modifier in the thermal anionic curing of DGEBA [26]. Hyperbranched poly(styrene)-*b*-poly(ϵ -caprolactone) showed a slightly decelerative effect on the curing, a homogeneous nanograined morphology and good processability when was used as reactive modifier of epoxy thermosets cured in the presence of tertiary amine. In another previous work, the influence of two multiarm star polymers, based on hyperbranched poly(glycidol)-*b*-poly(ϵ -caprolactone) on the cationic thermal curing and the cationic photocuring of the same epoxy resin was studied [27]. These polymers decelerated the thermal curing and the photocuring, but to a lesser extent than the poly(styrene)-*b*-poly(ϵ -caprolactone) polymer, studied in this work.

In addition to the kinetics of thermal and UV-induced curing and thermal properties of poly(styrene)-*b*-poly(ϵ -caprolactone)/DGEBA mixtures, the potential capacity of the star-like topology to enhance epoxy toughness is also discussed.

2. Experimental

2.1. Materials

DGEBA with an epoxy equivalent of 187 g/ee (EPIKOTE 828, Hexion Specialty Chemicals B.V., Hoogvliet, Netherlands) was dried in vacuum before use. A multiarm star poly(styrene)-*b*-poly(ϵ -caprolactone) (from now on PS-10) with 60 arms per molecule, a degree of polymerization of the poly(ϵ -caprolactone) arms of 10 and an average molecular weight in number of 76,200 g/mol was synthesized by us following a reported procedure [26]. Figure 1 shows the idealized chemical structure of this polymer. Ytterbium triflate (Yb(OTf)₃) (Aldrich, St. Louis, Missouri, USA) has been used as thermal cationic initiator. The photoinitiator used is CYRACURE UVI-6976 (triarylsulfonium hexafluoroantimonate, 50 wt% in propylene carbonate) and was received from Dow Chemical Company (Midland, Michigan, USA).

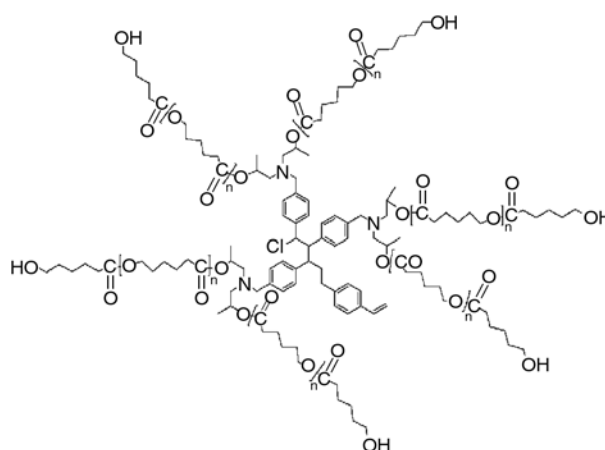


Figure 1. Idealized chemical structure of the multi arm star poly(styrene)-*b*-poly(ϵ -caprolactone)

2.2. Preparation of curing formulations

The mixtures of liquid DGEBA and solid star polymer were prepared by mixing and heating the desired quantities of these substances using a hot air blower and vigorous stirring. In the thermally curable samples, 1 phr (parts of initiator per 100 parts of resin) of the thermal initiator was added to the mixtures at room temperature and they were stirred and kept at -18°C to prevent polymerization. In the photocurable samples of neat DGEBA, 2 phr of CYRACURE UVI-6976 was added (because the concentration of photoinitiator was 50% in weight in the CYRACURE UVI-6976 solution, 2 phr of this solution was needed for a concentration of 1 phr of photoinitiator in the

reactive mixture) and they were stirred and kept in the dark at -18°C . In the photocurable samples of DGEBA with different proportions of PS-10, 4 phr of CYRACURE UVI-6976 was added (the concentration of the photoinitiator in the reactive mixture was 2 phr).

2.3. Thermal curing

The thermally curable samples were cured at different heating rates (2.5, 5, 7.5, 10 and $15^{\circ}\text{C}/\text{min}$) in a Mettler 822e calorimeter (Mettler-Toledo, Schwerzenbach, Switzerland) under a nitrogen atmosphere. The dynamic scans were performed from 0 to 250°C when the system was neat DGEBA. But when a proportion of 5 or 10% of PS-10 was added to DGEBA the dynamic scans were performed from 0 to 330°C at $15^{\circ}\text{C}/\text{min}$ and from 0 to 300°C at the other heating rates. The ultimate glass transition temperature of the cured materials ($T_{g\infty}$) was determined on the basis of a second dynamic run from -100 to 250°C at $10^{\circ}\text{C}/\text{min}$, as the temperature of the half-way point of the jump in the heat capacity when the material changed from glassy to the rubbery state under N_2 atmosphere and the error is estimated to be approximately $\pm 1^{\circ}\text{C}$.

2.4. Photocuring

The photocurable samples were photocured at different temperatures, in a Mettler DSC-821e (Mettler-Toledo, Schwerzenbach, Switzerland) calorimeter appropriately modified with a Hamamatsu Lightningcure LC5 (Hg-Xe lamp) (Hamamatsu Photonics K.K., Hamamatsu City, Japan) 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 four minutes of temperature conditioning, a period of time of irradiation and finally four minutes more without UV light. The light intensity used was calculated by irradiation of graphite-filled plans on only the sample side. The period of time of irradiation depended on the analyzed system. For the neat DGEBA, it was 30 min. For the DGEBA modified with 5% of PS-10 this period of time depended on temperature. This period changed between 80 min (at 120°C) and 160 min (at 40°C). These different periods of time were necessary to ensure a complete

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

When DGEBA was modified with 10% of PS-10 the system was photocured at 120°C for 30 min, and after that, it was thermally postcured at different heating rates from 30 to 300°C , with the exception of the heating rate of $15^{\circ}\text{C}/\text{min}$, where the final temperature was 330°C .

2.5. SEM (Scanning Electron Microscopy)

Some samples were photocured isothermally in a polypropylene mould ($2.35 \times 1.2 \times 0.3 \text{ cm}^3$, with a thickness of 0.5 mm) at room temperature. Each side of the sample was irradiated for 15 min with a monochromatic UV lamp of 365 nm wavelength and $4 \text{ mW}/\text{cm}^2$ of intensity. They were subsequently postcured at 180°C for two hours, cooled in liquid nitrogen and fractured. The fracture surface of these samples was coated with a conductive gold layer and then examined with a JEOL JSM-6400 SEM (JEOL Ltd., Tokyo, Japan), with a magnification of 20,000.

3. Theory

In the thermal curing processes the degree of conversion (α) was calculated according to Equation (1):

$$\alpha = \frac{\Delta h_T}{\Delta h_{\text{dyn}}} \quad (1)$$

where Δh_T is the heat released up to a temperature T , obtained by integration of the calorimetric signal up to that temperature and Δh_{dyn} is the total reaction heat of the experiment, associated with complete conversion of all reactive groups. Cure completion was confirmed by FTIR of the samples after dynamic curing.

The rate of conversion ($d\alpha/dt$) is proportional to a function of the degree of conversion ($f(\alpha)$) which depends on the mechanism governing the reactive process, as shown by Equation (2):

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

where k is the kinetic constant. If this constant is replaced by the Arrhenius equation, Equation (3) is obtained:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

where k_0 is the preexponential factor, E activation energy, R universal gas constant and T temperature. By reordering the so-called temperature integral can be written as in Equation (4):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

where β is the heating rate (dT/dt) and $g(\alpha)$ an integral function of the degree of conversion. Equation (4) may be integrated employing Doyle's approach [28] and rewritten in logarithm form as shown by Equation (5):

$$\ln\beta = \ln\left[\frac{k_0 E}{g(\alpha) R}\right] - 5.330 - \frac{1.0516E}{RT} \quad (5)$$

This equation enables to determine E and the kinetic parameter $\ln[k_0 E/(g(\alpha) R)]$ (Ozawa method [29]) for each degree of conversion. To determine the values of the preexponential factor for each degree of conversion the R_3 model (contracting volume mechanism) is applied. This kinetic model can be represented by its differential expression $f(\alpha) = 3(1 - \alpha)^{2/3}$ and its integral expression $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. This model has been previously determined for the resin/initiator system used in this work [30]. In this work it has been confirmed that the curing of PS-10/DGEBA formulations is also described by R_3 model.

In isothermal photocuring experiments the degree of conversion was calculated by Equation (6):

$$\alpha = \frac{\Delta h_t}{\Delta h_{ave}} \quad (6)$$

where Δh_t is the heat released up to a time t and Δh_{ave} is the average reaction heat obtained in the non-isothermal thermal curing (see Table 1). Equation (3) can also be used in the isothermal photocuring process and integrating this equation in isothermal conditions, Equation (7) is obtained [31]:

$$\ln t = \ln\left[\frac{g(\alpha)}{k_0}\right] + \frac{E}{RT} \quad (7)$$

which allows finding the activation energy for each degree of conversion from the slope of the linear relationship $\ln t$ vs. $1/T$.

Table 1. Hydroxyl equivalents per epoxy equivalent (eq OH/ee) of DGEBA modified with different proportions of PS-10. Average total reaction heat (Δh_{ave}), kinetic constant at 160°C at a degree of conversion of 0.5 ($k_{160^\circ\text{C}}$) and experimental maximum glass transition temperature (T_{g^∞}) of the thermal curing of DGEBA modified with different proportions of PS-10. Experimental maximum glass transition temperature (T_{g^∞}) of the photocuring of DGEBA modified with different proportions of PS-10

% PS-10	eqOH/ee	Thermal curing			Photocuring
		Δh_{ave} [kJ/ee]	$k_{160^\circ\text{C}}$ [s ⁻¹]	T_{g^∞} [°C]	T_{g^∞} [°C]
0	0.0545	99.6	$6.46 \cdot 10^{-4}$	134	162
5	0.0619	97.8	$3.74 \cdot 10^{-4}$	101	135
10	0.0692	99.1	$2.07 \cdot 10^{-4}$	98	119

In DGEBA modified with 10% of PS-10, as it has been commented in the experimental part, a dynamic post-curing (dark reaction) at different heating rates after photocuring the sample at 120°C has been made. The dynamic post-curing has also been studied by an isoconversional procedure using Equation (5) to find the activation energy and the preexponential factor, but these magnitudes have been found at different relative conversion degrees (α'), see Equation (8):

$$\alpha' = \frac{\Delta h_T}{\Delta h_{dyn}} \quad (8)$$

where in this case Δh_T is the heat released up to a temperature T during the dynamic post-curing and Δh_{dyn} the total reaction heat released during the dynamic post-curing part of the experiment.

4. Results and discussion

4.1. Thermal curing

Figure 2 shows the heat flow and the degree of conversion calculated using Equation (1) (see the inset in the figure) versus the temperature of neat DGEBA and DGEBA modified with 5 and 10% of PS-10, at a heating rate of 2.5°C/min. First of all, it must be noted that the curing process is complex, as detected by the presence of more than one peak in the thermograms and the changing slope in the conversion curves (see inset). On increasing the proportion of PS-10, the process broadens and extends to higher temperatures. However, the temperature of the first peak is hardly modified, while the second one moves towards higher temperatures on increasing

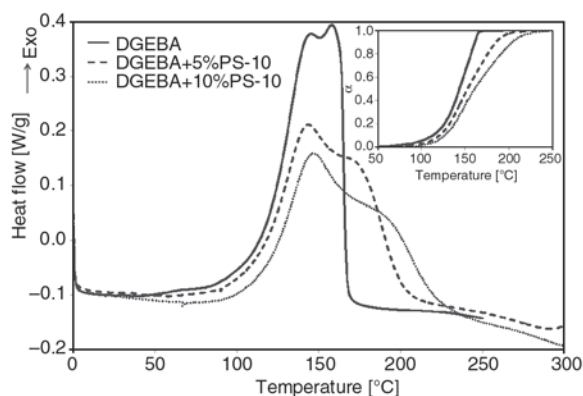


Figure 2. Heat flow and degree of conversion (as an inset) of the thermal curing at 2.5°C/min of neat DGEBA and DGEBA modified with different proportions of PS-10

the proportion of PS-10 and it becomes a shoulder. This is also observed in the conversion curves as a progressive retardation as the degree of conversion increases. The presence of two peaks can be rationalized in terms of the competition between two different propagation mechanisms, the activated chain-end (ACE) and the activated monomer (AM), which are described for cationic ring-opening polymerization. It is reported that the AM mechanism produces a proton-transfer reaction between a hydroxyl group and an activated epoxy group, which prevents subsequent chain growth and generates a new active species and growing chain, so a lower degree of crosslinking can be expected. In the absence of hydroxyl groups, the cationic epoxy curing only takes place via the ACE mechanism. In the ACE mechanism, propagation takes place through the reaction of epoxy groups with the active oxonium ion at the chain end [32]. In our case, the first peak can be related to AM mechanism and the second one with the ACE mechanism, since the first exotherm has a higher relative intensity than the second exotherm when hydroxyl content increases (see Table 1). Upon addition of a hydroxylic compound to the system, such as methanol, the first peak increases and this confirms that AM mechanism is the main process during this peak. As seen in Table 1, the number of hydroxyl groups increases with PS-10 proportion, then one would expect that the addition of PS-10 accelerated the thermal curing but the opposite effect is observed. The second curing exotherm, associated with the ACE propagation mechanism, is retarded due to the presence of PS-10, which suggests that PS-10 may participate in

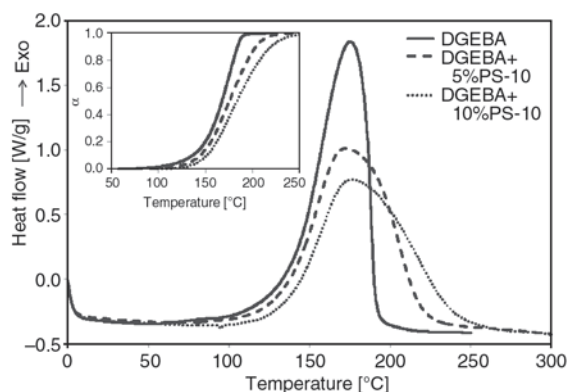


Figure 3. Heat flow and degree of conversion (as an inset) of the thermal curing at 10°C/min of neat DGEBA and DGEBA modified with different proportions of PS-10

the curing process leading to either less mobile or less active propagating species.

At the other heating rates analyzed, the thermogram of the neat DGEBA only presents one peak (see Figure 3, corresponding to a heating rate of 10°C/min) and the thermograms of the modified systems present only a shoulder. Although two maxima cannot be observed, it is expected that both mechanisms, AM and ACE, compete in a similar way as observed at low heating rates. This can be clearly appreciated in the inset of Figure 3, where it is observed the same behaviour as at the lower heating rates.

Table 1 shows that the reaction heat of all formulations (in kJJee^{-1}), obtained as the average of the reaction heat at different heating rates, is almost the same and close to the reference value of 100 kJJee^{-1} for epoxy formulations [33]. This suggests that complete curing is reached for all formulations and that the presence of the multi-arm star polymer does not have any effect on the completion of the thermal cure.

Table 2 shows the results of the isoconversional analysis of the thermal curing of the different formulations, using Equation (5). In the neat DGEBA and the DGEBA modified with 5% of PS-10 the activation energy increases with degree of conversion until $\alpha = 0.9$, after which it remains fairly constant. When DGEBA is modified with 10% of PS-10 the activation energy always increases with the degree of conversion. Until $\alpha = 0.4$ the values of the activation energy for the different systems are very similar, but after this degree of conversion, the increase of activation energy with PS-10 proportion

Table 2. Activation energy and pre-exponential factor of the thermal curing of DGEBA modified with different proportions of PS-10 at different degrees of conversion

% PS-10		$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$	$\alpha = 0.95$
0	E [kJ/mol]	74.8	79.7	83.7	85.5	86.9	88.4	91.0	94.5	97.8	99.6	98.6
	k_0 [s ⁻¹]	$7.59 \cdot 10^5$	$2.70 \cdot 10^6$	$7.90 \cdot 10^6$	$1.33 \cdot 10^7$	$1.94 \cdot 10^7$	$2.99 \cdot 10^7$	$5.96 \cdot 10^7$	$1.48 \cdot 10^8$	$3.50 \cdot 10^8$	$5.50 \cdot 10^8$	$4.38 \cdot 10^8$
5	E [kJ/mol]	79.4	81.8	85.4	87.9	91.1	96.7	104.9	114.6	123.6	130.0	129.7
	k_0 [s ⁻¹]	$1.47 \cdot 10^6$	$3.11 \cdot 10^6$	$8.95 \cdot 10^6$	$1.81 \cdot 10^7$	$4.19 \cdot 10^7$	$1.70 \cdot 10^8$	$1.30 \cdot 10^9$	$1.33 \cdot 10^{10}$	$1.02 \cdot 10^{11}$	$3.52 \cdot 10^{11}$	$2.32 \cdot 10^{11}$
10	E [kJ/mol]	76.5	81.6	86.2	89.0	93.3	101.6	115.1	132.9	152.4	170.4	182.7
	k_0 [s ⁻¹]	$3.86 \cdot 10^5$	$1.94 \cdot 10^6$	$7.68 \cdot 10^6$	$1.64 \cdot 10^7$	$4.82 \cdot 10^7$	$3.74 \cdot 10^8$	$9.50 \cdot 10^9$	$6.26 \cdot 10^{11}$	$5.16 \cdot 10^{13}$	$1.96 \cdot 10^{15}$	$1.85 \cdot 10^{16}$

is considerable. Activation energy is higher at higher star polymer content, in agreement with the decelerative effect of the modifier on the kinetics of thermal curing. The observed increase in activation energy during curing, which is more pronounced in formulations with 10% of PS-10, should be attributed to either a change in the curing mechanism by the participation of PS-10, leading to less active propagating species, or mobility restrictions occurring as a consequence of the participation of PS-10, rather than simply a change in the balance between the AM and ACE mechanisms due to the different hydroxyl content of the formulations.

In Table 2 the values of the preexponential factor using the R_3 model has also been reported. From the values of the activation energy and the preexponential factor the kinetic constant at 160°C and $\alpha = 0.5$ has been calculated using the Arrhenius equation and these values are collected in Table 1. In agreement with the results presented in Figures 2 and 3, the kinetic constant decreases significantly on increasing the content in star polymer. These values are smaller than those found when a multiarm star poly(glycidol)-b-poly(ϵ -caprolactone) polymer was used as modifier [27]. It is hypothesized that the higher rigidity of the poly(styrene) core in comparison with the poly(glycidol) core can justify the observed differences between both modifiers, leading to more mobility restrictions caused by the participation of PS-10 in the curing process. However, on the basis of the results so far, in which PS-10 participates in a different way, the formation of a less active species should not be discarded.

In Table 1 the ultimate glass transition temperatures of the different systems are reported. The ultimate glass transition temperature is lower than the predicted by the Fox equation [34] and other common mixing rules. This indicates a strong modification of the structure of the epoxy matrix on samples thermally cured containing PS-10. Before curing, the star polymer has a compact structure due to the large

number of intermolecular H-bonds and intramolecular H-bond interactions. These types of interactions decrease when the terminal hydroxyl groups react with the epoxy groups. The PS-10 molecules incorporated into the network increase the free volume and reduce considerably the crosslinking density and consequently the T_g of the cured materials, even below the T_g calculated with Fox equation and other common mixing rules. The difference between $T_{g\infty}$ and the calculated T_g is much lower in the case of DGEBA modified with 10% of PS-10. Probably, this behaviour can be related to the fact that in some extent a part of OH groups in PS-10, in formulations containing a 10% of PS-10, are not completely covalently bonded to the epoxy matrix.

4.2. Photocuring

Figure 4 shows the heat flow and the degree of conversion (see inset) versus the photocuring time of DGEBA and DGEBA modified with different proportions of PS-10 at 120°C. Although the modified systems have a higher proportion of photoinitiator, PS-10 produces a strong deceleration of the photocuring process. In the case of neat DGEBA, vitri-

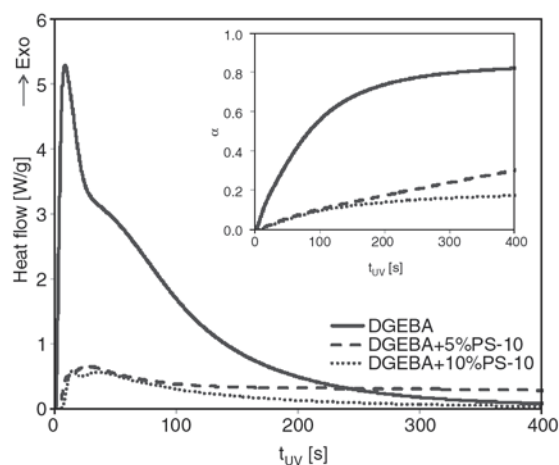


Figure 4. Heat flow and degree of conversion (as an inset) of the photocuring process of neat DGEBA and DGEBA modified with different proportions of PS-10 at 120°C

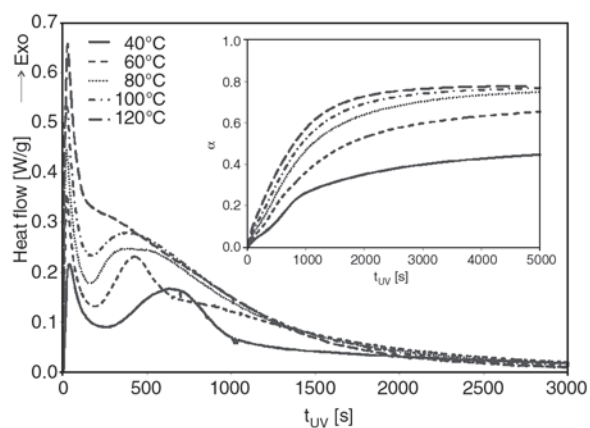
Table 3. Values of Δh_{iso} in kJ/ee for the photocuring of DGEBA modified with different proportions of PS-10 and temperatures

% PS-10	40°C	60°C	80°C	100°C	120°C
0	55.3	67.3	75.5	80.8	85.3
5	46.3	66.0	74.2	75.3	75.9
10					19.4

Table 4. Values of α_{iso} for the photocuring of DGEBA modified with different proportions of PS-10 and temperatures

% PS-10	40°C	60°C	80°C	100°C	120°C
0	0.555	0.676	0.758	0.811	0.856
5	0.473	0.674	0.759	0.770	0.776
10					0.196

fication was achieved at the end of the 30 min of irradiation time. However, in the case of DGEBA with 5% of PS-10, the photocuring process needed to be extended to longer irradiation times (see Figure 4), as described in the experimental section, in order to reach vitrification. As can be seen in Tables 3 and 4, the values of Δh_{iso} (isothermal curing heat) and α_{iso} (degree of conversion after the photocuring experiment) are only slightly lower than the attained ones when the formulation is the neat DGEBA. The photocuring process practically ends at the same time in the case of neat formulation and DGEBA modified with 10% of PS-10, as it can be appreciated from the inset of Figure 4. But, as observed in Tables 3 and 4, the values of Δh_{iso} and α_{iso} for the modified system at 120°C are much smaller than the corresponding to neat DGEBA. The heat of reaction is very low for temperatures below 120°C for DGEBA modified with 10% of PS-10 which indicates that the formulations with 10% of PS-10 hardly react even at high temperatures, whereas photocuring of neat DGEBA is near complete and only restricted by vitrification. For all these reasons the photocuring process of DGEBA modified with 5% of PS-10 has been analyzed as in the case of neat DGEBA. On the other hand, in the case of DGEBA with 10% of PS-10 the kinetics of the photocuring process has not been studied due to the low value of the heat involved in the photocur-

**Figure 5.** Heat flow and degree of conversion (as an inset) of the photocuring process of DGEBA modified with 5% of PS-10 at different temperatures

ing and only the kinetics of a subsequent thermal post-curing has been analyzed instead.

Figure 5 shows the heat flow and the degree of conversion (see inset) versus the photocuring time of DGEBA with 5% of PS-10 at different temperatures. As usually reported for other photocuring systems [35], at the beginning of the process the heat flow and the degree of conversion increase with temperature. At the lower temperatures two peaks appear, probably related to the existence of two propagation mechanisms, AM and ACE. The time corresponding to the second peak decreases on increasing the temperature. At 120°C this second peak disappears and it becomes a shoulder of the mean peak.

The kinetics of the photocuring process for neat DGEBA and DGEBA with 5% of PS-10 between 80 and 120°C has been analyzed using the isoconversional methodology explained above. Using Equation (7), the activation energy for every degree of conversion has been found. The results are collected in Table 5. While for neat DGEBA formulation the activation energy increases with the degree of conversion, when a 5% of PS-10 is added the activation energy fluctuates, reaching slightly different values than the neat formulation. The different behaviour in the curing of both formulations can be explained by the complex influence of the time-dependent irradiation and subsequent photoinitia-

Table 5. Activation energy of the photocuring of DGEBA and DGEBA modified with 5% of PS-10 at different degrees of conversion

% PS-10	$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$	$\alpha = 0.6$
0	8.3	8.1	10.3	14.0	15.9	16.8	17.3
5	12.4	18.5	13.9	10.9	9.5	9.7	11.7

tion in the photocuring process, which is not, in consequence, only a temperature-dependent process [36]. It can also be hypothesized that the presence of PS-10 may interfere with the curing process, resulting in the formation of different active species, as discussed below. The competition between AM and ACE mechanism and the different protogenic nature of the reaction medium can also help to explain the observed differences [37].

Figures 6 and 7 show the heat flow of the dynamic postcuring experiment of neat DGEBA and the formulation with 5% of PS-10, respectively, made after the photocuring experiences at the temperatures indicated. In the case of neat DGEBA (Figure 6), it can be observed that the post-curing process begins at temperatures above the temperature of isothermal photocuring and shows two maxima that appear at the lower temperatures (40, 60 and 80°C). The height of the first one decreases on increasing the curing temperature. At 100°C this first peak becomes a shoulder and at 120°C this shoulder completely disappears. The height of the

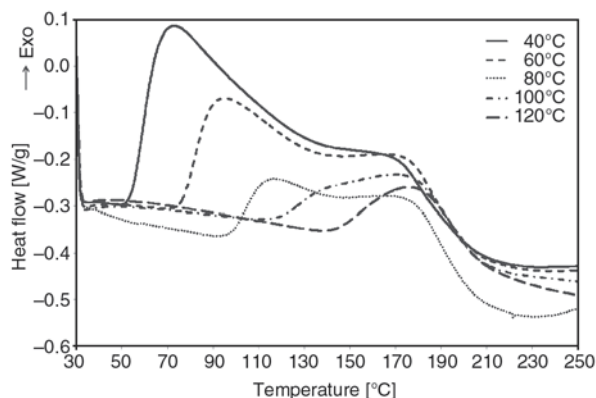


Figure 6. Dynamic postcuring of neat DGEBA after photocuring process at different temperatures

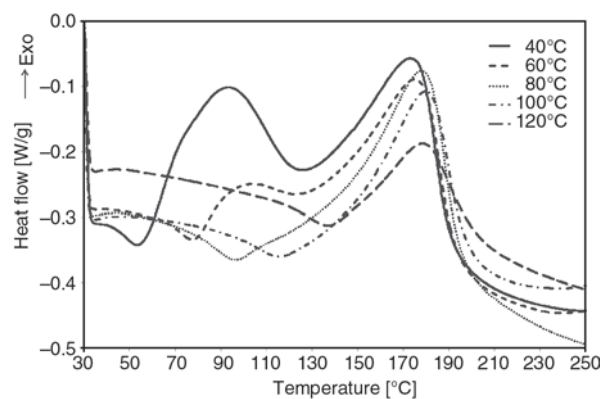


Figure 7. Dynamic postcuring of DGEBA modified with 5% of PS-10 after photocuring process at different temperatures

second peak hardly varies, because its temperature is higher than that of the photocuring process. The first exotherm, which starts at a temperature close to the photocuring temperature [38], can be associated with the propagation of active species formed during photocuring and entrapped in the vitrified material, and the second one with the propagation of less mobile species after structural relaxation of the network [39] or reactivation of dormant tertiary oxonium cations by increasing the temperature [32]. When DGEBA is modified with 5% of PS-10, a glass transition is clearly observed before the onset of the first exothermic peak, which is displaced towards higher temperatures when photocuring temperature increases (Figure 7). At the lower temperatures (40 and 60°C) two peaks appear. The first one becomes a shoulder at 80°C and at higher temperatures it disappears. The height of the second peak decreases on increasing the temperature. With the exception of the curve registered after a photocuring at 40°C, the size of the second peak is always larger than that of the first peak. However, in the case of neat DGEBA, the size of the first peak is higher than the second peak at the lower temperatures (see Figure 6). Although the nature of two peaks in 5% of PS-10 formulation is expected to be the same as in the neat formulation, the high intensity of the second peak for all photocuring temperatures suggests the formation of a dormant species during photocuring, which can be reactivated when the temperature increases (during second peak). It was previously described that the presence of nitrogen in the chemical structure of the epoxy monomers prevents photopolymerization or photocrosslinking reaction to occur. The degree of retardation depends both on the amount and basicity of the amine concerned [40]. Thus, the presence of nitrogen in the structure of stars could be the reason for the inactivation of the photocuring process, because nitrogen atoms in the form of tertiary amine can interact with the protons generated by the irradiation on the photocuring initiator, producing ammonium salts, because of their basic character. However, it should be commented that the study was done with monomers containing nitrogen in the structure, which leads to a high proportion of this heteroatom in the mixtures and no reactivation by heating of the sample was tested. Endo and Sanda [41] reported that benzyl ammonium salts can act as latent thermal initiators. Thus, it seems reasonable that the inacti-

vation of the photocuring process by the presence of benzylic amine moieties in the multiarm star structure can be followed by the reactivation at high temperature by the breakage of the benzylic ammonium salt. This breakage produces benzylic cations capable of initiating the thermal cationic polymerization of epoxides. The low nucleophilicity of the anion, hexafluoroantimonate, helps to increase the reactivity of these species.

The *in situ* generation of a thermal initiator by a photoirradiation process by addition of the PS-10 stars to the epoxy formulation opens the way to a new dual curing system, related to another previously described [42]. In that case, the responsible of the dual behaviour was the presence of a hyperbranched modifier in the formulation with thioether as repeating unit, which can be transformed into alkyl sulfonium species upon photolysis of the photoinitiator. Sulfonium cations can also act as cationic thermal latent initiators. However, the structure of the hyperbranched modifier with a huge proportion of thioether groups in the modifier structure led to a higher functionality as macroinitiator, which is not the case of the star structures, having an only benzylamine group per arm.

Figure 8 shows the heat flow and the relative conversion degree (as an inset) of the postcuring scan at different heating rates, made after photocuring samples of DGEBA with 10% of PS-10 at 120°C

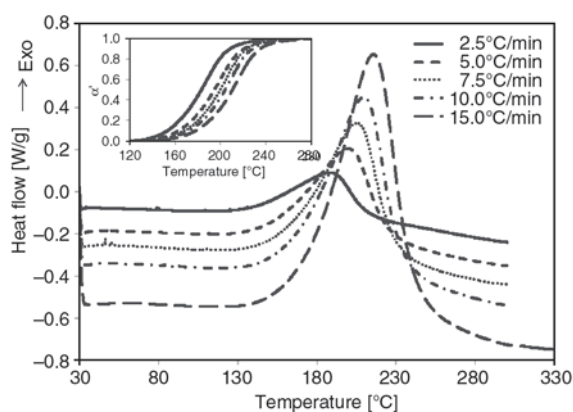


Figure 8. Dynamic postcuring (after UV irradiation) at different heating rates and relative conversion degree (as an inset) of DGEBA modified with 10% of PS-10

Table 6. Activation energy and pre-exponential factor of the thermal curing of DGEBA modified with 10% of PS-10 after photocuring at 120°C at different relative conversion degrees

	$\alpha' = 0.05$	$\alpha' = 0.1$	$\alpha' = 0.2$	$\alpha' = 0.3$	$\alpha' = 0.4$	$\alpha' = 0.5$	$\alpha' = 0.6$	$\alpha' = 0.7$	$\alpha' = 0.8$	$\alpha' = 0.9$	$\alpha' = 0.95$
E [kJ/mol]	119.4	114.8	112.9	114.3	117.0	120.0	123.2	126.4	130.5	139.1	148.1
k_0 [s ⁻¹]	$1.45 \cdot 10^{10}$	$4.07 \cdot 10^9$	$2.25 \cdot 10^9$	$2.91 \cdot 10^9$	$5.32 \cdot 10^9$	$1.06 \cdot 10^{10}$	$2.15 \cdot 10^{10}$	$4.32 \cdot 10^{10}$	$1.00 \cdot 10^{11}$	$5.44 \cdot 10^{11}$	$2.61 \cdot 10^{12}$

for 30 min. It can be observed that only one strong peak appears at high temperature. When the same formulation was thermally cured without previous UV-irradiation, the thermogram did not show any exotherm. These results suggest, as it had been hypothesized, that in presence of PS-10, UV irradiation promotes the formation of a thermal macroinitiator (dormant species), by reaction between the amine groups of PS-10 and the proton resulting from the photolysis of the photoinitiator upon irradiation, which can be subsequently activated by heating. However, this curing system shows a small latency since the slope of the stimulation-activity curve is small (see inset in Figure 8) [41].

Table 6 shows the results of the isoconversional analysis based on DSC thermograms of Figure 8. Using Equation (5), the activation energy has been found for some values of relative conversion degrees. This magnitude first decreases, but after $\alpha' = 0.2$ it increases. The high activation energy values obtained in comparison with those obtained during photocuring (Table 5) suggests again the formation of dormant species during UV irradiation which can act as thermal initiator upon heating. In the same table the values of the preexponential factor using R_3 model are also collected.

Table 1 shows the $T_{g\infty}$ of DGEBA with 5% of PS-10. These values are lower than those calculated using common mixing rules, indicating a modification of the structure of the epoxy matrix. However, the difference between $T_{g\infty}$ and the calculated T_g is smaller than in the case of the thermal curing. As it has been stated, the number of intermolecular and intramolecular H-bond interactions and the degree of chemical incorporation of PS-10 to the epoxy matrix, can justify the differences between the experimental and calculated $T_{g\infty}$. The value of the $T_{g\infty}$ of DGEBA with 10% of PS-10 is also smaller than the calculated ones, indicating a structural modification of the epoxy matrix. In fact, the breakage of the star structure by formation of benzylic cations should lead to the separation of the arms from the hyperbranched core. This process can occur to some extent, but should produce a plasticization of the matrix that counteracts the effect of the multifunc-

tional character of the benzylic hyperbranched initiator formed. Although the reason of this behaviour can be rationalized in a similar way to 5% PS-10 formulation, the fact that some part of PS-10 phase separates during curing, (as it will be seen later by scanning electron microscopy) can probably have an influence on the $T_{g\infty}$ value. The values of $T_{g\infty}$ found after photocuring are higher than those found after thermal curing (Table 1), because ytterbium triflates are able to induce reorganization, cyclization and/or degradation reactions when the curing reaches too high temperatures, which results in a network structure with a lower degree of crosslinking and consequently with a lower $T_{g\infty}$ [43, 44].

4.3. Fracture morphology by SEM

The topography of photocured and postcured samples of neat DGEBA and DGEBA with 10% of PS-10 have been investigated by SEM. The microphotographs of the fracture surface are collected in Figure 9 and 10, respectively. The existence of an only homogeneous phase in the neat DGEBA and the presence of two phases in DGEBA with 10% of PS-10 can be observed. This material shows a rougher appearance than the neat formulation, based on rod-like particles with a size of ca 50–500 nm homogeneously dispersed. It is worth to state that thermally cured samples do not show evidences of a second phase. So, it is expected that PS-10 modifier can improve the fracture properties of DGEBA by a phase-separation mechanism, only when the material is previously UV irradiated.



Figure 9. Surface morphology obtained by SEM of neat DGEBA

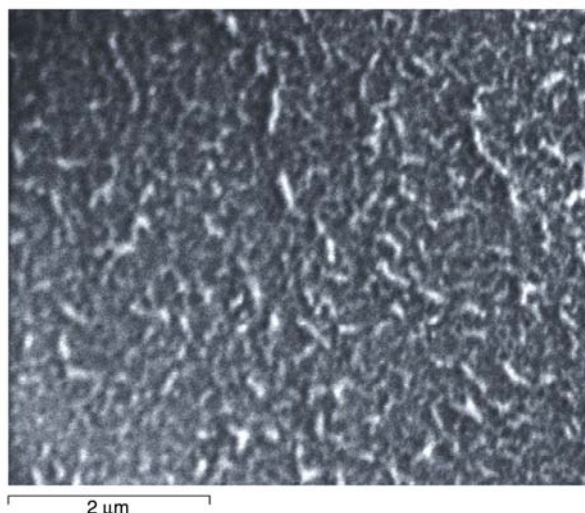


Figure 10. Surface morphology obtained by SEM of DGEBA modified with 10% of PS-10

5. Conclusions

PS-10 decelerates the thermal curing of DGEBA, modifying significantly the structure of the epoxy matrix in terms of ultimate glass transition temperature. PS-10 also decelerates the photocuring process of DGEBA but in a different way. With a 5% of PS-10, the process is significantly delayed but can proceed to vitrification, as in modified DGEBA. With a 10% of PS-10 the photocuring is strongly limited and it is necessary a subsequent thermal curing to reticulate the sample. The decelerating effect on the photocuring process is explained in terms of the formation of dormant species by protonation of the amine groups in the multiarm star molecule. The benzylic ammonium salts formed are reactivated upon heating, thus acting as a thermal initiator. Thus the addition of PS-10 to the epoxy formulation leads to a new dual photo-thermal curing system. Upon irradiation a benzylic cationic multifunctional initiator is formed, which can act a thermal curing system. In the photocuring process the addition of PS-10 also modifies the structure of the epoxy matrix, but in a lower extent than in the thermal curing.

Depending on the initiation conditions, thermal or UV induced, and on the amount of PS-10 it is possible to obtain tailor-made thermosets with different thermal and mechanical properties and morphology. The resulting morphology of DGEBA/PS-10 formulations UV-cured is that of nanosize ‘rod-like’ of homogeneously dispersed particles in the epoxy matrix, with a potential capacity of increasing toughness of UV-cured DGEBA thermosets.

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