CrossMark

Thermal curing of an epoxy-anhydride system modified with hyperbranched poly(ethylene imine)s with different terminal groups

J. M. Morancho[1] · X. Fernández-Francos[1] · C. Acebo[2] · X. Ramis[1] · J. M. Salla[1] · À. Serra[2]

Abstract New hyperbranched polymers (HBP) have been synthesized by reaction of a poly(ethylene imine) with phenyl and *t*-butyl isocyanates. These HBPs have been characterized by ^{1}H-NMR (nuclear magnetic resonance of hydrogen) and Fourier transform infrared spectroscopy. Their influence on the curing and properties of epoxy-anhydride thermosets has been studied by different techniques: differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetry (TG). The curing kinetics has been studied with DSC. Integral isoconversional method and the Šesták–Berggren model have been used to determine the activation energy and the frequency factor. The kinetic parameters are very similar for all the studied systems at the middle stage of the process, but changes are observed at the beginning and at the end of the process when these modifiers are used. The HBPs reduce the glass transition temperature of the cured materials. In addition, from the DMA analysis it can be seen that the HBP modifier obtained from phenyl isocyanate hardly changes the storage modulus, but the obtained ones from *t*-butyl isocyanate decrease it. TG analysis reveals a decrease in the onset temperature of the degradation process upon addition of the HBPs.

Introduction

Epoxy resins are widely used in applications such as adhesives, coatings, electric laminates, encapsulation of semiconductor devices, matrix material for composites, structural components [1–12], and cryogenic engineering [13–15] because of their mechanical properties, adhesion, and chemical resistance.

However, epoxy resins are inherently brittle due to their high cross-link density. To increase their toughness different modifiers such as rubber, thermoplastic and glass particles can be added, but they always limit the processability of the formulation [16–20]. Hyperbranched polymers (HBP) are a new kind of polymers used as modifiers of epoxy resins to increase their toughness without sacrificing the processing ability of the formulation due to their highly branched dendritic structure, which is a key point in coating applications [9–11, 21–23]. HBPs have several advantages as their low viscosity compared with their liner counterparts, the possibility of tailoring their core and branched structures and the functionalization of the end groups so that they can be made compatible with the surrounding matrix [24, 25]. These modifiers can also reduce the shrinkage of the resin during the curing process [26] and the generation of internal stress [9]. HBPs can also maintain the glass transition of the epoxy resin [9], but in some cases a significant reduction was observed [24]. In previous works of our group, the influence of some HBPs in the thermal curing and the photocuring of diglycidyl ether of bisphenol A (DGEBA) has been studied [27–31]. Using HBP polyester partially blocked with benzoyl groups

A1 ✉ J. M. Morancho
A2 morancho@mmt.upc.edu

A3 1 Thermodynamics Laboratory, Heat Engines Department,
A4 ETSEIB, Universitat Politècnica de Catalunya, Av. Diagonal
A5 647, 08028 Barcelona, Spain

A6 2 Department of Analytical and Organic Chemistry, Universitat
A7 Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona,
Spain

as epoxy modifier, a phase-separated morphology, with a part of the HBP segregate into particles, was obtained. The π-π stacking interactions between phenyl groups and the different hydrophilic character of HBP core and terminals groups were the forces that drive the phase separation process. The existence of some hydroxyl terminal groups improved the compatibility with the epoxy matrix due to the formation of covalent linkages and, as a consequence, thermosetting materials with improved flexibility and toughness were obtained [30]. Hyperbranched poly (ethylene imine) polymers were used as reactive polymeric modifiers in epoxy thermosetting systems using a tertiary amine as anionic initiator. These HBPs were able to get incorporated into the network structure by condensation of amine and epoxy groups. The densely branched architecture of PEI and grafting between the condensed epoxy-amine and polyether network reduced significantly the network mobility, but a positive effect in terms of impact resistance could be observed [31].

Taking all of these into account, in the present work three new hyperbranched poly(ethylene imine) polymers with different terminal groups (two of them with different amounts of t-butyl terminal groups and the other one with phenyl terminal groups) have been synthesized. Phenyl and t-butyl groups are introduced to block active amines of poly(ethyleneimine) structure and therefore reduce the extent of covalent linkage between the HBP and the epoxy matrix, with the purpose of promoting phase separation and enhancing impact strength [32]. The synthetic procedure to prepare the polymeric modifiers is quite easy and consists in reacting commercial poly(ethylene imine) with the corresponding isocyanate in acetonitrile solution at room temperature. The obtained HBPs have been characterized by ^{1}H-NMR (proton nuclear magnetic resonance) and Fourier transform infrared spectroscopy (FTIR). The influence of these new HBPs on the thermal curing of an epoxy-anhydride system has been studied. The kinetics of the thermal curing has been analyzed using isoconversional methods. The effect of these HBPs over the storage modulus, and the thermal degradation has also been studied.

Experimental

Materials

Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent of 187 g ee^{-1} (EPIKOTE 828, Herion Specialty Chemicals B. V.) was dried in vacuum before use. Hexahydro-4-methylphthalic anhydride of 186.19 g eq^{-1} (Aldrich) was used as hardener, and N,N-dimethylbenzylamine (DMBA) (Aldrich) was used as catalyst.

Poly(ethylene imine) (PEI) (Lupasol®FG, 800 g/mol, BASF) (see Fig. 1a) was donated by the producer and used after drying under vacuum. From the molar mass of the polymer and of the repeating unit, an average degree of polymerization of 18.6 was calculated. According to the data sheet, the relationship (NH$_2$/NH/N) was (1/0.82/0.53) and thus by calculations the equivalent number of primary, secondary and tertiary amines resulted to be 0.010, 0.00837, and 0.0053 eq g^{-1}. Phenyl isocyanate and *tert*-butyl isocyanate were purchased from Sigma-Aldrich and used as received. Acetonitrile (ACN) was dried and distilled under CaH$_2$ before used.

Modification of poly(ethylene imine) with phenyl isocyanate (PEI-PhNCO) (Scheme 1)

The modification of PEI with the selected isocyanate was performed according to a general reported procedure [33]. The synthesis of PEI-PhNCO was performed by solving 3.24 g (58.3 meq of –NH) of PEI in 20 mL of acetonitrile in a three-necked flask magnetically stirred. The solution was brought to 0 °C, and phenyl isocyanate (6.95 g, 58.3 mmol) was added drop-wise. Once the addition was finished, the mixture was left at room temperature overnight. The solvent was eliminated in the rotary evaporator, and the white powder obtained was dried in vacuum overnight. In Scheme 1, the reaction between PEI and phenyl isocyanate is shown.

PEI-PhNCO ^{1}H-NMR (400 MHz, CDCl$_3$), δ (ppm): 7.7–6.7 (**H$_{ar}$**, i–l), 3.5–1.6 (–**CH$_2$**–NHCO–, g, –**CH$_2$**–N(**CH$_2$**)CO–, f), and PEI (–NH–**CH$_2$CH$_2$**–NH–, e) (see Fig. 1b).

Modification of poly(ethylene imine) with t-butyl isocyanate (PEI-t-butylNCO)

The synthetic procedure was similar to that used in the previous description, but two different quantities of t-butyl isocyanate were employed: 5.78 g (58.3 mmol) to reach a 100 % of modification (from now on PEI-BuNCO100) and 4.33 g (43.68 mmol) to reach a modification degree of 75 % (from now on PEI-BuNCO75).

PEI-BuNCO100 ^{1}H-NMR (400 MHz, CDCl$_3$), δ (ppm): 3.5–1.6 (–**CH$_2$**–NHCO–, g, –**CH$_2$**–N(**CH$_2$**)CO–, f) and PEI (–NH–**CH$_2$CH$_2$**–NH–, c–e) and 1.3 (CH$_3$ of t-butyl groups) (see Fig. 1c).

Average molar mass and thermal data of all the modified HBPs obtained are collected in Table 1.

Preparation of curing formulations

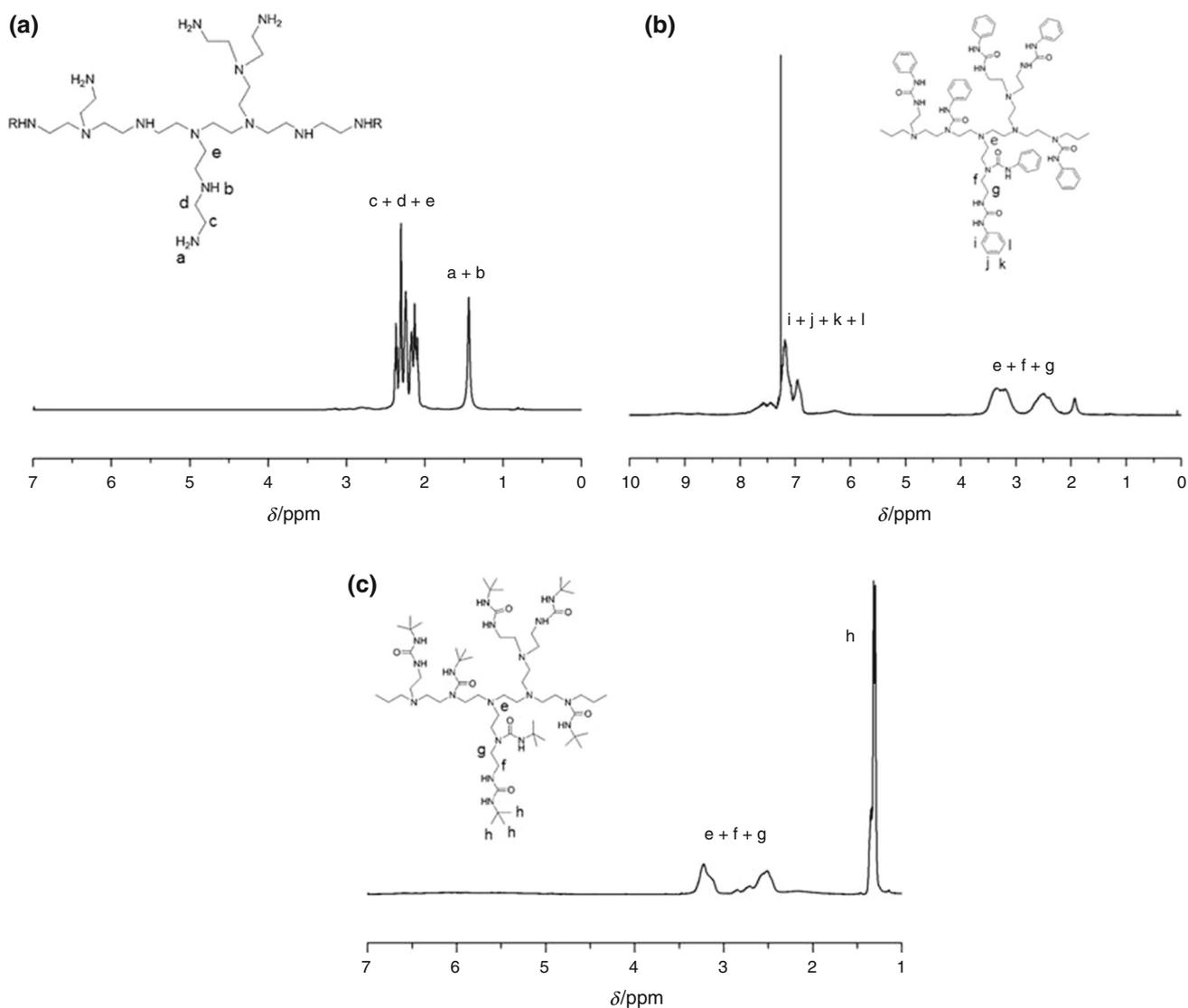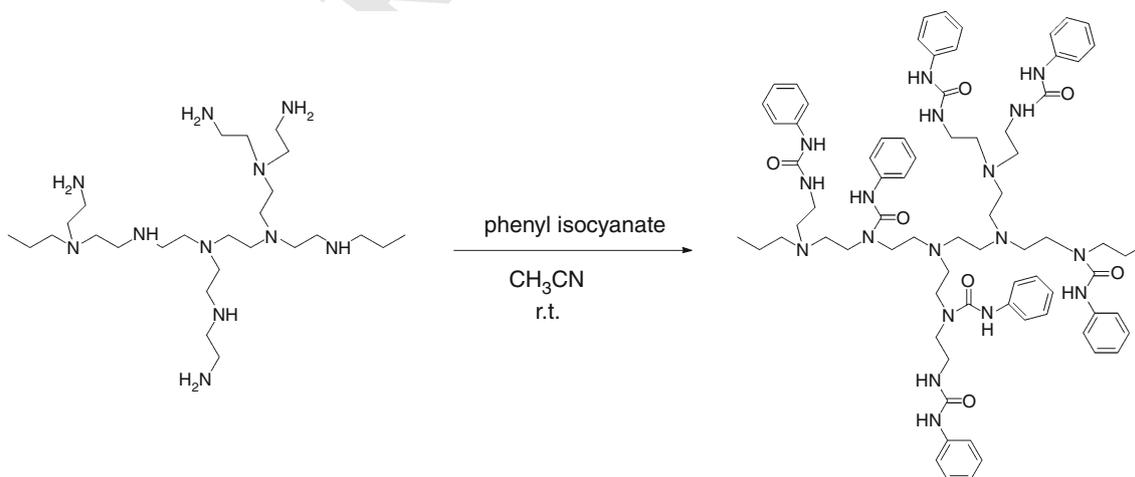First, the desired quantities of DGEBA and solid HBP were mixed, heated using a hot air blower, and vigorously

Fig. 1 ^{1}H-NMR spectra of PEI (**a**), PEI-PhNCO (**b**), and PEI-BuNCO100 (**c**) in CDCl$_3$

Scheme 1 Modification of PEI with phenyl isocyanate to obtain PEI-PhNCO

Table 1 Characteristics of the modified HBPs synthesized

Modifier	DA[a]/%	M_n^a/g mol^{-1}	$T_{5\%}^b$/°C
PEI-BuNCO100	99	2174	204
PEI-BuNCO75	74	1827	196
PEI-PhNCO	100	2468	238

[a] Determined by ^{1}H-NMR

[b] Temperature of the 5 % of mass loss

stirred. When this mixture reached room temperature, the anhydride (in a stoichiometric proportion with respect to DGEBA) and 1 phr of the tertiary amine (one part per hundred of DGEBA and anhydride mixture) were added. Immediately after, the mixture obtained was introduced in a vacuum oven to completely remove bubbles of air. The proportion of the different HBPs used was 5 and 10 %. The prepared mixtures were kept at −18 °C to prevent polymerization and used subsequently in the corresponding studies.

Nuclear magnetic resonance of hydrogen

^{1}H-NMR measurements were carried out at 400 MHz and in a Varian Gemini 400 spectrometer. CDCl$_3$ was used as the solvent. For internal calibration, the middle solvent signal corresponding to CDCl$_3$ was taken as δ (^{1}H) = 7.26 ppm.

Fourier transform infrared spectroscopy

FTIR spectrometer FTIR-680PLUS from Jasco with a resolution of 4 cm^{-1} in the absorbance mode was used to confirm that the reaction of isocyanate with polyethyleneimine was completed. This device was equipped with an attenuated-total-reflection accessory with thermal control and a diamond crystal (Golden Gate heated single reflection diamond ATR, Specac Teknokroma).

Differential scanning calorimetry

The kinetics of the thermal curing were evaluated by DSC analysis (differential scanning calorimetry, Mettler DSC-822e calorimeter) from 0 to 300 °C at different heating rates (2.5, 5, 7.5, 10, and 15 °C min^{-1}). The samples cured at 10 °C min^{-1} were used to determine the maximum glass transition temperature reached in a second scan from 0 to 300 °C at 10 °C min^{-1}.

Dynamic mechanical analysis

To prepare the specimens, the mixtures were completely cured in a rectangular mold, first at 100 °C for 2 h and then at 150 °C for 1 h. Before curing, PEI-PhNCO was completely solubilized in the epoxy matrix, but PEI-BuNCO75 and PEI-BuNCO100 were not. After the heating and curing, all the modifiers are apparently solubilized in the epoxy matrix. The materials obtained were homogeneous and transparent to the naked eye. The dimensions of the specimens were $20 \times 11 \times 2$ mm^3, approximately. The samples were tested in a DMA (dynamic mechanical analysis, TA instruments Q800) from −120 to 220 °C at 3 °C min^{-1} using the 3-point bending mode, with an amplitude of 10 μm and a frequency of 1 Hz.

Thermogravimetric analysis

Small specimens (8–10 mg) of the completely cured samples (following the procedure described above for the DMA analysis) were analyzed from 30 to 800 °C at 10 °C min^{-1} in a thermobalance (Mettler TGA/DSC1) in nitrogen atmosphere (60 cm^3 min^{-1}) to study the degradation process. Only the neat epoxy resin and the ones with 10 % of the different HBPs were analyzed.

Theory

In the thermal curing studied, the degree of conversion is defined as:

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

where Δh_T is the heat released up to a temperature T and Δh_{dyn} is the total reaction heat released during the curing. The kinetics of this curing has been analyzed by means of an integral isoconversional method, using the Kissinger–Akahira–Sunose equation [34]:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{g(\alpha)E_\alpha}\right) - \frac{E_\alpha}{RT_\alpha} \quad (2)$$

where is the heating rate, R is the gas constant and at a determined value of degree of conversion, T_α is the temperature attained, A_α is the frequency factor, E_α is the activation energy and $g(\alpha)$ is the following integral obtained from a function of the degree of conversion $f(\alpha)$:

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

The activation energy at a given conversion can be obtained from the slope of the representation of $\ln (\beta/T_\alpha^2)$ versus the reciprocal of the temperature [see Eq. (2)]. Providing the kinetic model is known; the frequency factor can also be determined from the intercept at the origin.

237 This analysis can be repeated at different degrees of con-
238 version throughout the curing process.

Results and discussion

Characterization of the obtained HBPs

241 Commercially available hyperbranched poly(ethylene
242 imine) (PEI, Lupasol® FG) contains primary, secondary,
243 and tertiary amine functional groups. From the degree of
244 polymerization of PEI and the molar ratio of primary,
245 secondary, and tertiary amines, we calculated the average
246 number of active groups per molecule, NH and NH_2, which
247 resulted to be 6.4 secondary amines and 7.9 primary ami-
248 nes in average per molecule. From this number and the
249 desired degree of modification, the quantity of phenyl and
250 *t*-butyl isocyanates was calculated, taking into account that
251 primary and secondary amines react with an only iso-
252 cyanate group to form the corresponding urea. The reaction
253 was performed by reacting the isocyanates with the PEI at
254 low temperature using ACN as solvent (see Scheme 1).

255 By FTIR analysis, we could confirm that the desired
256 modification was achieved due to the complete disappear-
257 ance of the isocyanate band at 2271 cm^{-1} and the new urea
258 groups formed that gives absorptions at 3321 cm^{-1} (N–H
259 st) and at 1623 cm^{-1} (C=O st).

260 To evaluate the real degree of modification, ¹H-NMR
261 spectra were registered (Fig. 1b, c). In the PEI-PhNCO
262 spectrum, it can be observed the aromatic protons intro-
263 duced in the 6.8–7.8 ppm (i, j, k, l) and the total absence of
264 NH protons. In the case of PEI-BuNCO100, the signal
265 (h) due to the methyl protons of the *t*-butyl groups allows
266 the calculation of the degree of modification. The signals
267 corresponding to the protons of the PEI structure shift
268 because of the transformation of amines into urea groups.

269 The complete absence of amine protons (a + b signals)
270 in the spectrum of PEI-PhNCO indicates that a 100 % of
271 modification was reached. For the PEI-BuNCO polymers,
272 the degree of modification was calculated by ¹H-NMR,
273 following a previously reported method [35]. From the
274 integration of the signals coming from the methyl groups
275 and the PEI structure, we determined the ratio of urea
276 formed by amine moiety according the following
277 equation:

$$x = \frac{I(\text{h})/9}{I(\text{c} + \text{d} + \text{e} + \text{f} + \text{g})/4} \tag{4}$$

279 where $I(\text{h})$ is the integration of methyl protons of butyl
280 groups and $I(\text{c} + \text{d} + \text{e} + \text{f} + \text{g})$ is the total integration of
281 the protons coming from the PEI structure. From x and the
282 values of the primary amine end groups (T), secondary
283 amine linear units (L), and tertiary amine branched units

284 (D), it is possible to calculate the degree of amidation (DA)
285 by using the following equation:

$$DA = \frac{x(L + T + D)}{L + T} \tag{5}$$

287 A complete and 74 % of modification were achieved in
288 PEI-BuNCO HBPs. Primary amines are mainly located in
289 the periphery, whereas secondary amines are in the middle
290 of the spheroid-like structure. Because of the steric hin-
291 drance of the secondary amines and the higher nucle-
292 ophilicity of primary amines, the latter should be much
293 more reactive than the secondary ones and then most
294 unreacted amines in PEI-BuNCO75 should be secondary,
295 and therefore less active on further reaction in epoxy cur-
296 ing. In Table 1, the degree of modification achieved and
297 the average molar mass calculated are collected. The initial
298 decomposition temperature ($T_{5\%}$) was evaluated to confirm
299 that during the curing process the PEI modifiers were
300 enough stable to be cured without breakage of urea groups.

Thermal curing

302 Figures 2, 3, and 4 show the DSC scans at 10 °C min^{-1} or
303 the epoxy system modified with different proportions of the
304 HBPs used (in the insets, degree of conversion versus
305 temperature). PEI-BuNCO100 (Fig. 2) hardly modifies the
306 thermal curing, but PEI-BuNCO75 (Fig. 3) and PEI-
307 PhNCO (Fig. 4) accelerate and decelerate the thermal
308 curing, respectively. In PEI-BuNCO75, there are some
309 remaining amine groups that facilitate the opening of the
310 epoxy ring increasing the reaction rate. PEI-PhNCO is the
311 only modifier completely solubilized in the epoxy resin
312 before the beginning of the thermal curing and it has a
313 dilution effect on the reaction rate. Moreover, the high
314 molar mass of PEI-PhNCO and the rigidity of phenyl
315 groups hinder the mobility of the reactive species, decel-
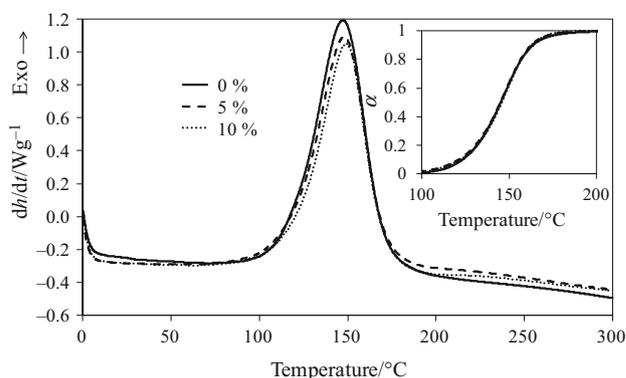316 erating the curing specially at lower temperatures [36].

Fig. 2 Heat flow of thermal curing of the epoxy resin with different proportions of PEI-BuNCO100 at 10 °C min^{-1}. In the *inset*, degree of conversion versus temperature

Fig. 3 Heat flow of thermal curing of the epoxy resin with different proportions of PEI-BuNCO75 at 10 °C min^{-1}. In the *inset*, degree of conversion versus temperature
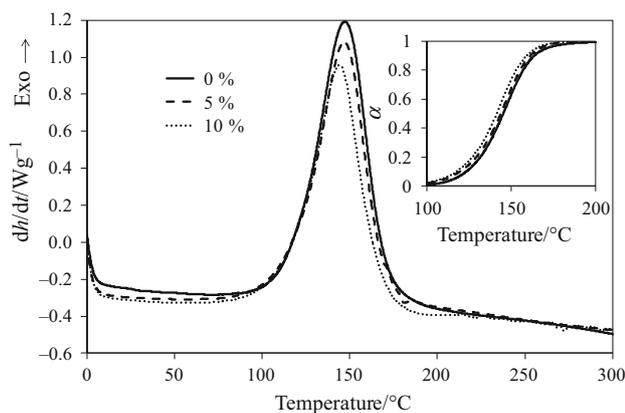

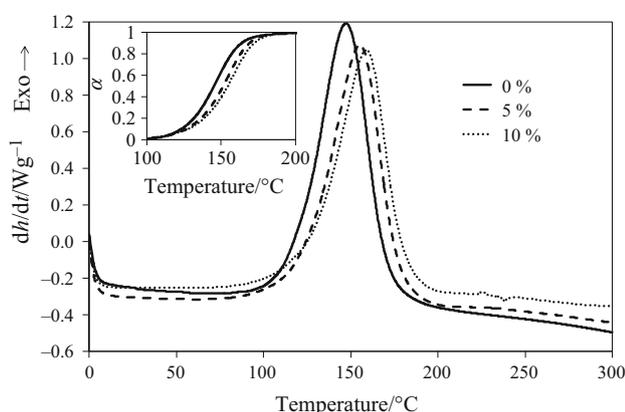**Fig. 4** Heat flow of thermal curing of the epoxy resin with different proportions of PEI-PhNCO at 10 °C min^{-1}. In the *inset*, degree of conversion versus temperature

To analyze the kinetics of the process, an integral iso-conversional method is used as it has been commented in the theoretical part. To find the frequency factor, model-fitting method and the Šesták–Berggren equation ($f(\alpha) = \alpha^m(1-\alpha)^n$) [34] have been used with $m + n = 2$ [37]. With this condition, the following expression for $g(\alpha)$ is obtained:

$$g(\alpha) = \frac{1}{1-m}\left(\frac{\alpha}{1-\alpha}\right)^{1-m} \tag{6}$$

This kinetic model has been selected since that the curing of epoxy-anhydride has been satisfactorily modeled in previous works [37–39]. As it can be seen in Table 2, the values of the parameters m and n are similar for the studied systems, an indication of the fact that the curing mechanism is not significantly affected by the presence of the star HBP modifier. Only the autocatalytic parameter m slightly decreases when a 10 % of PEI-PhNCO is added, probably due to the restrictions imposed by the modifier to the

mobility of the reactive species. Table 3 shows the values of the activation energy and the frequency factor for all the studied systems obtained using Eq. (2) for some degrees of conversion. The values of the activation energy and the frequency factor are very similar for all the studied systems at the middle stage of the process. At the beginning, these parameters decrease on increasing the proportion of modifier and at the end, they increase with the modifier proportion, but these differences are small and they are not significant. This can be explained by uncertainties in the determination of the baseline and in consequence of the measurement of the reaction heat at the beginning and the end of the curing process. In many reactions, due to the compensation effect between the activation energy and the frequency factor [40], the activation energy does not reflect exactly the reaction rate and it is better to discuss the rate constants.

In Table 4, the values of the rate constant at 150 °C and $\alpha = 0.5$ are indicated. These values have been found using the Arrhenius equation ($k = A \exp(-E/RT)$) and the values of the activation energy and the frequency factor of Table 3. These rate constants are in agreement with the results shown in Figs. 2 to 4: PEI-BuNCO100 hardly modifies the thermal curing (the rate constants are practically the same than that of the neat system), PEI-BuNCO75 accelerates it (the rate constant increases with the modifier proportion), and PEI-PhNCO decelerates it (the rate constant decreases increasing the modifier proportion). Equivalent results have been obtained in all range of conversions. The acceleration observed on adding PEI-BuNCO75 could be attributed to the effect of unreacted NH groups in the modifier structure, which can react with epoxides and anhydrides because of their nucleophilic character. The deceleration observed can be explained on the basis of the dilution effect of reactive groups and the increase in viscosity on adding the PEI modifier.

In Table 4, the values of the ultimate glass transition temperature are also indicated. All the HBPs produce a decrease in the glass transition temperature, indicating that

Table 2 Values of the parameters m and n of the Šesták–Berggren equation, regression coefficient (r) of the model-fitting method, and standard deviation (SD) for all the studied systems

Modifier/%	m	n	r	SD
0 %	0.487	1.513	0.995	0.200
5 % PEI-BuNCO100	0.478	1.522	0.990	0.247
10 % PEI-BuNCO100	0.479	1.521	0.986	0.276
5 % PEI-BuNCO75	0.495	1.505	0.990	0.256
10 % PEI-BuNCO75	0.480	1.520	0.989	0.240
5 % PEI-PhNCO	0.491	1.509	0.988	0.243
10 % PEI-PhNCO	0.449	1.551	0.981	0.281

Table 3 Activation energies and frequency factors at different degrees of conversion for all the studied systems

Modifier/%		$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.4$	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$	$\alpha = 0.95$
0 %	$E_\alpha/$kJ mol^{-1}	68.2	70.4	70.7	71.2	71.5	71.7	71.6	71.3	70.6	69.9	71.0
	$A/$s^{-1}	6.00×10^6	1.14×10^7	1.14×10^7	1.27×10^7	1.38×10^7	1.45×10^7	1.43×10^7	1.33×10^7	1.13×10^7	1.01×10^7	1.44×10^7
5 % PEI-BuNCO100	$E_\alpha/$kJ mol^{-1}	63.1	66.4	68.8	70.2	71.0	71.4	71.6	71.5	71.3	71.6	73.4
	$A/$s^{-1}	1.25×10^6	3.28×10^6	6.25×10^6	9.11×10^6	1.14×10^7	1.29×10^7	1.38×10^7	1.41×10^7	1.41×10^7	1.72×10^7	3.22×10^7
10 % PEI-BuNCO100	$E_\alpha/$kJ mol^{-1}	56.0	62.9	66.6	68.3	69.3	69.9	70.3	70.4	70.6	72.1	74.9
	$A/$s^{-1}	1.27×10^5	1.06×10^6	3.15×10^6	5.06×10^6	6.78×10^6	8.23×10^6	9.31×10^6	1.02×10^7	1.16×10^7	2.02×10^7	5.07×10^7
5 % PEI-Bu NCO75	$E_\alpha/$kJ mol^{-1}	58.2	63.9	66.8	67.8	68.5	68.8	68.8	68.6	68.2	67.6	66.7
	$A/$s^{-1}	2.88×10^5	1.65×10^6	3.79×10^6	4.93×10^6	5.85×10^6	6.47×10^6	6.69×10^6	6.49×10^6	6.02×10^6	5.63×10^6	4.85×10^6
10 % PEI-BuNCO75	$E_\alpha/$kJ mol^{-1}	53.9	61.5	66.3	68.1	68.9	69.3	69.6	69.9	70.5	72.9	75.2
	$A/$s^{-1}	7.35×10^4	8.05×10^5	3.51×10^6	5.78×10^6	7.31×10^6	8.53×10^6	9.54×10^6	1.07×10^7	1.37×10^7	2.98×10^7	6.51×10^7
5 % PEI-PhNCO	$E_\alpha/$kJ mol^{-1}	56.2	62.5	65.8	67.2	68.3	69.0	69.5	69.9	70.3	71.7	74.1
	$A/$s^{-1}	1.07×10^5	7.50×10^5	1.93×10^6	2.82×10^6	3.79×10^6	4.69×10^6	5.54×10^6	6.48×10^6	7.85×10^6	1.30×10^7	2.94×10^7
10 % PEI-PhNCO	$E_\alpha/$kJ mol^{-1}	53.9	61.5	66.3	68.5	70.0	71.2	72.1	73.1	74.2	76.5	79.5
	$A/$s^{-1}	4.26×10^4	4.36×10^5	1.74×10^6	3.28×10^6	5.10×10^6	7.20×10^6	9.78×10^6	1.35×10^7	2.05×10^7	4.60×10^7	1.22×10^8

Table 4 Rate constants at 150 °C and $\alpha = 0.5$, maximum glass transition ($T_{g\infty}$) for all the studied systems and heating of cure (in kJ by equivalent epoxy)

Modifier/%	$k_{150°C}/$s^{-1}	$T_{g\infty}/$°C	$\Delta h/$kJ ee^{-1}
0 %	2.04×10^{-2}	136	124
5 % PEI-BuNCO100	1.98×10^{-2}	126	117
10 % PEI-BuNCO100	1.91×10^{-2}	117	117
5 % PEI-BuNCO75	2.09×10^{-2}	121	117
10 % PEI-BuNCO75	2.36×10^{-2}	107	113
5 % PEI-PhNCO	1.43×10^{-2}	123	121
10 % PEI-PhNCO	1.18×10^{-2}	112	120

they are solubilized in the epoxy matrix acting as plasti- 378
cizers. The flexible PEI structure can also account for the 379
lowering of $T_{g\infty}$. PEI-BuNCO75 is the modifier that 380
decreases more this magnitude, but PEI-BuNCO100 is the 381
modifier that decreases less it. It should be considered that 382
the introduction of a modifier with reactive groups affects 383
the stoichiometry of the formulation: since the epoxide and 384
anhydride groups were maintained at stoichiometric pro- 385
portions, the addition of PEI-BuNCO75 can leave some 386
groups unreacted and a more open structure of the ther- 387
mosetting network. Moreover, the covalent linkages 388
between PEI-BuNCO75 and matrix can produce a more 389
expanded structure with a lower amount of cross-link 390
points per unit mass. As it can be seen in Table 4, the 391
introduction of HBP slightly decreases the reaction heat, 392
possibly because of the topological restrictions leading to 393
incomplete curing and, in consequence, to a lower cross- 394
linking density. 395

Dynamic mechanical analysis 396

Figures 5, 6 and 7 show the DMA experiments of the 397
materials prepared. The presence of PEI-BuNCO75 and 398
PEI-BuNCO100 in the material decreases the storage 399
modulus (E') before the glass transition, but the addition of 400
PEI-PhNCO hardly changes it. After glass transition, all the 401
modifiers decrease E', especially PEI-BuNCO75. As stated 402
above, the chemical incorporation of PEI-BuNCO75 into 403
the matrix reduces the cross-linking density. All modifiers 404
decrease the glass transition temperature (temperature of 405
the tan δ peak). This result is in agreement with the trend 406
observed in the values of the ultimate grass transition 407
temperature obtained by DSC and agrees with the flexibi- 408
lizing effect exerted by the modifiers on the matrix. 409

In the insets of these Figures, an enlargement of tan δ at 410
low temperatures is shown. These peaks correspond to the 411
β transition and increasing the modifier proportion, their 412
temperature decreases, according to the fact that the HBP 413
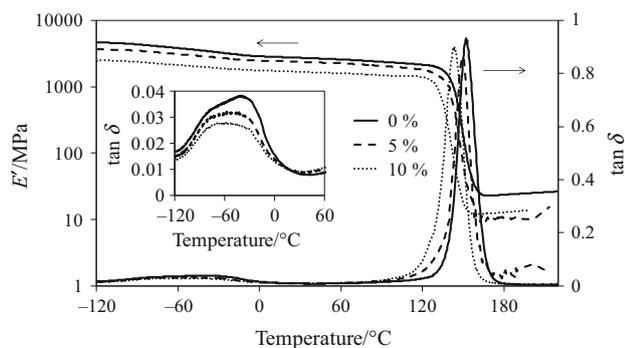act as an internal plasticizer. 414

Fig. 5 Storage modulus (E') and loss tangent (tan δ) of samples completely cured of the epoxy resin modified with different proportions of PEI-BuNCO100
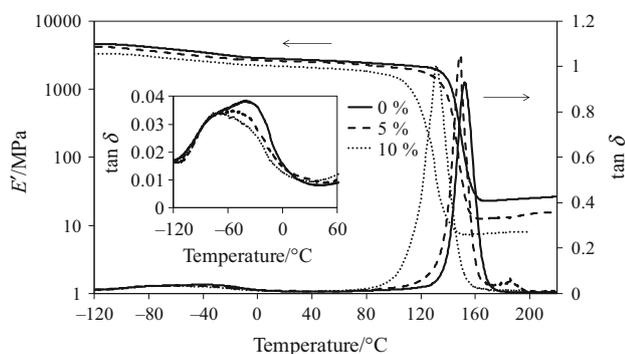

Fig. 6 Storage modulus (E') and loss tangent (tan δ) of samples completely cured of the epoxy resin modified with different proportions of PEI-BuNCO75
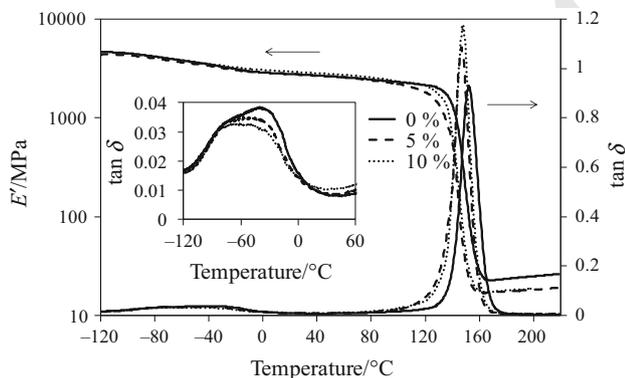

Fig. 7 Storage modulus (E') and loss tangent (tan δ) of samples completely cured of the epoxy resin modified with different proportions of PEI-PhNCO

415   In all the studied systems, there is only one glass tran-
416   sition and only β transition. Then, all the cured materials
417   are homogeneous with apparently only one phase or else is
418   present to a very limited extent and not detectable by
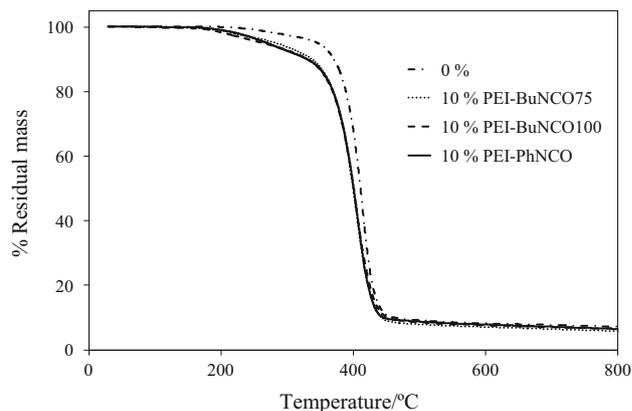419   DMA.

Fig. 8 Thermogravimetry at 10 °C min^{-1} in nitrogen atmosphere of samples completely cured of the neat epoxy resin and of the same resin modified with 10 % of the different modifiers

Thermogravimetric analysis   420

In Fig. 8, the thermal degradation process of the neat epoxy   421
resin and the modified thermosets with 10 % of the dif-   422
ferent HBPs is shown. The curves of this Figure are   423
obtained subtracting a blank one to the corresponding to   424
the samples. With the addition of the modifiers, the onset   425
temperature of the degradation decreases, but this onset   426
temperature is still greater than the curing temperature   427
(150 °C). This decrease is due to the decomposition of the   428
urea groups of the modifier in a isocyanate group and the   429
corresponding amine and of the poly(ethylene imine) at   430
lower temperatures than the epoxy/anhydride matrix [41].   431
Tentatively, and according to the $T_{5\%}$ values of the neat   432
HBPs (Table 1), it can be considered that the thermal   433
degradation of the cured materials starts by the decompo-   434
sition and volatilization of the modifier, followed by the   435
degradation of the epoxy/anhydride matrix at higher tem-   436
peratures. In Fig. 8, it is shown that at the first part of the   437
decomposition process, the decrease in mass is approxi-   438
mately 10 %, the same as the proportion of modifier in the   439
formulation.   440

Conclusions   441

The reaction between poly(ethylene imine) and two dif-   442
ferent isocyanates is a practical method to obtain new   443
hyperbranched polymers with blocked amino groups.   444
Using ^{1}H-NMR, their structures have been elucidated.   445

    The kinetics of curing has been correctly established   446
using an integral isoconversional procedure and a model-   447
fitting method and well fitted using an autocatalytic model.   448
The addition of these novel HBPs synthesized to epoxy/   449
anhydride systems, in the presence of a tertiary amine as   450

catalyst, barely modified the curing rate, which is controlled primarily by the mobility and concentration of the reactive species.

The addition of modified PEIs with phenyl and *t*-butyl terminal groups to epoxy/anhydride formulations allows obtaining thermosets with improved flexibility, due to the plasticizing influence of HBPs, with a slight reduction in glass transition temperature and cross-linking density and without affecting negatively processability. The final properties of the material obtained depend on the amount and type of modifier used.

References

1. Riew CK, Siebert AR, Smith RW, Fernando M, Kinloch AJ. Toughened epoxy resins: performed particles as tougheners for adhesives and matrices. In: Riew CK, Kinloch AJ, editors. Toughened plastics II novel approaches in science and engineering. Advances in chemical series, vol. 252. Washington: American Chemical Society; 1996. p. 33–44.

2. Saiki N, Yamazaki O, Ebe K. UV/heat dual-curable adhesive tapes for fabricating stacked packages of semiconductors. J Appl Polym Sci. 2008;108:1178–83.

3. Kang B-U. Interfacial fracture behavior of epoxy adhesives for electronic components. J Korea Acad Ind Cooper Soc. 2011;12:1479–84.

4. May CA, Tanaka GY. Epoxy resins. In: May CA, editor. Chemistry and technology, chap 1. New York: Marcel Dekker; 1988.

5. Petrie EM. Epoxy adhesive formulations. New York: McGraw-Hill; 2006.

6. Pascault JP, Williams RJJ. Epoxy polymers: new materials and innovations. Weinheim: Wiley-VCH; 2010.

7. Kinloch AJ, Shaw SJ, Tod DA, Hunston DL. Deformation and fracture behavior of a rubber-toughened epoxy: 1. Microstructure and fracture studies. Polymer. 1983;24:1341–54.

8. Ho T-H, Wang C-S. Toughening of epoxy resins by modification with dispersed acrylate rubber for electronic packaging. J Appl Polym Sci. 1993;50:477–83.

9. Mezzenga R, Boogh L, Månson JAE. A review of dendritic hyperbranched polymer as modifiers in epoxy composites. Compos Sci Technol. 2001;61:787–95.

10. Guo QP, Habrard A, Park Y, Halley PJ, Simon GP. Phase separation, porous structure, and cure kinetics in aliphatic epoxy resin containing hyperbranched polyester. J Polym Sci B. 2006;44:889–99.

11. Ratna D, Varley R, Simon GP. Toughening of trifunctional epoxy using an epoxy-functionalized hyperbranched polymer. J Appl Polym Sci. 2003;89:2339–45.

12. He S, Shi K, Bai J, Zhang Z, Li L, Du Z, Zhang B. Studies on the properties of epoxy resins modified with chain-extended ureas. Polymer. 2001;42:9641–7.

13. Evans D, Canfer SJ. Radiation stable, low viscosity impregnating resin systems for cryogenic applications. Adv Cryog Eng. 2000;46:361–8.

14. Ueki T, Nishijima S, Izumi Y. Designing of epoxy resin systems for cryogenic use. Cryogenics. 2005;45:141–8.

15. Nishijima S, Honda Y, Okada T. Application of the positron annihilation method for evaluation of organic materials for cryogenic use. Cryogenics. 1995;35:779–81.

16. Wu SH. Phase structure and adhesion in polymer blends; a criterion for rubber technology. Polymer. 1985;26:1855–63.

17. Pearson RA, Yee AF. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide). Polymer. 1993;34:3658–70.

18. Hedrick JL, Yilgor I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulphone) modified epoxy networks. Polymer. 1991;32:2020–32.

19. Wilkinson SP, Ward TC, McGrath JE. Effect of thermoplastic modifier variables on toughening a bismaleimide matrix resin for high-performance composite materials. Polymer. 1993;34:870–84.

20. Kunz SC, Sayre JA, Assink RA. Morphology and toughness characterization of epoxy resins modified with amine and carboxyl terminated rubbers. Polymer. 1982;23:1897–906.

21. Voit B. New developments in hyperbranched polymers. J Polym Sci A. 2000;38:2505–25.

22. Boogh L, Pettersson B, Månson JAE. Dendritic hyperbranchesd polymers as tougheners for epoxy resins. Polymer. 1999;40:2249–61.

23. Zhang D, Liang E, Li T, Chen S, Zhang J, Cheng X, Zhou J, Zhang A. The effect of molecular weight of hyperbranched epoxy resins with a silicone skeleton on performance. RSC Adv. 2013;3:9522–9.

24. Sörensen K, Pettersson BO, Boogh L, Månson JAE. Dendritic polyester macromolecule in thermosetting resin matrix. PCT Pat./SE94/04440; 1994.

25. Zhang D, Jia D, Chen S. Kinetics of curing and thermal degradation of hyperbranched epoxy (HTDE)/diglycidyl ether of bisphenol-A epoxy hybrid resin. J Thermal Anal Calorim. 2009;98:819–24.

26. Zhang Y, Zhang D, Qin C, Xu J. Physical and mechanical properties of dental nanocomposites composed of aliphatic epoxy resin and epoxidized aromatic hyperbranched polymers. Polym Compos. 2009;30:176–81.

27. Fernández-Francos X, Salla JM, Cadenato A, Morancho JM, Serra A, Mantecón A, Ramis X. A new strategy for controlling shrinkage of DGEBA resins cured by cationic copolymerization with hydroxyl-terminated hyperbranched polymers and ytterbium triflate as an initiator. J Appl Polym Sci. 2009;111:2822–9.

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

29. Morancho JM, Cadenato A, Ramis X, Fernández-Francos X, Flores M, Salla JM. Effect of a hyperbranched polymer over the thermal curing and the photocuring of an epoxy resin. J Thermal Anal Calorim. 2011;105:479–88.

30. Foix D, Fernández-Francos X, Salla JM, Serra A, Morancho JM, Ramis X. New thermosets obtained from bisphenol A diglycidyl ether and hydroxyl-ended hyperbranched polymers partially blocked with benzoyl and trimethylsilyl groups. Polym Int. 2011;60:389–97.

31. Fernández-Francos X, Santiago D, Ferrando F, Ramis X, Salla JM, Serra A, Sangermano M. Network structure and thermomechanical properties of hybrid DGEBA networks cured with 1-methylimidazole and hyperbranched poly(ethyleneimine)s. J Polym Sci B Polym Phys. 2012;50:1489–503.

32. Flores M, Fernández-Francos X, Ferrando F, Ramis X, Serra A. Efficient impact resistance improvement of epoxy/anhydride

thermosets by adding hyperbranched polyesters partially modified with undecenoyl chains. Polymer. 2012;53:5232–41.

33. Vandenabeele-Trambouze O, Mion L, Garrelly L, Commeyras A. Reactivity of organic isocyanates with nucleophilic compounds: amines; alcohols thiols; oximes; and phenols in dilute organic solutions. Adv Envir Res. 2001;6:45–55.

34. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta. 2011;520:1–19.

35. Liu H, Chen Y, Shen Z. Thermoresponsive hyperbranched polyethylenimines with isobutyramide functional groups. J Polym Sci A Polym Chem. 2007;45:1177–84.

36. Santiago D, Fernández-Francos X, Ramis X, Salla JM, Sangermano M. Comparative curing kinetics and thermal-mechanical properties of DGEBA thermosets cured with a hyperbranched poly(ethyleneimine) and an aliphatic triamine. Thermochim Acta. 2011;526:9–21.

37. Flores M, Fernández-Francos X, Ramis X, Serra A. Novel epoxy-anhydride thermosets modified with a hyperbranched polyester as toughness enhancer. Thermochim Acta. 2012;544:17–26.

38. Montserrat S, Andreu G, Cortes P, Calventus Y, Colomer P, Hutchinson JM, Malek J. Addition of a reactive diluent to a catalyzed epoxy-anhydride system. I. Influence on the cure kinetics. J Appl Polym Sci. 1996;61:1663–74.

39. Xu J, Holst M, Wenzel M, Alig I. Calorimetric studies on an anhydride cured epoxy resin from diglycidyl ether of bisphenol-A and diglycidyl ether of poly(propylene glycol). I. Onset of diffusion control during isothermal polymerization. J Polym Sci B Polym Phys. 2008;46:2155–65.

40. Vyazovkin S, Wight CA. Kinetics in solids. Annu Rev Phys Chem. 1997;48:125–49.

41. Schaber PM, Colson J, Higgins S, Thielen D, Anspach B, Brauer J. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. Thermochim Acta. 2004;424:131–42.

Springer

the language of science

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	Figure 1 (low res) is poor in quality as it looks fuzzy. Please supply a high-resolution version of the said figure preferably in .tiff or .jpeg format with 300 dpi resolution.	

Author Proof