Influence of end groups in hyperbranched polyesters used as modifiers in the characteristics of epoxy thermosets cured by adipic dihydrazide

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Abstract. Mixtures of diglycidylether of bisphenol A (DGEBA) resin and different ratios of aliphatic-aromatic hyperbranched polyester (HBP) were cured by a latent curing agent, adipic dihydrazide (AH). The HBPs prepared have hydroxyl groups or 10-undecenoyl or allyl groups as chain ends. The curing mixtures were investigated by differential scanning calorimetry (DSC) to study the curing process and to evaluate the kinetic parameters of the different formulations. These studies suggest that HBPs decrease the curing rate of epoxy/AH in the case of vinyl terminated HBP, whereas OH terminated HBP accelerates the first stages and delays the lasts.

The thermosets obtained showed an improvement in microhardness and impact strength without any reduction of the T_g and thermal parameters. Microparticle phase separation was observed with the undecenoyl HBP derivatives or when a 10% of allyl HBP derivative was in the formulation.

Keywords: thermosetting resins, toughness, hyperbranched polymers, latency, dihydrazides

1. Introduction

Epoxy resins are widely used in several applications: adhesives, coatings, castings, electric laminates, encapsulation of semiconductor devices, matrix materials for composites, structural components and engineering [1, 2], because of their good characteristics such as adhesion and chemical resistance. However, due to their high cross-link density they are inherently brittle, which limits their applicability. With the aim to increase their toughness different types of modifiers have been added to epoxy formulations such as rubber, thermoplastic and core-shell particles. The addition of liquid rubbers and thermoplastics was one of the first attempts to improve toughness, but usually this method has a

detrimental effect on the thermomechanical characteristics of the thermosets and the processability of the formulation [3], which is a drawback for coatings applications [4, 5]. To solve the limitations related to processability, hyperbranched polymers (HBPs) were introduced as toughness modifiers [6–8]. The advantage is that their highly branched structure prevents entanglement, reducing the viscosity of the formulation in comparison to the use of their linear analogues. Moreover, the great number of terminal groups has a significant effect on the reactivity, can increase the compatibility with the resin and helps to maintain thermomechanical characteristics [9, 10]. Based on their unique properties, HBPs have been applied not only as tougheners for ther-

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mosets but also in cross-linking or adhesive agents [11], compatibilizers [12], dispersers [13], processing aids, and rheology modifiers [14, 15].

One of the most effective methods of inhibiting crack growth after impact is the addition of a second phase that induces the formation of particles that absorb the impact energy and deflect the crack [5]. Usually, the particles are generated from a homogeneous solution composed of the resin, curing agent and modifiers, which on curing causes a reaction-induced phase separation (RIPS) to take place. The phase separated morphology is highly dependent on the kinetics of curing and on the dynamics of the phase separation process.

The synthesis and characterization of aromatic-aliphatic hyperbranched polyesters modified with long and short vinylic chains and their use as modifiers of DGEBA thermosets cured with hexahydro-4-methylphthalic anhydride was reported by us [16]. The addition of these modifiers led to significantly increased rates of cure. However, the materials obtained were homogeneous and the increase in impact strength was only modest. In addition, the HBPs led to a plasticization and to a considerable decrease in the T_g .

In a previous paper we demonstrated the latent character of a series of dihydrazides in the thermal curing of DGEBA [17]. Several dihydrazides were synthesized and used as stoichiometric curing agents of epoxy resins. From the dihydrazides synthesized, AH was the one that leads to curing at the lowest temperature (maximum of the curing exotherm at 165°C) and led to materials with good characteristics. However, dihydrazides possess a high crystalline character and they are difficult to disperse or dissolve, because on melting (at 181–184°C) the curing process is extremely fast.

In the present work, the influence of the addition of aromatic-aliphatic hyperbranched polyesters modified with long and short vinylic chains (see Figure 1) to the epoxy formulation has been studied with two different aims: to increase toughness and help to disperse AH in the DGEBA resin. In addition, it was expected from the fast curing process caused by the dihydrazides at the appropriate temperature that could induce phase separated morphologies, when the HBP structure cannot be covalently incorporated to the epoxy matrix, because of its solubility and the end group characteristics.

Figure 1. Structure of the HBP modifiers added to the formulations

2. Experimental

2.1. Materials

4,4-Bis(4-hydroxyphenyl) valeric acid, N,N'-dicyclohexylcarbodiimide (DCC), triethyl amine, allyl bromide, 10-undecenoyl chloride, diethyl adipate and hydrazine hydrate were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification. Diglycidyl ether of Bisphenol A (DGEBA) Epikote Resin 828 was provided by Momentive Speciality Chemicals Inc. (Barbastro, Spain) with an epoxy equivalent of 184 g/eq and was dried in vacuum before use. All the organic solvents were purchased from Scharlab and purified by standard procedures. 4-(N,N-dimethylamino) pyridinium p-toluenesulfonate (DPTS) was prepared as described in the literature [18].

2.2. Synthesis of adipic dihydrazide (AH)

50.5 g (0.25 mol) of the diethyl adipate were dissolved in 200 mL of absolute ethanol and 0.9 mol of hydrazine hydrate (90%) were added drop by drop. Once the addition was complete the heating was turned on and the mixture was kept 6 h at reflux. During this time a white precipitate was formed, which was filtered through a Buchner funnel and then washed twice with cold ethanol. The white powder was dried in the vacuum oven at 50°C. The obtained yield was higher than 90%. m.p. 181–4°C (recrystallized from ethanol). ^1H NMR (DMSO- d_6 , δ in ppm): 8.93 s (2H, –NH–); 4.14 s (4H, –NH₂); 1.97 t (4H, –CH₂–) 1.41 m (4H, –CH₂–); ^{13}C NMR (DMSO- d_6 , δ in ppm): 171.49 (–CONH–); 33.27 (–CH₂–); 24.99 (–CH₂–). FTIR-ATR (cm^{–1}): 3310, 3288, 3197, 1626, 1529, 1376, 1273, 1166, 1033, 690.

2.3. Hyperbranched polyester synthesis (HBP-OH)

The HBP-OH (Figure 1) was synthesized according to a previously described procedure [19] from 4,4-bis(4-hydroxyphenyl) valeric acid as AB₂ monomer. The ^1H and ^{13}C NMR data are in accordance with those published [20].

M_n : 8700 g/mol, M_w : 12300 g/mol. T_g 121°C (by DSC). The amount of hydroxyl groups was determined according to ISO 2554-1974 standards. The number of hydroxyl groups per molecule found by titration was 36 [16].

2.4. Derivatization of HBP-OH with 10-undecenoyl chain ends (HBP-Und)

The derivatization was done from HBP-OH (Figure 1) synthesized previously by reacting with 10-undecenoyl chloride in the presence of triethylamine, as previously described [16]. The product was dried in a vacuum oven at 50°C overnight and a pale brown viscous liquid was obtained. Yield: 94% T_g 18°C (by DSC).

^1H NMR (400 MHz, CDCl_3), δ (ppm): 1.26 m (–CH₂–); 1.41 m (–CH₃); 1.68 m (–CH₂–); 2.06 m (–CH₂–); 2.34 m (–CH₂–); 2.55 m (–CH₂–); 5.10 dd (CH₂=); 5.87 m (=CH–); 7.11 m (CH Ar).

^{13}C NMR (100.6 MHz, CDCl_3), δ (ppm): 24.7 (–CH₂–); 27.6 (–CH₂–); 28.9 (–CH₂–); 33.6 (–CH₂–); 34.3 (–CH₂–) 36.2 (–CH₂–); 45.4 (=C=); 113.9 (CH₂=); 121.2 (Ar) ; 128.2 (Ar); 139.0 (=CH–); 145.6 (Ar); 148.6 (Ar); 172.3 (C=O).

2.5. Derivatization of HBP-OH with allyl chain ends (HBP-Allyl)

The derivatization was performed by nucleophilic substitution on allyl bromide by the phenolate end groups, formed by treating HBP-OH (Figure 1) with K₂CO₃ in a mixture of THF and acetone, as previously reported [16]. HBP-Allyl was obtained by precipitating the THF solution on water. The polymer was dried in a vacuum oven at 50°C overnight and a white powder was obtained. Yield: 90%. T_g 81°C (by DSC).

^1H NMR (400 MHz, CDCl_3), δ (ppm): 1.65 s (–CH₃–); 2.36 m (–CH₂–); 2.53 (–CH₂–); 4.53 s (–CH₂–); 5.35 dd (CH₂=); 6.07 m (=CH–); 6.8–7.2 m (CH Ar).

^{13}C NMR (100.6 MHz, CDCl_3), δ (ppm): 28.0 (–CH₂–); 30.6 (–CH₂); 36.6 (–CH₂–); 45.1 (=C=); 68.9 (–CH₂–); 114.3 (Ar); 117.9 (CH₂=) ; 128.4 (Ar); 133.5 (=CH–); 141.2 (Ar); 156.9 (Ar); 172.5 (C=O).

2.6. Preparation of the curing mixtures

The neat DGEBA/AH formulation was prepared by adding the stoichiometric amounts of each reactant to a mortar and homogenizing them by mechanical mixing while heating at 90°C. For the preparation of the formulations with the HBP modifiers, first of all the corresponding proportion was dissolved in DGEBA by adding a little amount of THF. The sol-

vent was then eliminated in vacuum at 50°C overnight and then the stoichiometric amount of AH was added and homogenized by mixing in a mortar while heating at 90°C. The proportions of HBPs added were a 5 and 10% w/w in reference to DGEBA. AH was added in a molar proportion to DGEBA of 1:2.

2.7. Measurements

The 400 MHz ^1H NMR and 100.6 MHz ^{13}C NMR spectra were obtained with a Varian Gemini 400 spectrometer with Fourier Transformed (Palo Alto, California USA). ^1H NMR spectra were acquired in 1 min and 16 scans with a 1.0 s relaxation delay (D1). ^{13}C NMR spectra were obtained using a D1 of 0.5 s and an acquisition time of 0.2 s. A total of 500 accumulations were recorded. CDCl_3 was used as a solvent and tetramethylsilane (TMS) as internal standard.

Calorimetric analyses were carried out on a Mettler DSC-821e calorimeter (Greifensee, Switzerland). Samples of approximately 10 mg were cured in aluminium pans in a nitrogen atmosphere. Non-isothermal experiments were performed from 0 to 225°C at heating rates of 2, 5, 10, and 15°C/min to determine the reaction heat and the kinetic parameters. In the non-isothermal curing process, the degree of conversion at a given temperature T was calculated as the quotient between the heat released up to T and the total reaction heat associated with the complete conversion of all reactive groups. The precision of the given enthalpies is $\pm 3\%$. The T_g s of the cured materials were determined with a second scan at 20°C/min after dynamic curing by the mid-point method and the error is estimated to be approximately $\pm 1^\circ\text{C}$. The T_g s of the pure HBPs were determined by a similar procedure.

Dynamic mechanical thermal analysis (DMTA) was carried out with a TA Instruments DMTA 2980 analyzer (New Castle, USA). The samples were cured isothermally in a mould at 190°C for 1 h and then post-cured for 0.5 h at 200°C. Before the samples were prepared, they were degassed in a vacuum oven at 50°C for 3 h. Single cantilever bending at 1 Hz was performed at 3°C/min from 30 to 220°C on prismatic rectangular samples ($1.5 \times 20 \times 5 \text{ mm}^3$). Thermogravimetric analysis was carried out with a Mettler-Toledo TGA/SDTA 851e thermobalance

(Greifensee, Switzerland). Cured samples with an approximate mass of 5 mg were heated from 30 to 800°C at a heating rate of 10°C/min in a nitrogen atmosphere.

Impact tests were performed at room temperature by means of a Zwick 5110 impact tester (Altamonte Springs, USA) according to ASTM D 4508-05 using rectangular samples ($25 \times 12 \times 2.5 \text{ mm}^3$). The pendulum employed had a kinetic energy of 1 J. For each material, 9 determinations were made. The impact strength (IS) was calculated from the energy absorbed by the sample upon fracture according to Equation (1):

$$IS = \frac{E - E_0}{S} \quad (1)$$

where E and E_0 are the energy loss of the pendulum with and without sample respectively, and S is the cross-section of the samples.

The fracture area of impacted samples was metalized with gold and observed with a scanning electron microscope (SEM) Jeol JSM 6400 (Tokyo, Japan).

The kinetic triplet (pre-exponential factor, activation energy, and the kinetic model) of the curing was determined using integral isoconversional non-isothermal kinetic analysis, Kissinger-Akahira-Sunose equation, combined with the Coats-Redfern procedure. Details of the kinetic methodology are given in previous studies [21].

Microhardness was measured with a Wilson Wolpert (Micro-Knoop 401MAV) device (Massachusetts, USA) following the ASTM D1474-98 (2008) standard procedure. For each material 10 determinations were made with a confidence level of 95%. The Knoop microhardness (HKN) was calculated from Equation (2):

$$HKN = \frac{L}{A_p} = \frac{L}{l^2 C_p} \quad (2)$$

where L is the load applied to the indenter (0.025 kg), A_p is the projected area of indentation in mm^2 , l is the measured length of long diagonal of indentation in mm, and C_p is the indenter constant ($7.028 \cdot 10^{-2}$) relating l^2 to A_p . The values were obtained from 10 determinations with the calculated precision (95% of confidence level).

3. Results and discussion

3.1. Calorimetric study of the curing process and the thermosets obtained

In the preparation of epoxy thermosets, the selection of the curing agent is crucial to obtaining good thermoset properties but especially when a HBP modifier is added to the formulation, because of the role played by the chemistry of the curing agent in the possible reaction of the terminal groups in the HBP structure. A number of authors used primary amines as curing agents, which did not allow the covalent incorporation of hydroxyl terminated HBPs to the epoxy matrix and thus microphase separation in the final material could be observed [22, 23]. In the present study, the addition of a 5 or 10% in weight of HBP-OH and its derivatives with allyl and 10-undecenoyl chain ends should not react with dihydrazides and phase separation could also be expected. However, not only the chemistry of the terminal groups but also the structure of the HBP and the curing rate can influence the phase separation process.

In a previous paper, we reported the study of the curing process of DGEBA with some dihydrazides and concluded that the stoichiometric proportion is 2 mol of DGEBA per each mol of dihydrazide. The structure of the network formed was confirmed by FTIR analysis and is represented in Figure 2.

The curing could be catalyzed by acidic and basic catalysts but the latent character was reduced, and therefore some effects on the curing evolution can be expected on adding HBP modifiers.

We studied the curing process by non-isothermal scanning calorimetry. The calorimetric curves col-

lected in Figure 3 show the curing exotherms for all the formulations studied. The plot of conversion against temperature for all the studied formulations is represented in Figure 4 and the calorimetric data are collected in Table 1. In this plot, we can observe

Figure 3. Calorimetric curves for the formulations studied obtained in DSC scans at 10°C/min under N₂

Figure 4. Conversion against temperature of the dynamic curing at 10°C/min of all the formulations studied

Figure 2. Structure of the network formed by reaction of the epoxy resin and the adipic dihydrazide

Table 1. Calorimetric data and kinetic parameters obtained in the curing of all the formulations

Thermoset	$T_{\max}^a$ [°C]	Δh^b [J/g]	Δh^b [kJ/eq]	T_g^c [°C]	T_{gFox}^d [°C]	E_a^e [kJ/mol]	$\ln A^f$ [s ⁻¹]	$k_{170^\circ C}^g$ [min ⁻¹]
Neat	165	408	96	128	128	170	49.2	21.3
HBP-OH-5%	170	352	90	130	128	114	33.0	7.1
HBP-OH-10%	167	331	89	138	127	99	29.0	7.3
HBP-Und-5%	172	355	91	127	121	117	33.4	5.0
HBP-Und-10%	176	327	88	123	113	117	33.1	4.5
HBP-Allyl-5%	180	273	70	123	125	161	45.3	4.7
HBP-Allyl-10%	177	285	78	128	121	127	35.7	3.0

^aTemperature of the maximum of the curing exotherm registered at 10°C/min.^bEnthalpy of the curing exotherm registered at 10°C/min.^c T_g determined after curing in a dynamic scan registered at 20°C/min.^d T_g calculated by the Fox equation.^eValues of activation energy at 50% of conversion, evaluated by the isoconversional non-isothermal procedure.^fPre-exponential factors calculated for autocatalytic model ($n = 2.1$, $m = 0.9$) with $g(\alpha) = [(1-\alpha)\alpha^{-1}]^{-0.9}(0.9)^{-1}$.^gValues of rate constants at 170°C using the Arrhenius equation at 50% conversion.

that the latent character of the curing of the neat formulation is slightly reduced on adding the HBP modifiers. The effect on the latency seems to be more noticeable on adding HBP-OH, which catalyzes the first stages of the curing process. However, a delay is observed at higher conversions. The catalytic effect is increased with the proportion of HBP-OH in the formulation. This can be explained by the presence of phenolic groups, which can facilitate the nucleophilic attack of the nitrogen on the epoxy ring by the formation of hydrogen bonds, as is described for epoxy-amine formulations [24]. Since during curing of epoxy resins with active NH_2 moieties OH groups are always formed, the effect of the phenolic groups of the HBP is not as noticeable when the conversion reaches a certain extent. Moreover, the viscosity of the reactive mixture increases and can delay the curing process. The addition of HBP-Und and HBP-Allyl leads to a significant reduction of the curing rate, and higher temperatures are needed to cure these formulations. However, there is not a clear dependence of the curing rate with the amount of modifier. In a previous study in epoxy-anhydride thermosets with both modified HBPs an acceleration of the curing was observed in spite of the higher viscosities of the formulations. This acceleration was attributed to the presence of carboxylic groups in the focal point of the HBPs, which can catalyze the curing process [16]. In the present case using dihydrazides, the dilution effect on adding the modifiers and the increase in the viscosity seem to greatly influence the curing rate in comparison to the acidic catalysis produced by carboxylic groups [17].

From the values in Table 1 we can observe that the curing enthalpy of the formulations containing HBP modifiers is somewhat lower than that measured for the neat formulation, but in all cases the curing was complete, as identified by the complete disappearance of the band at 910 cm^{-1} in the FTIR of the final thermosets. It should be stressed that the T_g measured for the modified thermosets does not decrease significantly, and even increases in the case of adding HBP-OH to the formulation. If we consider the T_g s of the different hyperbranched T_g^{HBP} and the T_g of the neat material and apply these values and the corresponding proportions (w) in the Fox equation [25] (Equation (3)) we can predict the T_g values of the homogeneously blended modified thermosets:

$$\frac{1}{T_g} = \frac{w}{T_g^{HBP}} + \frac{1-w}{T_g^{neat}} \quad (3)$$

As can be seen in Table 1, only the thermoset with a 5% of Allyl-HBP has an experimental value of T_g similar to that predicted by this equation, whereas the addition of the other vinylic modified HBPs does not significantly influence the T_g determined for the neat material. This result can be explained by a phase separation of the HBPs due to the incompatibility produced during the curing reaction, which will be further confirmed by SEM. Since the initial solution was fully compatible, the separation of the particles is originated by a reaction-induced phase separation process (RIPS), which is highly dependent on the kinetics of curing and on the dynamics of the phase separation process. It should be pointed out, that the same HBP-Allyl and HBP-Und were

used as modifiers of DGEBA/anhydride thermosets, leading to completely homogeneous materials [16]. The higher curing rate when dihydrazides are used as curing agents and the highly polar structure of the network produced with this agent could both be responsible for the phase separation process, since these HBPs cannot be chemically incorporated into the epoxy network and have non-polar characteristics, especially in case of HBP-Und, as a result of the presence of the long aliphatic chains. Thus, the addition of a 5% of HBP-Allyl to the formulation leads to a homogeneous material because of its higher compatibility, due to its shorter aliphatic structure. On adding HBP-OH to the formulation, the T_g of the final thermosets is even higher than that predicted by the Fox equation. This unexpected result in fully homogeneous materials can be rationalized by the reduction in free volume due to the hydrogen bonding established between the OH groups of HBP and the epoxy-dihydrazide network [26].

In Table 1, the kinetic parameters calculated for the curing of the different formulations are collected. The kinetics of these systems was studied by the non-isothermal isoconversional procedure, as explained in the experimental part and in a previous article [21]. Figure 5 shows the evolution of the activation energy against conversion for the formulations studied.

As is shown in the Figure 5, the activation energy remains, during curing, nearly constant for all formulations. This result suggests that the reaction mechanism is the same in the whole range of curing and only a single kinetic model is needed to describe the curing. In many reaction processes the values of

Figure 5. Apparent activation energies against conversion of all the formulations studied

activation energy, due to the compensation effect between the activation energy and the pre-exponential factor [27], do not reflect exactly the reaction rate and it is better to discuss the rate constants calculated using the Arrhenius equation and the aforementioned kinetic parameters. To calculate the frequency factors, we selected the kinetic model that best fits the experimental data, which for all formulations was the autocatalytic kinetic model with $n = 2.1$ and $m = 0.9$. This kinetic model is consistent with the accelerative effect of the hydroxyl groups generated during curing.

The calculated values of the rate constants (Table 1) illustrate the order of reactivity on curing at a conversion of 0.5 and agree with the experimental conversion-temperature curves. In this conversion, all the HBP modifiers show a delaying effect on the curing rate, as can be also observed in Figure 4. However, this effect is not produced at the beginning of curing in the case of the formulations containing HBP-OH, where hydroxyl terminal groups accelerate the curing.

3.2. Characterization of the materials by TGA and DMTA

Table 2 and Figure 6 present the thermogravimetric data and the derivatives of the TGA curves, respectively.

The thermosets obtained show a higher resistance to thermal degradation than the neat material, since the ester groups introduced are aromatic and therefore there is no β -elimination process that finally leads to the formation of little fragments that can be lost on heating. There is also no effect on the temperature of the maximum degradation rate, but the shape of the curves changes on modifying the mate-

Table 2. Thermogravimetric data for all the thermosets obtained

Thermoset	$T_{5\%}^a$ [°C]	T_{max}^b [°C]	Char yield ^c [%]
Neat	287	337–390	12.2
OH-5%	292	344–407	13.2
OH-10%	290	352–398	14.1
Und-5%	293	355–404	14.5
Und-10%	291	356–402	14.6
Allyl-5%	297	360–400	13.7
Allyl-10%	296	350–410	13.8

^aTemperature of the 5% of weight loss in N_2 atmosphere.

^bThe temperature of the peaks of the derivative on the thermogram registered in N_2 atmosphere.

^cChar yield after a dynamic scan until 600°C in N_2 atmosphere.

Figure 6. Derivatives of the TGA curves in N_2 atmosphere for the thermosets obtained

rials. As we can see, all the degradation curves are bimodal, indicating two different degradative processes. In case of the neat material, the peak at lower temperature is more pronounced than the one occurring at higher temperature, whereas in case of the material containing a 10% of HBP-Und the contrary trend is observed. This can be related to the lower proportion of OH groups in the latter.

Figures 7 and 8 show the curves of the storage modulus and $\tan \delta$, respectively, for all the thermosets prepared obtained by DMTA. In Figure 7 we can see that the modulus in the rubbery state is similar for the neat and HBP-OH formulations, which seems to indicate that the crosslinking density, either covalently or by hydrogen bonding, is quite similar. On the contrary, the presence of HBP-Allyl and HBP-Und leads to a reduction of the modulus. From Figure 8, it can be seen that the temperature of the maximum of the $\tan \delta$ peak is quite similar for all the thermosets studied, but the values are higher

Figure 7. Evolution of storage modulus against temperature at 1 Hz for all the thermosets obtained

Figure 8. Evolution of $\tan \delta$ against temperature at 1 Hz for all the thermosets obtained

than those obtained by DSC, because of the differences in the frequency applied in DMTA technique. It should be noted that the materials containing a 10% of HBP-Allyl or HBP-Und show a much broader curve indicating their lower homogeneity.

3.3. Mechanical and morphological characterization

Microhardness measurements are very useful in rating coatings on rigid substrates as a measure of the resistance that one body offers against penetration by another under static loads. These measurements were carried out with a Knoop microindenter and the results are shown in Figure 9.

As can be seen, the addition of all the HBP modifiers does not reduce this parameter but even increases it, which is advantageous in the performance of the coatings. The best formulation in terms

Figure 9. Microhardness values of the thermosets prepared. The increase in microhardness respect to the neat formulation is also indicated.

Figure 10. Impact strength values of the thermosets prepared

of microhardness enhancement is the one containing a 10% of HBP-Allyl.

The results of the impact tests are collected in Figure 10 for all the materials prepared. The values correspond to the energy absorbed by the material during crack propagation. It is possible to prove that the modification of DGEBA/AH thermosets with all the HBPs synthesized improves this value, as it was reported in previous publications on epoxy/amine or anhydride systems [28].

As we can see, all the modified thermosets present a higher value than the neat material. The highest values were obtained with a 10% of HBP-Und or a 5% of HBP-Allyl. In reference to the impact strength values, it should be pointed out that the neat system is tougher than the DGEBA/MHHPA neat material studied in a previous publication (2.4 to 3.9 kJ/m²) [16]. This illustrates the important role of the curing agent in the characteristics of the thermosets. Moreover, the addition of HBP-Und and HBP-Allyl to DGEBA/dihydrazide materials results in a greater improvement of the toughness characteristics in comparison with DGEBA/MHHPA thermosets.

The SEM micrographs of the impacted fracture surfaces are collected in Figure 11. These show a fracture surface with cracks and river-line structures in different planes in the neat material in accordance with the impact strength measured. In agreement with our earlier interpretations, on comparing the experimental T_g s which are higher than those predicted by the Fox equation, materials containing a 5% of HBP-Und or a 10% of both vinylic modifiers show a clear phase separation of the HBP from the epoxy matrix. Usually, particle phase separated

materials have enhanced toughness characteristics [5, 29]. However, the thermoset containing a 10% of HBP-OH shows a notable improvement in impact strength, quite similar to phase separated materials, but it presents a homogeneous appearance with a patterned roughness. This type of morphology was previously observed by us in materials obtained with 1-methylimidazole, which cured very fast as is also the case here [30]. The T_g measured for this thermoset does not indicate plasticization, related to ductility, that dictate its toughness characteristics [31]. However, the rougher surface appearance observed in the fractographs containing HBP-OH blends, suggests that the impact specimens experienced more plastic deformation during fracture in comparison with the unmodified epoxy network.

As we can see, materials with a 5 or a 10% in weight of HBP-Allyl show very different fracture morphologies. Whereas the first one, present a homogeneous appearance with unidirectional cracks, river-line structures and striations, the second present nanoparticles (of about 300 nm) distributed in the surface, which leads to high expanded cracks. In both materials containing HBP-Und a microphase separation is observed which stops or deflects the crack propagation. In both cases, the size of the particles has a broad distribution, and more particles with a bigger size (average about 1.5 μ m) can be observed for the material containing a larger proportion of modifier.

In Figure 12, a more detailed micrograph of the fracture surface for the material containing a 10% of HBP-Und is shown. As we can see, when the crack reaches the particle, it terminates and the energy is dissipated around the particle of HBP. This indicates that there is no interfacial adhesion between epoxy network and HBP-Und as expected as a result of the loss of hydrogen bonding by derivatization of phenolic groups. Some authors reported that the improvement in the interfacial adhesion of epoxy resin and HBP particles contributes to an improvement of the fracture behaviour of epoxy resin/HBP blends [27]. According to that argument, the nano/microphase separation reached in the present study does not very effectively enhance the toughness, as was expected. HBP-OH modifiers do not separate because of the compatibility with the epoxy matrix. However, the improvement in toughness is achieved in all the materials obtained in the present work without any decrease of T_g or deterioration of the

Figure 11. SEM micrographs from impacted fracture surfaces of the thermosets prepared at 2000 magnifications

Figure 12. SEM micrograph of the impacted fracture surface for the thermoset containing a 10% of HBP-Und at 20000 magnifications

thermal characteristics and microhardness without forgetting that the addition of HBPs helps to reach a good dispersion of the dihydrazide in the formulation.

4. Conclusions

A series of HBPs with OH or vinyl groups of different length as chain ends were synthesized and used as modifiers in DGEBA/AH formulations. The addition of the HBPs helped to disperse and to compatibilize the crystalline dihydrazide in the reactive mixture.

The addition of HBP-OH to the formulation increased the curing rate at the beginning of the curing but decreased it at high conversion, and slightly reduced the latency of the adipic dihydrazide as DGEBA curing system. The addition of HBP-Allyl and HBP-Und led to a significant reduction of the curing rate and higher curing temperatures were needed to reach the complete curing of these formulations.

The T_g values of the modified thermosets were not significantly lower than that of the neat material and were even higher when HBP-OH was blended in the thermoset. This was attributed to the hydrogen bonding of the phenolic groups with the epoxy matrix. When 5 or 10% of HBP-Und or 10% of HBP-Allyl was incorporated into the material a nano or microphase separation was observed by SEM, which explains why no reduction in the T_g was observed. The materials showed a higher resistance to thermal degradation on adding the modifiers.

Microhardness and impact strength values were improved by adding all the HBP modifiers to the formulations.

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