Epoxy/anhydride thermosets modified with end-capped star polymers with poly(ethyleneimine) cores of different molecular weight and poly(ϵ -caprolactone) arms

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Abstract. Multiarm star polymers, with a hyperbranched poly(ethyleneimine) (PEI) core and poly(ϵ -caprolactone) (PCL) arms end-capped with acetyl groups were synthesized by ring-opening polymerization of ϵ -caprolactone from PEI cores of different molecular weight. These star polymers were used as toughening agents for epoxy/anhydride thermosets. The curing process was studied by calorimetry, thermomechanical analysis and infrared spectroscopy. The final properties of the resulting materials were determined by thermal and mechanical tests. The addition of the star polymers led to an improvement up to 130% on impact strength and a reduction in the thermal stresses up to 55%. The structure and molecular weight of the modifier used affected the morphology of the resulting materials. Electron microscopy showed phase-separated morphologies with nano-sized fine particles well adhered to the epoxy/anhydride matrix when the higher molecular weight modifier was used.

Keywords: thermosetting resins, star polymers, epoxy resin, toughness, thermal stress

1. Introduction

Epoxy resins are extensively used in technological fields such as electricity and electronics. They are employed as adhesives, matrices in advanced composites, surface coatings and device assemblies because of their combination of high strength and stiffness, excellent corrosion resistance and good electrical properties [1–3]. However, their inherent rigidity and high crosslinking density makes them brittle, thus limiting their potential range of applications. In addition, when epoxy thermosets are used as coatings, thermal stresses generated from the mismatch between the thermal expansion coefficients

(CTE) of the coating and of the metallic substrate can lead to the appearance of defects that can limit their service life, such as the generation of microvoids and microcracks, the loss of adhesion due to warping. Thermal stress generated during cooling from the curing temperature down to operating conditions, typically room temperature, tends to be more severe than that consequence of heating or during service at constant temperature, especially when the temperature is below glass transition temperature (T_g) of the thermoset [4].

One of the most successful routes towards toughness improvement is to incorporate polymeric mod-

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ifiers into the thermosetting matrix to form fine morphological structures. Some effective polymer modifiers are liquid rubber [5], thermoplastics [6] or core-shell particles [7]. In general, these modifiers are initially miscible with the uncured thermoset precursors but partially or completely phase-separate to typically form spherical structures or bicontinuous structures. The problem of this strategy is a sharp increase of the viscosity of the blends, the drop in the modulus and glass transition temperature and sometimes the poor interfacial adhesion between phases. Recently, a significant toughening effect has been achieved without compromising other properties and processability by using dendritic polymers, especially if the structure and properties of the modifier have been tailored to enhance the physical and chemical interaction between them and the matrix. The improvement in toughness can be achieved by chemically induced phase separation (CIPS) or by *in situ* homogeneous reinforcing and toughening mechanism, but in both cases covalent linkages or a good compatibility between the modifier and the matrix are necessary [8–16].

The thermal stresses generated during cooling of thermosetting coatings applied over metal can be minimized by reducing the *CTE* and elastic modulus in the glassy state of the coating, as well as by decreasing its T_g , which in certain applications may not be desired. We recently reported the use of multiarm stars with poly(ethyleneimine) core and poly(ϵ -caprolactone) or poly(lactide) arms as modifiers in the curing of DGEBA using a tertiary amine as anionic curing agent [17, 18]. Upon addition of the modifiers, the decrease on T_g and glassy modulus led to a significant reduction in internal stresses, in spite of the increase in the glassy *CTE*. In another work, it could be seen that the addition of hyperbranched poly(ester-amide)s to epoxy/anhydride systems allowed reaching a significant reduction of the *CTE* in the glassy state and consequently on the thermal stress [19], the effect being more important when higher molecular weight modifiers were used. Recently, we used multiarm star polymers with hyperbranched poly(ethyleneimine) core and poly(ϵ -caprolactone) arms of different length with reactive and unreactive terminal groups as modifiers of epoxy/anhydride thermosets [20]. The overall stresses, measured on a steel substrate using the beam bending technique, were significantly reduced with modifiers containing reactive hydroxyl terminal groups

and low degree of polymerization of the poly(ϵ -caprolactone) arms.

Taking all these precedents into account, in the present work we synthesized, following the ‘core-first’ approach, multiarm star polymers with hyperbranched poly(ethyleneimine) cores of different molecular weight and poly(ϵ -caprolactone) short arms. All the end hydroxyl groups resulting from the polymerization of ϵ -caprolactone were end-capped with acetyl moieties, but some amine groups of the poly(ethyleneimine) remain unmodified and can potentially react with epoxy groups. These multiarm star polymers were used to modify diglycidylether of bisphenol A/methyl hexahydrophthalic anhydride formulations in the presence of benzyl dimethyl amine as catalyst.

The synthesis of an amphiphilic modifier with hydrophilic core and hydrophobic shell, aimed at reaching phase-separated morphologies. The existence of reactive amino groups in the hyperbranched core would permit the incorporation of the modifier into the network structure, enhancing the interfacial adhesion between phases, if present. Moreover, the hydrophobic poly(ϵ -caprolactone) arms could contribute to the good interfacial adhesion between the hydrophobic matrix and the modifier-rich phase. To summarize, the goal of the present work is to enhance the toughness and reduce the internal stress in epoxy/anhydride formulations using amphiphilic star polymers with cores of different molecular weight, end-capped arms and reactive amine groups in the core structure.

The curing process was studied by calorimetry, infrared spectroscopy and thermomechanical analysis and the curing kinetics was analyzed by model-free and model-fitting methods. The final properties of the resulting materials were characterized by means of thermogravimetry, thermomechanical analysis and electron microscopy on the fracture surface. Impact resistance was evaluated by Izod impact tests and thermal stresses were estimated on the basis of *CTE*, T_g and elastic modulus measurements.

2. Experimental

2.1. Materials

Poly(ethyleneimine) (PEI) Lupasol®FG (M_w = 800 g/mol, data sheet) and Lupasol®WF (M_w = 25 000 g/mol, data sheet) were kindly donated by BASF (Ludwigshafen, Germany) and used without

further purification. From the molecular weight of the polymer and of the repeating unit, average degrees of polymerization of 18.3 for Lupasol[®]FG and 581.4 for Lupasol[®]WF were calculated. According to the data sheet, the relationship (NH₂/NH/N) was (1/0.82/0.53) for Lupasol[®]FG and (1/1.2/0.76) for Lupasol[®]WF, therefore the equivalent number of primary, secondary and tertiary amines is 10, 8.4, and 5.3 meq/g for Lupasol[®]FG and 8.0, 9.6, and 6.1 meq/g for Lupasol[®]WF.

ϵ -Caprolactone (ϵ -CL, 97%) was distilled under vacuum before use. Tin (II) 2-ethylhexanoate (Sn(oct)₂, 98%), *N,N*-dimethylbenzylamine (BDMA, >99%) and methyl hexahydrophthalic anhydride (MHHPA) were used without further purification. All these chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). For the end-capping process by acetylation, extra pure acetic anhydride was used and purchased from Scharlau (Sentmenat, Spain). Triethyl amine (TEA) and *N,N*-dimethylamino pyridine (DMAP) were purchased from Fluka (Sentmenat, Spain). Chloroform (CHCl₃) was dried under CaCl₂ and distilled before use. Solvents were purchased from Scharlab (Sentmenat, Spain).

Diglycidylether of bisphenol A (DGEBA) with an epoxy equivalent of 187 g/eq (Epikote 828, Hexion Speciality Chemicals B.V. Louvain, Belgium) was dried for 4 hours at 40°C under vacuum before use.

2.2. Synthesis of

poly(ethyleneimine)-poly(ϵ -caprolactone) end-capped multiarm stars (PEIX)

In the acronyms for both types of stars (PEIX), X accounts for the data sheet molecular weight times 10⁻² and take the values of 8 and 250 for Lupasol[®]FG and Lupasol[®]WF, respectively.

The hydroxyl terminated star polymers were synthesized by ring-opening polymerization of ϵ -capro-

lactone from a hyperbranched poly(ethyleneimine) core in bulk at 130°C. The acetylation to obtain PEIX was performed with acetic anhydride at room temperature overnight in the presence of TEA and a catalytic amount of DMAP in CHCl₃ solution as previously described [17, 20]. Figure 1 depicts the synthetic procedure applied in the preparation of the stars.

For both PEIX star polymers ¹H NMR (400 MHz, CDCl₃, δ in ppm): 4.08 (–CH₂–OCO–), 2.32 (–NHCO–CH₂–, –CH₂–COO), 1.92 (OCO–CH₃), 1.70–1.30 (–CH₂–, CL chain) and 3.5–1.5 (PEI core). The structural data of the stars prepared determined by ¹H NMR and values in data sheet were as follows:

PEI8: polymerization degree of arms is 11.8. Fraction of unmodified primary/secondary amines of 0.15. *T_g* = –54°C, *T_m* = 58°C, Δh_m = 96 J/g, *T_{max}* = 390°C (temperature of the maximum rate of weight loss calculated by TGA).

PEI250: polymerization degree of arms is 13.5. Fraction of unmodified primary/secondary amines of 0.26. *T_g* = –59°C, *T_m* = 50°C, Δh_m = 75 J/g, *T_{max}* = 390°C.

2.3. Preparation of curing formulations

Mixtures containing MHHPA and the selected proportion of the star polymer were heated mildly until the modifier was dissolved and the solution became clear. The mixture was then cooled down to room temperature and added to the corresponding amount of DGEBA and catalyst. Finally, samples were carefully stirred and degassed under vacuum (at 40°C) during 15 min to prevent the appearance of bubbles during curing. The catalyst, BDMA, was used at a concentration of 1 phr (1 part of catalyst per hundred parts of DGEBA/MHHPA mixture). The modifier was added at concentrations of 5, 10 and 20% with

Figure 1. Synthetic procedure for the preparation of the multiarm stars PEI8 and PEI250

Table 1. Notation and composition of the neat and modified formulations in weight percentage [wt%] and in equivalents per gram of mixture. The weight percentage of the star polymer is indicated in formulation.

Formulation	DGEBA		MHHPA		BDMA		NH from SP
	[wt%]	[eq/g]	[wt%]	[eq/g]	[wt%]	[eq/g]	[eq/g]
Neat	52.1	$2.79 \cdot 10^{-3}$	46.9	$2.79 \cdot 10^{-3}$	0.99	$7.32 \cdot 10^{-5}$	0
5% PEI8	49.6	$2.65 \cdot 10^{-3}$	44.7	$2.65 \cdot 10^{-3}$	0.94	$6.97 \cdot 10^{-5}$	$3.95 \cdot 10^{-6}$
10% PEI8	47.4	$2.53 \cdot 10^{-3}$	42.6	$2.53 \cdot 10^{-3}$	0.90	$6.66 \cdot 10^{-5}$	$7.54 \cdot 10^{-6}$
20% PEI8	43.4	$2.32 \cdot 10^{-3}$	39.1	$2.32 \cdot 10^{-3}$	0.83	$6.10 \cdot 10^{-5}$	$1.38 \cdot 10^{-5}$
5% PEI250	49.6	$2.65 \cdot 10^{-3}$	44.7	$2.65 \cdot 10^{-3}$	0.94	$6.97 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$
10% PEI250	47.4	$2.53 \cdot 10^{-3}$	42.6	$2.53 \cdot 10^{-3}$	0.90	$6.66 \cdot 10^{-5}$	$1.92 \cdot 10^{-5}$
20% PEI250	43.4	$2.32 \cdot 10^{-3}$	39.1	$2.32 \cdot 10^{-3}$	0.83	$6.10 \cdot 10^{-5}$	$3.51 \cdot 10^{-5}$

respect to DGEBA/MHHPA/BDMA mixture. Table 1 collects the notation and composition of the different formulations studied.

Fully cured samples for DMA, TMA, TGA, DSC, impact and SEM assays were prepared by isothermal curing in oven at 100°C for 2 h followed by a postcuring at 180°C for one hour.

2.4. NMR Spectroscopy

^1H NMR and ^{13}C NMR measurements were carried out at 400 and 100.6 MHz, respectively, in a Varian Gemini 400 spectrometer (Palo Alto, USA). CDCl_3 was used as solvent. For internal calibration the solvent signals were used: $\delta (^{13}\text{C}) = 77.16$ ppm and $\delta (^1\text{H}) = 7.26$ ppm for CDCl_3 .

2.5. Calorimetric measurements (DSC)

Calorimetric analyses were carried out on a Mettler DSC-822e thermal analyser (Greifensee, Switzerland). The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-zinc standard (temperature calibration).

Samples of approximately 10 mg were placed in aluminium pans with pierced lids and cured non-isothermally from 0 to 300°C at heating rates of 2, 5, 10 and 15°C/min, under nitrogen atmosphere, to determine the reaction heat associated with the complete conversion of all reactive groups and study the curing kinetics. In a non-isothermal curing process, the degree of conversion by DSC 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 this temperature, and Δh_{dyn} is the total reaction heat associated with the complete conversion of all reactive groups. The reaction rate $d\alpha/dt$ was calculated

as the first derivative of the conversion with respect to time.

The glass transition temperatures ($T_{\text{g}\infty}$ s) of the obtained thermosets, uncured materials and star polymers were determined by means of a scan at 10°C/min under nitrogen atmosphere, 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 $\pm 1^\circ\text{C}$.

In order to predict the theoretical glass transition temperature of the formulations, Fox equation (Equation (2)) was used:

$$\frac{1}{T} = \frac{w}{T_{\text{g,SP}}} + \frac{1-w}{T_{\text{g,matrix}}} \quad (2)$$

where $T_{\text{g,SP}}$ and $T_{\text{g,matrix}}$ are the glass transition temperatures of the star polymer and neat epoxy/anhydride matrix respectively and w is the weight fraction of star polymer in the formulation.

2.6. Curing kinetics (DSC)

The linear integral isoconversional, model-free method of Kissinger-Akahira-Sunose (KAS) was used for the determination of the activation energy based on the non-isothermal curing curves, as shown by Equation (3):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A \cdot R}{g(\alpha) \cdot E}\right) - \frac{E}{RT} \quad (3)$$

β is the heating rate, T the temperature, E the activation energy, A the pre-exponential factor, R the gas constant, and $g(\alpha)$ the integral conversion function. For each conversion degree, the representation of $\ln(\beta/T^2)$ versus $1/T$ produces a straight line and makes it possible to determine E and $\ln[A \cdot R/(g(\alpha) \cdot E)]$ from the slope and the intercept without knowing the kinetic model.

Isoconversional isothermal curing times, t , were estimated taking the non-isothermal data $\ln[A \cdot R/(g(\alpha) \cdot E)]$ and E , determined from Equation (3), and applying the rate equation integrated in isothermal conditions, as shown by Equation (4):

$$\ln t = \ln \left(\frac{g(\alpha)}{A} \right) + \frac{E}{RT} \quad (4)$$

Assuming that the approximation given by expression (3) is valid, we can determine the kinetic model that best describes the curing process by rearranging expression (3) as shown in Equation (5):

$$\ln \left(\frac{g(\alpha) \cdot \beta}{T^2} \right) = \ln \left(\frac{A \cdot R}{E} \right) - \frac{E}{RT} \quad (5)$$

which is the basis for the composite integral method for the determination of the kinetic model. Given that the curing of epoxy-anhydride can be satisfactory modelled using autocatalytic-like models with an overall reaction order around 2, we have fitted using Equation (5) the experimental data to autocatalytic kinetic models with $n + m = 2$, where n and m are the order of reaction.

The results of the kinetics analysis were used to model the curing and to determine the optimum curing times to achieve fully cured thermosets. In addition, isothermal curing times determined by simulation of non-isothermal kinetic data (Equations (3) and (4)) were compared with experimental isothermal curing times obtained by means of FTIR experiments.

Details of the kinetic methodology used can be found in previous works [21, 22].

2.7. FTIR spectroscopy

A Bruker Vertex FTIR spectrometer (Ettlingen, Germany) equipped with an attenuated-total-reflectance accessory with a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma, Sant Cugat del Vallés, Spain) was used to monitor the curing process. Spectra were acquired in the mid-infrared region (spectral range of 600–4000 cm^{-1}) with a resolution of 4 cm^{-1} . 20 scans were averaged for each spectrum. The evolution of the functional groups was monitored during isothermal curing at 100°C, taking the band at 1508 cm^{-1} , attributed to the DGEBA aromatic rings, as a reference. The conversion was determined by the Lambert-Beer law from the normalized change of absorbance at 1732 cm^{-1} (formation ester groups) and at

1860+1785 cm^{-1} (disappearance of anhydride group) as explained in a previous work [22].

2.8. Thermomechanical analysis (TMA)

A thermo-mechanical analyzer Mettler thermomechanical analysis SDTA840 (Greifensee, Switzerland) was used to determine the conversion at the gel point and the thermal expansion coefficients.

A silanized glass fiber disc about 5 mm in diameter was impregnated with the liquid formulation and sandwiched between two aluminium discs. The sample was heated up from 40 to 200°C at 2°C/min and subjected to an oscillatory force from 0.005 to 0.01 N with an oscillation frequency of 0.083 Hz. The gel point temperature was taken as the onset in the decrease of the oscillation amplitude measured by the probe. The conversion at the gel point was determined from the gel point temperature and a dynamic curing experiment in the DSC at 2°C/min.

Cured samples (1.5×8×8 mm^3) were supported by two silica discs and heated at 5°C/min from 30 up to 150°C by application of a force of 0.02 N. Two heating scans were performed, the first one to erase the thermal history and the second one to determine the thermal expansion coefficients (CTEs), below and above the T_g , calculated according to Equation (6):

$$CTE = \frac{1}{L_0} \cdot \frac{dL}{dT} = \frac{1}{L_0} \cdot \frac{\frac{dL}{dt}}{\frac{dT}{dt}} \quad (6)$$

where, L is the thickness of the sample, L_0 the initial length, t the time, T the temperature and dT/dt the heating rate.

2.9. Dynamic mechanical analysis (DMA)

DMA was carried out with a TA Instruments DMA Q800 (New Castle, DE, USA). Three point bending of 10 mm at 1 Hz and 0.05% strain was performed at 3°C/min from –150 to 250°C on prismatic rectangular samples (ca. 2×12×20 mm^3).

2.10. Thermal stress

The thermal stress caused by the variation of the temperature, σ_{th} , in a bi-layer strip (epoxy-anhydride coating/steel substrate) was determined from the radius of curvature, R , in the assumptions of the simple beam theory and from the free body analysis of strains in the two layers. The calculation was made

taking account the dependence on the geometrical parameters and properties of the sample and substrate, according to Benabdi and Roche methodology [23], see Equations (7) and (8):

$$\frac{1}{R} = \frac{6(1+\beta)^2(SFT - T_{amb})(CTE_c - CTE_s)}{(t_c + t_s) \left[3(1+\beta)^2(1+\alpha\beta) \left(\beta^2 + \frac{1}{\alpha\beta} \right) \right]} \quad (7)$$

$$\sigma_{th} = \frac{1}{R} \cdot \frac{E_s \cdot t_s}{6} \left[\frac{1}{\beta(\beta + 1)} (\alpha\beta^3 + 1) + 3\alpha\beta \right] \quad (8)$$

where the subscripts *c* and *s* mean coating and substrate respectively, *t* is the thickness, *E* the elastic modulus, $\alpha = E_c/E_s$, $\beta = t_c/t_s$, *SFT* is the stress free temperature taken as the transition glass transition temperature determined by TMA and *T_{amb}* is the ambient temperature taken as 40°C.

In this study a stainless steel, with an elastic modulus of 180 053 MPa and thermal expansion coefficient of $16 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$, was selected as the substrate and the thickness of the steel substrate and the epoxy/anhydride coating was respectively 0.1 and 0.4 mm. The elastic modulus of epoxy/anhydride sample was determined by DMA.

2.11. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with a Mettler TGA/SDTA 851e/LF/1100 thermobalance (Greifensee, Switzerland). Samples with an approximate mass of 10 mg were degraded between 30 and 800°C at a heating rate of 10°C/min in a nitrogen atmosphere (50 cm³/min measured in normal conditions).

2.12. Impact resistance

The impact test was performed at room temperature by means of an Zwick 5110 impact tester (Ulm, Germany) according to ASTM D 4508-10 (2010) using rectangular samples (2×12×25 mm³). The pendulum employed had a kinetic energy of 0.5 J. For each material, nine determinations were made. The impact strength (*IS*) was calculated from the energy absorbed by the sample upon fracture according to Equation (9):

$$IS = \frac{E - E_0}{S} \quad (9)$$

where *E* and *E₀* are the energy loss of the pendulum with and without sample respectively, and *S* is the cross-section of the samples.

2.13. Electron microscopy analysis (SEM)

The fracture surface of the samples, previously fractured by impact at room temperature, was coated with a conductive gold layer and then examined with a Jeol JSM 6400 SEM (JEOL Ltd., Tokyo, Japan) with a resolution of 3.5 nm and different magnifications (100, 500 10 000 and 50 000).

3. Results and discussion

3.1. Synthesis and characterization of multiarm stars

The synthesis of the multiarm stars was performed as previously described in two different papers, one of them describing the growing of the poly(ε-caprolactone) arms from the PEI core and the other to the blocking of hydroxyl end-groups by reaction with acetic anhydride [17, 20]. The length of the arms can be adjusted, in principle, from the amount of ε-CL per reactive group in the core (NH and NH₂). In this paper, PEI cores of 800 and 25 000 g/mol of mass-average molecular weight were employed.

The multiarm star molecules were characterized by ¹H NMR spectroscopy as done in the previous works [17, 20]. It could be seen that the increase in the molecular weight of the core did not change significantly the ¹H NMR spectrum. From the spectra of the hydroxyl-ended stars we could determine the degree of polymerization of the arms. However, in both cases the arms were longer (*DP* = 11.8 and 13.5) than expected (*DP* = 10) and the difference was higher for the larger core. Since all the ε-CL reacts, the higher polymerization degree of the arms calculated from the spectra led us to the conclusion that part of the NH- and NH₂ groups could not initiate the growth of an arm. From these values we estimated a degree of modification of 0.85 for the PEI8 core and of 0.74 for the PEI250 core. The effect of the core size is noteworthy, as the degree of modification of the PEI250 core is significantly lower. The hydrogen bond interactions and the steric hindrance could be the responsible for these differences. Although the evaluation of the modification achieved in terminal and linear units could not be accomplished, linear units seem to be less reactive because of the lower nucleophilicity of secondary amines and the more internal position of these units in the PEI structure. Moreover, intra-molecular hydrogen bonding in PEI may make difficult the penetration of ε-CL into the core structure and the subsequent polymerization reaction.

The acetylation of the hydroxyl groups at the end of the arms was performed as described and the spectra obtained were similar to the ones published before [20]. The complete disappearance of $-\text{CH}_2\text{OH}$ signals showed that all hydroxyl groups were blocked. The intensity of the methyl signals (at 1.92 ppm) allowed us to determine that unreacted NH groups were still in PEI8 and PEI250 structures.

By using linear standards the molecular weight of star polymers are usually underestimated by GPC and this method does not render accurate molecular weights. However, the GPC analysis did not produce signals at low molecular weight, meaning that no detectable poly(ϵ -caprolactone) homopolymer was formed during the ring-opening polymerization. In addition, the shape of the curves was unimodal in both PEI8 and PEI250, due to the living characteristics of the ϵ -CL polymerization.

3.2. Study of the curing and thermal properties of DGEBA/MHHPA/PEIX mixtures

The presence of hydroxyl groups and tertiary amines in epoxy-anhydride formulations, leads to a complex competitive mechanism consisting of polycondensation, initiated by hydroxyl groups, and ring opening polymerization, initiated by tertiary amine [19, 24]. Moreover the existence of secondary and/or primary amines in the reaction medium may also lead to a polycondensation between these groups and epoxy resin or even anhydrides and the concomitant appearance of new tertiary amines or amides. In previous works we reported the use of hyperbranched poly(ethyleneimine)s as crosslinking agents in epoxy formulations [25, 26], reacting by an epoxy-amine condensation mechanism and getting thus incorporated into the network structure of the thermoset. The curing kinetics was slowed down by their lower mobility in comparison with smaller amines and they led to more densely crosslinked materials due to the presence of internal branching points in the hyperbranched polymer structure. However, the total number of reactive amino groups introduced in the formulation is very small taking into account the elevated molecular weight of the stars polymers, and the effect would be difficult to quantify. It should be also noticed that not all the amine groups would be able to react because of steric hindrance or topology restrictions.

Figure 2. Reaction rate da/dt (a) and degree of conversion (b) against temperature of neat and PEI250 formulations at $10^\circ\text{C}/\text{min}$

Figure 2 shows the plots of degree of conversion and reaction rate against temperature recorded at $10^\circ\text{C}/\text{min}$ of neat formulation and formulations containing different amounts of PEI250. Calorimetric curves for neat and 5% showed a unimodal shape, which indicates that, the different curing mechanism takes place at the same time or that one of them predominates, in particular the epoxy-anhydride alternating copolymerization mechanism, due to the presence of BDMA. Formulations containing 10 and 20% of PEI250 show a secondary process at conversions above 0.8. Because epoxy-amine condensation may take place at a relatively low temperature [25, 26] this process, at high temperature and slow rate, could be related with the non-catalytic epoxy/anhydride curing mechanism or epoxy homopolymerization, although this is generally observed in anhydride-deficient formulations [27].

In the presence of a small amount of star polymer the curing is slightly accelerated possibly due to the additional tertiary amines coming from the modifier. When a higher amount of modifier is used (10 and 20%) the reaction rate decrease and the conversion-temperature curves shift at higher temperatures (Figure 2). In these last cases the higher viscosity of the formulations, the lower mobility of the reactive species and the lower content of epoxides may contribute to decelerate the curing rate of the epoxy/anhydride/PEIX formulations. Although the differences between formulations are not large, the relative influence of the discussed parameters can lead to acceleration or deceleration of the curing.

When PEI8 was used as modifier a similar trend was observed (not shown), although both effects, accel-

Figure 3. Activation energy during curing of neat and PEI250 formulations obtained by using the Kissinger-Akahira-Sunose method

eration at low modifier content and deceleration at high modifier content, take place to a lesser extent. This result can be rationalized on the basis of the lower tertiary amine content and viscosity of PEI8 than PEI250.

The nonisothermal curing kinetics was analyzed using the isoconversional KAS methodology (Equation (3)). Figure 3 shows that E remains constant during the entire range of conversions for neat and 5% formulations, whereas for 10 and 20% E is maintained constant up to a conversion of 0.8, to decrease sharply between 0.8 and 1. This result is consistent with the existence of two curing mechanisms, activated at different temperatures, in modifier-rich formulations (Figure 2).

As described in the experimental section, model fitting was performed using suitable phenomenological model, autocatalytic model with $n + m = 2$ [22, 24], which may generally describe the autocatalytic behaviour of the catalyzed epoxy-anhydride curing. Non-isothermal data at different heating rates were simultaneously fitted by linear regression (Equation (5)), in the conversion range 0.1–0.8, where

activation energy is nearly constant for all formulations.

Table 2 summarizes the results of the linear fitting and other kinetic parameters. The linear regression coefficients get close to one and the similarity between fitted and isoconversional activation energies evidence the quality of the fitting and the suitability of the kinetic model chosen. All formulations show similar kinetic parameters, an indication of the fact that the curing mechanism is not significantly affected by the presence of the star polymer modifier. The values of da/dt and k , calculated using Arrhenius equation and the kinetic parameters, activation energy and pre-exponential factor obtained by adjustment, agree with the reactivity of the different formulations and with the experimental calorimetric curves (Figure 2). On increasing the content of star polymer up to 5%, the curing accelerates (k and da/dt increase), but gradually decelerates (k and da/dt decrease) at higher modifier contents. The kinetic effects of the modifier are more relevant when PEI250 is used, showing greater differences between the values of k and da/dt and those of the neat formulation.

The curing kinetics of all formulations were studied with FTIR spectroscopy at 100°C in order to identify the main reactions taking place during curing and compared with the curing kinetics obtained by non-isothermal procedure. Figure 4 shows FTIR spectra recorded during isothermal curing of neat formulation at 100°C. The general features of the epoxy-anhydride curing reaction can be observed: the decrease of the anhydride groups (bands at 1780 and 1860 cm^{-1}) that react giving rise to ester groups (1735 cm^{-1}). The disappearance of epoxy groups was also observed but not quantified because of the difficulty to separate its contribution from the different overlapping signals in the region around 910 cm^{-1} .

Table 2. Kinetic parameters of curing process

Formulation	E^a [kJ/mol]	$\ln A^a$ [min ⁻¹]	n^a	m^a	r^a	$k_{150^\circ\text{C}}^b$ [min ⁻¹]	$(da/dt)_{0.5}^c$ [min ⁻¹]	E_{iso}^d
Neat	82	22.92	1.58	0.42	0.999	0.66	0.165	83
5% PEI8	76	21.39	1.53	0.47	0.999	0.69	0.174	77
10% PEI8	77	21.42	1.54	0.46	0.999	0.65	0.161	77
20% PEI8	67	18.48	1.53	0.47	0.999	0.50	0.125	69
5% PEI250	81	22.64	1.55	0.45	0.999	0.75	0.187	82
10% PEI250	70	18.95	1.57	0.43	0.992	0.38	0.095	71
20% PEI250	75	20.95	1.57	0.43	0.999	0.45	0.113	75

^aKinetic parameters obtained by model-fitting using an autocatalytic model with $n + m = 2$

^bValues of rate constant at 150°C using the Arrhenius equation and the parameters E and $\ln A$

^cValues of reaction rate at 150°C obtained using the equation rate $da/dt = k \cdot f(\alpha) = k \cdot (1 - \alpha)^n \cdot \alpha^m$ at 50% conversion

^dAverage isoconversional activation energy.

Figure 4. FTIR spectra recorded during curing of neat formulation at 100°C

Figure 5 shows the evolution of ester and anhydride groups against time recorded during curing for the 10%PEI250 formulation at 100°C in the spectrometer. It can be observed that the formation of ester and the disappearance of anhydride groups take place almost at the same time up to 0.6 of conversion, showing little discrepancies at higher conversion. This result agrees with the fact the curing mainly follows an alternating epoxy-anhydride mechanism catalyzed by tertiary amines. The inset in Figure 5 plots the ester conversion with respect to the anhydride conversion at 100°C for neat and all the PEI250 formulations. It can be observed that the evolution of both groups follows the diagonal line, indicating again an alternating copolymerization mechanism. Figure 5 shows the conversion of epoxy groups determined by using Equation (4) from the non-isothermal isoconversional kinetic parameters obtained by DSC.

Figure 5. Conversion of the ester groups, α_{ester} , and reacted anhydride, α_{anh} , during curing of 10% PEI250 formulation at 100°C in FTIR. Epoxy conversion simulated using non-isothermal isoconversional DSC data. Inset: conversion of the ester groups against reacted anhydride for neat and PEI250 formulations.

It can be observed that the conversions are similar to those obtained by FTIR. The slight differences between the evolutions of the different reactive species observed at high conversions can be related with the activation of a second curing mechanism that takes place during non-isothermal curing in DSC (Figure 5) at higher temperatures, uncatalyzed epoxy-anhydride reaction or epoxy homopolymerization, a process that is not activated during isothermal curing at moderate temperatures. FTIR and DSC simulation of PEI8 formulations showed similar trends than those observed for PEI250.

It can be concluded that curing of epoxy-anhydride formulations containing PEI8 and PEI250 proceeds mainly by anionic alternating copolymerization catalyzed by tertiary amines. Rocks *et al.* [28] studied the curing of epoxy-anhydride formulations catalyzed by tertiary amines by Raman spectroscopy and concluded that, in spite of the complexity of the curing mechanism, the overall curing profile corresponded to an alternating epoxy-anhydride copolymerization. However, epoxy-amine condensation may take place, thus permitting the covalent linkage between the modifier and the matrix. The quantification of this process is not possible, since it may take place to a very low extent. The other processes, occurring at higher temperatures, as observed by DSC, may not be relevant depending on the isothermal curing schedule selected in the processing.

Table 3 shows the experimental heats of polymerization, Δh , calculated as the average heat of the experiments at different heating rates. On increasing the proportion of modifier Δh [J/g] decreases due to the lower content of reactive epoxy and anhydride groups, whereas Δh [kJ/ee] remains almost constant and similar to the values reported for other similar epoxy systems [29]. FTIR spectra of both isothermal and non-isothermal cured samples showed that the absorbance bands of oxirane and anhydride groups disappeared completely. Moreover, no residual heat was observed after a second dynamic scan made up to 250°C to determine T_g . These results indicate that all formulations reacted almost completely.

The T_g of the isothermally cured samples, determined by DSC, decreases progressively on increasing the proportion of star polymer in the formulation, but this decrease is more evident when PEI250 is used. The different flexibilities of both modifiers, the amount of physical entanglement and crosslinking density and the existence of separated phases of different size

Table 3. Calorimetric data, α_{gel} , thermal stability data and dynamomechanical properties of the formulation studied in this work

Formulation	Δh^a [J/g]	Δh^b [kJ/ee]	$T_{g\infty}^c$ [°C]	$T_{g\infty, \text{Fox}}^d$ [°C]	α_{gel}^e	T_{max}^f [°C]	$\tan \delta^g$ peak [°C]	$\tan \delta^h$ FWHM [°C]	E_r^i [MPa]
Neat	288	103	132	132	0.47	406	143	14	28
5% PEI8	272	103	126	115	0.55	406	139	17	24
10% PEI8	258	103	118	99	0.49	405	130	25	20
20% PEI8	249	112	111	71	0.52	405	124	32	16
5% PEI250	257	97	118	115	0.45	405	127	16	23
10% PEI250	255	102	111	99	0.45	404	124	25	18
20% PEI250	230	103	103	71	0.48	403	114	32	13

^aEnthalpies per gram of mixtures^bEnthalpies per equivalent of epoxy groups^cGlass transition temperature after isothermal curing^dCalculated glass transition temperature, using DSC data and Fox equation^eDegree of conversion at gelation determined as the conversion reached by non-isothermal TMA and DSC tests at 2°C/min^fTemperature of the maximum rate of weight loss calculated by thermogravimetry^gTemperature of maximum of $\tan \delta$ ^hFWHM stands for full width at half maximum of $\tan \delta$ ⁱStorage modulus in the rubbery state determined at $\tan \delta$ peak + 50°C

and structure could be responsible of this behaviour. In order to understand the effect of the star on the matrix, the Fox equation was applied to predict the T_g of the fully cured thermosets. Up to 5% of PEI250 content, the thermosets have an experimental value of T_g similar to the predicted by this equation, whereas formulations containing 10 and 20% of both modifiers show experimental T_g 's significantly higher than the theoretical ones. These results could be explained by a phase separation of the star polymer due to the incompatibility produced during the curing reaction, which was further confirmed by electron microscopy.

The results of the gelation tests are summarized in Table 3. The conversion at the gelation point α_{gel} is only little affected by the addition of both star polymers, and in all cases the obtained values are within the range commonly observed for epoxy-anhydride systems, around 0.3–0.5 [24, 30, 31]. This scattering of values can be explained not only by the differences and accuracy of the measuring techniques but from the presence of protic impurities or the occurrence of initiator regeneration reactions that tend to increase α_{gel} [30–32].

Figure 6 shows the thermogravimetric curves for neat and PEI250 formulations. It can be observed that the degradation takes place in only one step, indicating random breaking of bonds. Formulations containing PEI8 show similar TGA traces (not shown). The results of the thermogravimetric analysis of all formulations are summarized in Table 3. Although modified formulations contain C–N bonds that are less stable than the C–C bonds of the epoxy matrix,

Figure 6. Thermogravimetric curves at 10°C/min in nitrogen atmosphere of the neat and PEI250 formulations

all formulations show similar thermal stability (T_{max}). This is in agreement with previously reported results using poly(ϵ -caprolactone) modified polymers [17, 20]. This can be explained by the low proportion of hyperbranched core in the modifier structure (even lower in the formulation), the similar thermal stability of the ester bonds in the poly(ϵ -caprolactone) arms and the epoxy-anhydride polyester network structure, and the possible covalent linkage between the matrix and the modifier.

3.3. Thermomechanical properties and thermal stress

Table 3 collects the results of the DMA characterization of all the samples prepared. Figures 7 and 8 plot the evolution of $\tan \delta$ and storage modulus of PEI250 and PEI8 formulations, respectively. In

Figure 7. Storage modulus and $\tan \delta$ curve against temperature for neat and PEI250 modified materials. The inset shows a detail of loss modulus curves at low temperatures.

agreement with the calorimetric data, when the proportion of modifier increases, the network relaxation curves are shifted towards lower temperatures, indicating that T_g decreases on adding modifier, as seen with DSC. The effect is more remarkable in PEI250 formulations, probably due to an increase in the plasticization caused by the longer poly(ϵ -caprolactone) arms or a decrease in the crosslinking density. It can also be observed that the α -relaxations (related to the T_g) of all formulations are unimodal, indicating that all thermosets have homogeneous network structures, but modifier-rich formulations show a more disperse network, as seen from the broader α -relaxation and higher FWHM values. Meng and coworkers [33, 34] observed the contrary trend using hyperbranched polyethers as tougheners for epoxy/amine systems, but their materials showed a homogeneous morphology. Table 3

Figure 8. Storage modulus and $\tan \delta$ curve against temperature for neat and PEI8 modified materials

and Figures 7 and 8 show a decrease in the rubbery modulus and in the height of α -relaxation upon addition of the modifier. According to the rubber elasticity theory, the relaxed modulus is proportional to the crosslinking density, but deviations from the ideal network behaviour are likely to occur for a variety of reasons [26, 35, 36]. The decrease in rubbery modulus is not proportional to the modifier content, suggesting an additional decrease in the crosslinking density connected with the participation of the star polymer in the curing process.

The inset in Figure 7 shows a detail of loss modulus curves in the region of low temperature. It can be seen that the β -relaxation (attributed to glyceryl or diphenylpropane groups) decreases but it broadens on increasing the modifier content. This can be tentatively attributed to a new star polymer-rich phase formed during curing and to a restricted mobility of the matrix structure due to the additional bonding with star-polymer.

In order to determine the potential application of the prepared materials as coatings, the generation of thermal stress during cooling of neat and PEI250 and PEI8 formulations on steel as a rigid substrate were studied using the Benabdi and Roche methodology described in the experimental section [23]. In a previous work, we demonstrated that the intrinsic stress generated during curing of an epoxy system, due to rearrangement of molecular structure, and the thermal stress generated in the rubbery state, are much lower than the thermal stress generated on cooling down from the T_g to room temperature [14, 20], therefore in the present work we only calculate the thermal stress originated on cooling.

Table 4 collects the thermal stress values, σ_{th} , calculated using Equations (7) and (8) and the following experimental data of epoxy/anhydride/PEIX coating: CTE_c in the glassy state determined by TMA, elastic modulus determined by DMA at room temperature (40°C), E_c , and stress free temperature, SFT , taken as the glass transition temperature determined by TMA. It can be observed as σ_{th} decreases significantly on increasing the modifier content, due to a decreasing of some of these three parameters: CTE_c , E_c and SFT . In general, E_c and SFT regularly decrease on increasing PEIX content, according to the high flexibility and low crosslinking density of modified thermosets, whereas CTE_c does not follow a clear trend. While the CTE_c of PEI8 formulations hardly varies, CTE_c of PEI250 formulations

Table 4. Thermal data of the materials and thermal stresses generated during cooling for the different formulations

Formulation	E_c^a [MPa]	α^b	SFT ^c	CTE ^d	$1/R^e$ [mm ⁻¹]	σ_{th}^f [MPa]
Neat	3241	0.018	125	87	0.0169	16.4
5% PEI8	2796	0.016	119	83	0.0146	12.5
10% PEI8	2626	0.015	113	85	0.0137	11.2
20% PEI8	2203	0.012	104	92	0.0129	9.1
5% PEI250	2687	0.015	109	93	0.0145	12.1
10% PEI250	2505	0.014	105	95	0.0139	10.9
20% PEI250	1782	0.010	96	102	0.0123	7.4

^aElastic modulus determined by DMTA.^bRatio of coating and substrate module $\alpha = E_c/E_s$.^cStress free temperature taken as the transition glass transition temperature determined by TMA.^dThermal expansion coefficient in the glassy state determined by TMA.^eCurvature determined using Equation (7).^fThermal stress determined using Equation (8).

increases slightly. Although this increase tends to increase the stresses, the lower E_c and SFT values of PEI250 formulations compensate this effect leading to significant reduction of thermal stress. This reduction is higher for PEI250 formulations than for PEI8 formulations and the highest reduction of σ_{th} is achieved by adding a 20% of PEI250. These results agree, again, with the higher flexibility and lower crosslinking density induced by the presence of PEI250 and its possible participation in the curing process.

3.4. Mechanical characterization and morphology

The toughness behaviour of all cured formulations was investigated by impact test and the morphology was analyzed by SEM on the impacted fracture. Figure 9 shows that both PEI250 and PEI8 produce a significant increase in the impact strength of the cured materials, proportional to the amount of modifier used. This increase is more than 100% with respect to the neat formulation, for thermosets containing a 20% of both modifiers. This result is consistent with a phase-separated morphology, where soft particles of modifier adhered to the epoxy/anhydride matrix absorb energy during impact test, although the DMA and DSC results showing a decrease in the T_g of the cured material suggest also some enhancement in the matrix shear yielding. The degree of interfacial adhesion between the soft phase and the matrix is critical in toughening. Effective toughening is believed to occur with an intermedi-

Figure 9. Impact strength for neat DGEBA/anhydride and thermosets with PEI250 and PEI8

ate interfacial bonding, since an excessive adhesion can deteriorate the interfacial adhesion between the toughener phase and the matrix [36]. In previous works we observed that polymeric modifiers with excessive physical-chemical compatibility with the matrix led to their covalent incorporation into the network structure, preventing phase separation and producing very little toughness enhancement, whereas polymers that phase-separate during curing but with certain physical-chemical compatibility with the matrix led to the highest increase in impact strength [14]. Although it is not possible to know the amount of amine groups that react during curing, it is reasonable assuming the formation of some covalent bonds between the remaining amine groups at the core of the star polymer and the epoxy groups. Although the addition of both stars increases toughness characteristics the improvement achieved with PEI250 is higher. The amount of covalent bonds formed between matrix and modifier, the higher flexibility of PEI250 and the resulting polymer matrix and the lower thermal stress in PEI250 formulations can justify the differences observed between PEI250 and PEI8 thermosets.

Figure 10 shows some SEM micrographs of the fractured surfaces of materials after impact tests. In previous works it was observed that the fracture of the neat DGEBA/anhydride formulation is relatively smooth and glassy and does not show any significant morphological features, due to the formation of a homogeneous material [20, 37]. On the contrary, materials containing PEI8 and PEI250 (Figure 7) show a characteristic morphology completely differ-

Figure 10. SEM micrographs at 50 000 magnifications of the fractured surfaces of the materials obtained from a) neat, b) 10% PEI8 and c) 10% PEI250 formulations

ent from that of the neat formulation. PEI8 micrographs present nanograined morphology with nano-sized grains. This nanopatterned organization can be attributed to the presence of amino groups, which can react during curing with epoxides changing the morphology in the surrounding of the star polymer. In a previous study [20] on the modification of DGEBA/anhydride thermosets with star polymers we could observe that the presence of reactive groups in the star led to homogeneous materials, whereas the blocking of these reactive groups produced nanograined morphology. In the present case, PEI8 has a high content of blocked groups and a low content of amine reactive groups, leading to the nanostructure observed by SEM inspection. PEI250 thermosets show a phase-separated morphology with nano-sized (75 to 150 nm) fine particles well adhered to the epoxy/anhydride matrix. It can be hypothesized that these particles are formed by PEI250 surrounded by epoxy/anhydride matrix covalently bonded to PEI250 but some aggregation of star polymers cannot be excluded. The differences between two morphologies can be attributed to the different molecular weight of the star polymer and to the amount of amine groups of star polymer that reacts during curing. Although both morphologies lead to significant toughness enhancement in the materials, phase-separated morphology produces a slightly higher improvement than nanograined morphology.

4. Conclusions

The curing of epoxy/anhydride systems in the presence of PEI8 and PEI250 and tertiary amines mainly proceeds by anionic alternating copolymerization catalyzed by tertiary amines, although the uncatalyzed epoxy-anhydride polycondensation and the epoxy-amine reaction can take place to some extent.

The addition of star polymers with poly(ethyleneimine) cores and blocked poly(ϵ -caprolactone) arms to epoxy/anhydride formulations allows to obtain thermosets with significant improved toughness and low thermal stress generation during cooling, with only a slight reduction on glass transition temperature and crosslinking density.

The flexibility and molecular weight of the star modifiers used, as well as the amount of amino reactive groups in the modifier affect the morphology of the

resulting thermosets but only slightly their thermomechanical properties and curing process. The use of high molecular weight modifier with blocked terminal groups leads to phase-separated morphologies with nano-sized fine particles well adhered to the epoxy/anhydride matrix by the presence of unreacted amine groups.

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