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New epoxy thermosets modified with hyperbranched poly(ester-amide) of different molecular weight

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ABSTRACT

The influence of hydroxy-functionalized hyperbranched poly(ester-amide) (HBP) of different molecular weight on the curing process of diglycidylether of bisphenol A (DGEBA) was studied using methyltetrahydrophthalic anhydride (MTHPA) as curing agent. By Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) the curing reaction was monitored and the covalent incorporation of the modifier in the matrix was proved. By thermomechanical analysis (TMA) the reduction of the contraction after gelation on changing the HBP proportion was observed. The incorporation of HBP increased the glass transition temperature (T_g) and reduced the overall shrinkage. The modified materials showed a higher thermal degradability than neat DGEBA thermosets allowing reworkability. Thermal expansion coefficient, Young's modulus, impact strength and microhardness were improved. The water uptake behavior was also evaluated.

1. Introduction

Epoxy resins are ideal materials for structural applications. However, when applied as coatings, they have some drawbacks such as brittleness and shrinkage, which reduce their performance and dimensional stability, leading to a final reduction of their protection capability [1]. During the past decades considerable efforts have been made to improve the toughness of these materials. One of the most successful approaches to decrease the brittleness of epoxy resins is to blend them with rubbers, elastomers or core–shell particles able to stand energy absorption mechanisms [2–4]. However, this results in a high increase in the viscosity of the uncured blends and/or to a decrease in the T_g of the thermosets. Some years ago, the use of hyperbranched polymers (HBPs) has been proposed in order to overcome the limitations of traditional modifiers [5] and a lot of research groups adopted this strategy to improve the mechanical characteristics of epoxy resins [6–8]. It has been reported that the toughness increased while the Young's modulus and the glass transition temperature remained unaffected [5].

Another advantage of HBPs is their low viscosity compared to linear analogues, due to reduced entanglements between molecules caused by their highly branched architecture [5]. This characteristic allows improving the processability of HBP/epoxy thermosets which is very important in the field of coatings.

One of the technological ways to reduce shrinkage during epoxy curing is the addition of fillers but produces a great change on the mechanical properties and leads to the loss of transparency. Some authors proposed the use of expandable monomers, but a reduction of the T_g was al-

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ways observed, because of their flexible structure [9–11]. As an alternative, the reduction of the shrinkage has been achieved by the addition of hyperbranched polymers [12,13] although in some papers the contrary behavior has been described [14,15].

The improvement of the toughness in addition with the reduction of the shrinkage can minimize the generation of stresses during curing. Månson's group [16] investigated the applicability of HBPs as a stress-reducing agent in epoxy-based composite materials to prevent void formation. They observed that by adding 10 wt% of Boltorn E1, with a flexible aliphatic polyester structure and epoxy groups at the chain ends, a reduction of 5 °C in the T_g value and a strongly reduction of the shrinkage during curing and the internal stress level was achieved.

Apart from their structure, a parameter that should influence the effect of the HBPs on the characteristics of the thermosets is their average molar mass. If the molar mass increases, maintaining the repetitive unit, the number of reactive chain ends per molecule increases as well. Some authors studied the mechanical properties of epoxy thermosets modified with HBPs of different molar masses [17,18]. They reported that the addition of HBP to the epoxy matrix improved tensile, flexural and impact strength and fracture toughness. These properties improve with the proportion of HBP and its molecular weight until reaching a maximum. This maximum should also depend, predictably, on the chemical structure of the HBP added and therefore this cannot be taken as a general trend.

In addition to that, one of the main limitations of the thermosetting materials is their low degradability. Coating degradability is required when the reworkability of the coated electronic components is desired. The improvement on this property could be achieved by the introduction of labile groups such as esters of secondary or tertiary alkyl moieties in the network [19]. Ester groups can be thermally broken by a β-elimination process allowing removing the coating from the substrate. If their structure is appropriately selected, HBPs can help to solve this drawback. In previous studies we could increase the thermal degradability of epoxy thermosets by adding hyperbranched polyesters [13,20]. Besides hyperbranched polymers which have a large number of functional groups at the end of the branches, such as hydroxyls, which allow covalently linking the modifier to the epoxy matrix by the use of anhydrides as curing agents. In the present work, we have selected as modifiers two hydroxyl-ended hyperbranched poly(ester-amide)s with cycloaliphatic rings in their structure. One of them is the commercial Hybrane® H1500 with a molecular weight (M_n) of 1500 g/mol and the other with a molecular weight of about 30,000 g/mol synthesized by us. The presence of cycloaliphatic rings in the structure reduces the flexibility and the polarity compared to Hybrane® S1200, which affects the characteristics of the modified epoxy thermosets previously reported by us [20].

To our knowledge, there are no studies reported in the literature related with the effect of adding these structures to diglycidylether of bisphenol A (DGEBA)/anhydride thermosets.

2. Experimental

2.1. Materials

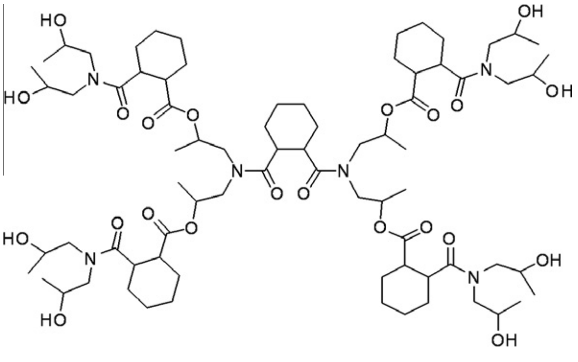
Diisopropanolamine (DIPA) and *cis*-hexahydrophthalic anhydride (HHPA) were purchased from commercial sources (Fluka and Sigma–Aldrich, respectively) and were used without further purification.

Diglycidylether of bisphenol A (DGEBA) EPIKOTE RESIN 827 was provided by Shell Chemicals (EEW = 182.08 g/eq). Methyltetrahydrophthalic anhydride (MTHPA) (Ciba-Huntsman) (HY918) and *N*,*N*-benzyldimethylamine (BDMA) (Aldrich) were used as received. The hydroxyl terminated hyperbranched poly(ester-amide) Hybrane® H1500 (DSM) has an average molecular weight (M_n) and polydispersity index (PDI), as reported on the data sheet, of about 1500 g/mol and 3.5, respectively. The hydroxyl index of 402 mg KOH/g and the T_g value of 75 °C were determined experimentally.

Xylene (mixture of isomers) was purified by vacuum distillation and dried over molecular sieve. Tetrahydrofuran (THF) and diethylether were used as received. All solvents were purchased from Scharlab.

2.2. Synthesis of hyperbranched H30000

The synthesis of hyperbranched polymer H30000 (represented in Scheme 1) was done similarly to the procedure described by Fang et al. [21]. Diisopropanolamine (15.32 g, 0.115 mol) and xylene (50 mL) were introduced into a three-necked flask equipped with a thermometer, a single water dispenser and a gas inlet to fill the flask with nitrogen and 15.42 g (0.10 mol) of *cis*-hexahydrophthalic anhydride dissolved in 50 mL xylene were added dropwise. The reaction mixture was gradually heated in an oil bath to 80 °C and reacted for 6 h under nitrogen at this temperature. For better stirring and mixing, small amounts of dry xylene were added if necessary. Then, the reaction mixture was heated to 180 °C until no more water could be azeotropically removed through the single water dispenser. To drive the reaction to higher conversion, vacuum (~5 mbar) was applied for further 15 min. After cooling, xylene was removed in vacuum yielding an almost colorless glassy substance. The crude product was purified twice by precipitation from THF into diethylether and



Scheme 1. Idealized structure of H1500.

dried under vacuum at 50 °C. The yield of the resulting polymer was about 24.32 g (79%);

^{1}H NMR (CDCl$_3$) δ ppm 1.09–1.24 (complex m), 1.76 (broad s), 2.00–2.13 (broad s), 2.49 (complex m), 2.74 (complex m), 2.99 (complex m), 3.24 (complex m), 3.41–3.46 (complex m), 3.87 (complex m), 3.99 (complex m), 4.95–5.05 (complex m); ^{13}C NMR (CDCl$_3$) δ ppm 15.39, 18.04, 21.29, 25.36, 28.94, 42.38, 44.85, 49.15–59.65 (broad), 65.98, 69.91, 174.6–177.25 (broad); IR-ATR: 3429, 2930, 1727, 1660 cm^{-1};

Hydroxyl index: 754 mg KOH/g.

$$\text{GPC}: \overline{M_n} = 30{,}000\ \text{g/mol};\ \text{PDI} = 3.1$$

2.3. Preparation of DGEBA/MTHPA/HBP mixtures

The mixtures were prepared by adding the required amount of HBP (H1500 or H30000) into the epoxy resin. These mixtures were heated until the modifier was dissolved and the solutions became clear. Then, MTHPA was added and the resulting solutions were stirred and degassed under vacuum for 15 min at 70 °C. Finally, BDMA was added and the mixtures were stirred and cooled down to −10 °C maintaining them at this temperature until use to prevent polymerization. Mixtures containing 0–20 wt% (by weight) of H1500 or 0–10 wt% of H30000 were prepared and the equivalent stoichiometric relation between MTHPA, DGEBA and HBP was kept for all materials. When amine (BDMA) was added, the amine/anhydride molar ratio was kept unchanged. The compositions of the formulations studied are collected in Table 1.

2.4. Characterization techniques

^{1}H NMR and ^{13}C NMR measurements were carried out at 500.13 and 125.75 MHz, respectively, using a Bruker DRX 500 NMR spectrometer. CDCl$_3$ was used as solvent for all NMR measurements. For internal calibration the solvent signals of CDCl$_3$ were used: $\delta(^{13}\text{C}) = 77.0$, $\delta(^{1}\text{H}) = 7.26$ ppm. Quantitative ^{13}C NMR spectra were recorded using inverse gated decoupling and a relaxation delay of 8 s.

The determination of molecular weights and molecular weight distributions was carried out on a modular build SEC-system coupled with a multi-angle laser light scattering (MALLS) detector DAWN EOS (Wyatt Technologies, USA) and a refractive index (RI) detector (Knauer, Germany) in combination with a PL-GEL 5 mm mixed C column, 300 × 7.5 mm (Polymer Laboratories, UK) using a flow rate of 1 mL min^{-1} and THF as eluent. Calibration in the case of RI detection was performed using linear polystyrene standards.

The amount of hydroxyl groups was determined according to ISO 2554–1974. An acetylating solution was prepared by dissolving 11.8 mL of acetic anhydride in 100 mL of pyridine. About 0.4–0.6 g of the polymer sample was dissolved in 5 mL of the acetylating solution. The mixture was stirred for 20 min at 130 °C. Thereafter, at the same temperature, 8 mL of water was added in order to hydrolyze the excess acetic anhydride. Finally, the solution was titrated with 1 N ethanolic KOH solution to determine the equivalence point. An analogous "blank experiment" was performed without the polymer sample with exactly the same amount of the acetylating mixture. The hydroxyl number (HN) was calculated from the results of both titrations using the formula:

$$\text{HN} = \frac{(V_0 - V_1)\cdot C \cdot M_{\text{KOH}}}{m} + \text{AN} \tag{1}$$

where V_0 and V_1 are the equivalence titration volume of KOH in mL from the blank experiment and from the sample titration, respectively; C is the concentration of KOH in eq/l; M_{KOH} is the molecular weight of KOH in g/mol; m is the mass of polymer sample in grams; and AN is the acid number, which has not been taken into account in this case because it is very low.

Calorimetric analyses were carried out on a Mettler DSC-821e thermal analyzer. Samples of approximately 5 mg in weight were cured in aluminum pans in a nitrogen atmosphere. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration).

In the dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha_{\text{DSC}} = \frac{\Delta H_T}{\Delta H_{\text{dyn}}} \tag{2}$$

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.

Table 1
Composition of the formulations with different weight percentage of H1500 or H30000. In percentage by total weight (%wt) of the mixture and in equivalent ratio, (*X*eq).

Formulation	DGEBA		MTHPA		BDMA		OH from HBP	
	*X*eq	wt%	*X*eq	wt%	*X*eq	wt%	*X*eq	wt%
DGEBA/MTHPA	1	50	1	50	0.0065	0.50	–	–
	H1500							
DGEBA/MTHPA/5%	0.95	48.5	1.05	46.5	0.0061	0.50	0.10	5
DGEBA/MTHPA/10%	0.90	44.8	1.11	45.2	0.0061	0.50	0.21	10
DGEBA/MTHPA/15%	0.85	40.8	1.18	44.0	0.0061	0.50	0.33	15
DGEBA/MTHPA/20%	0.80	37.2	1.24	42.8	0.0061	0.50	0.44	20
	H30000							
DGEBA/MTHPA/5%	0.88	46.7	1.13	48.3	0.0062	0.50	0.23	5
DGEBA/MTHPA/10%	0.77	41.2	1.30	48.8	0.0061	0.50	0.47	10

The glass transition temperatures (T_gs) were calculated, after complete curing, by means of a second scan at 20 °C/min as the temperature of the half-way point of the jump in the heat capacity when the material changed from glassy to the rubbery state.

A FTIR spectrophotometer FTIR-680PLUS from JASCO with a resolution of 4 cm^{-1} in the absorbance mode was used to monitor the isothermal curing process at 120 °C. 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). The disappearance of the absorbance peak at 913 cm^{-1} was used to monitor the epoxy equivalent conversion. The consumption of the reactive carbonyl group of anhydride was evaluated by the absorbance at 1777 cm^{-1}. The peak at 1508 cm^{-1} of the phenyl group was chosen as an internal standard. Conversions of the different reactive groups, epoxy and anhydride, were determined by the Lambert–Beer law as reported previously by us [20].

Thermomechanical analyses were carried out on a Mettler TMA40 thermomechanical analyzer. The samples were supported by two small circular ceramic plates and silanized glass fibers, which were impregnated with the samples. Isothermal experiments at 120 °C were undertaken using TMA by application of a force of 0.01 N in order to monitor contraction during the curing process. The degree of shrinkage ($\alpha_{\text{shrinkage}}$) can be calculated as follows:

$$\alpha_{\text{shrinkage}} = \frac{L_t - L_0}{L_\infty - L_0} \tag{3}$$

where L_t, L_0 and L_∞ represent, respectively, the thickness of the sample at time t, at the onset and at the end of the reaction.

The conversion at the gel point was evaluated by means of non-isothermal experiments performed between 40 and 225 °C at a heating rate of 5 °C/min applying a periodic force that changes (cycle time = 12 s) from 0.0025 to 0.01 N. The gel point was taken in TMA as the temperature at which a sudden decrease in the amplitude of the oscillations was observed. The gel conversion, α_{gel}, was determined as the DSC conversion at the temperature in which the gelation is observed in TMA in a non-isothermal experiment.

The linear thermal expansion coefficients in the glassy and rubbery states measurements of the cured samples were performed using samples with a size of ($4 \times 4 \times 2$ mm^3). The samples were mounted on the TMA and heated at a rate of 10 °C/min. The linear coefficient of thermal expansion (CTE) can be determined as:

$$\text{CTE} = \frac{1}{L_0}\frac{dL}{dT} = \frac{1}{L_0}\frac{dL/dt}{dT/dt} \tag{4}$$

where L is the thickness of the sample, L_0 is the initial length, t *is* the time and T *is* the temperature.

The overall shrinkage was calculated from the densities of the materials before and after curing, which were determined using a Micromeritics AccuPyc 1330 Gas Pycnometer thermostatized at 30 °C.

Thermogravimetric analyses (TGAs) were carried out in a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 8 mg were degraded between 30 and 800 °C at a heating rate of 10 °C/min in N_2 (100 cm^3/min measured under normal conditions).

Thermal–dynamic–mechanical analyses (DMTAs) were carried out with a Rheometrics PL-DMTA MKIII analyzer. The samples were cured isothermally in a mould at 150 °C for 4 h and then post-cured for 2 h at 200 °C. Single cantilever bending at 1 Hz was performed at 2 °C/min, from 30 to 200 °C on prismatic rectangular samples ($2 \times 0.5 \times 0.15$ cm^3).

The Izod impact test was performed at 23 °C by means of a Zwick 5110 impact tester. The test specimens has a rectangular section according to ASTM 256-05a. The pendulum employed had a kinetic energy of 2.75 J.

The fracture area of the specimens for impact tests was observed with an environmental scanning electron microscope (ESEM) model FEI Quanta 600.

The modulus of elasticity was determined using a Houndsfield 10ks universal testing machine. The unnotched specimens were the same rectangular bars used in Izod test. A three point bending assembly has been constructed for this test in order to obtain flexural modulus of elasticity in a non-destructive test. The tests were performed at a crosshead speed of 5 mm/min.

The modulus of elasticity is calculated using the slope of the stress–strain curve in accordance with Eq. (7). In this testing configuration, the maximum stress in central section of the beam is:

$$\sigma \equiv \frac{3FL}{2bd^2} \tag{5}$$

and the corresponding strain is:

$$\varepsilon \equiv \frac{6Dd}{L^2} \tag{6}$$

using a couple of points in the linear region, the slope of the curve and thus the modulus of elasticity can be obtained from:

$$E_B \equiv \frac{\Delta\sigma}{\Delta\varepsilon} \tag{7}$$

where E_B is the modulus of elasticity in bending (N/mm^2), L (mm) is the support span, b (mm) is the width of beam tested, d (mm) is the depth of beam tested, D (mm) is the deflection of the beam, and F (N) is the force.

Microhardness was measured with a Wilson Wolpert (Micro-Knoop 401MAV) device following the ASTM D1474-98 (2002) standard procedure. For each material 10 determinations were made with a confidence level of 95%. The Knoop microhardness (HKN) was calculated from the following equation:

$$\text{HKN} = L/A_p = L/l^2C_p \tag{8}$$

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 (7.028×10^{-2}) relating l^2 to A_p. The values were obtained from 10 determinations with the calculated precision (95% of confidence level).

Water uptake was evaluated by immersion tests according to ASTM D 570-98. To carry out this test three square samples of each thermoset ($1 \times 1 \times 0.1\ \text{cm}^3$) were cut and thermally conditioned at 50 ± 1 °C during 24 h in an oven. Then, the samples were cooled and immediately weighed to get the initial weight. The samples were immersed under water at 50 ± 1 °C during the selected times and then were dried with a dry cloth and weighed. The weightings were repeated until constant weight, at which the specimens can be considered substantially saturated. The increase in weight can be calculated as follows:

$$\text{Increase in weight}(\%) = \frac{\text{weight}_{\text{wet}} - \text{weight}_{\text{initial}}}{\text{weight}_{\text{initial}}} \times 100 \tag{9}$$

The diffusion coefficient was determined according to Ref. [20].

3. Results and discussion

Hyperbranched polymers have been studied as modifiers of epoxy thermosets with the commercial aliphatic polyester Boltorn® H30 being the most studied samples [5,6,13,15,22]. In a previous study [20], we selected as a HBP modifier the poly(ester-amide) Hybrane® S1200 obtained from succinic anhydride due to the presence of secondary alkyl esters in the structure which help to improve the thermal degradability of epoxy thermosets necessary for reworkability. Secondary alkyl ester groups are also present in the structure of Hybrane® H1500 (Scheme 1) and therefore, it can be interesting for the same purpose. Moreover this HBP, which derives from *cis*-hexahydrophthalic anhydride, contains cycloaliphatic units in the structure which can tailor several characteristics and this motivated us to initiate the present study and to extend it to the use of an analogous hyperbranched structure but with a higher molecular weight (H30000).

As in the previous study, we used a well established curing procedure: methyltetrahydrophthalic anhydride (MTHPA) as curing agent, catalyzed by a tertiary amine, benzyldimethylamine (BDMA) [20]. The presence of two reactive groups, epoxide and hydroxyl, leads to the adoption of a complex curing mechanism. In this mechanism polycondensation and ring-opening polymerization compete (Scheme 2) and the relative proportion of epoxy/hydroxyl groups in the curing mixture can favor one of them. This finally affects the morphology of the network and the characteristics of the final materials. The introduction of hydroxyl-ended HBPs in an epoxy/anhydride system favors the polycondensation mechanism [15,20]. To know the influence of the HBP in the reaction kinetics and mechanism, the curing process was studied by means of DSC and FTIR.

3.1. Studies on the curing of DGEBA/MTHPA/BDMA mixtures with several proportions of HBP

In a previous work [15] we determined that the maximum degree of curing was reached when one anhydride reacted either with an epoxide or with two hydroxyl groups of the HBP. In all the formulations prepared 0.5 wt% of BDMA was added as catalyst. This optimal ratio has been selected to prepare the formulations studied, which are collected in Table 1. As we can see in the table, on increasing the proportion of HBP in the formulation or/and the molecular weight of the HBP the hydroxyl/epoxy ratio increases as well.

The calorimetric curves of the curing process of all the formulations studied showed a unimodal shape, which seems to indicate that all the participating mechanisms take place simultaneously. However, there is a little difference among them, the addition of the HBPs generally leads to a slight increase in the conversion at a given temperature, especially until conversions of 80%. Fig. 1 shows the plot of conversion degree against temperature recorded at 10 °C/min of neat DGEBA/MTHPA and the formulations containing different proportions of H1500.

The monitoring along the curing process by FTIR spectroscopy allowed to confirm that anhydride groups disappeared faster than epoxides, which can be attributed to an initial esterification of hydroxyl groups by the mechanism depicted in Scheme 2(a) similarly as observed in previous studies [15,20]. The evolution of the characteristic functional groups taking part in the curing process confirmed the disappearance of the absorptions peaks of the anhydride (1777 and 1859 cm^{-1}) and epoxide (913 cm^{-1}) indicating the complete curing.

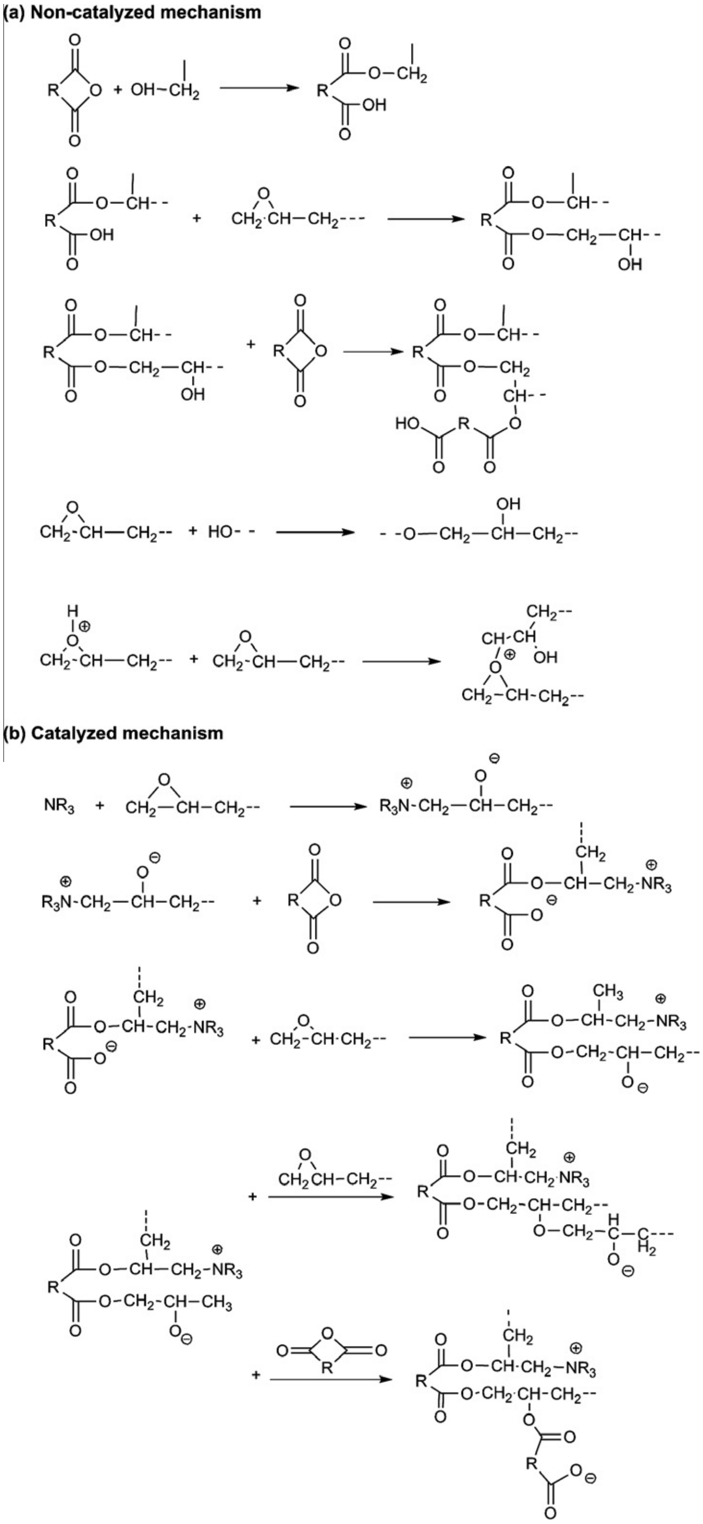
Table 2 collects the calorimetric data of the curing process of all the formulations studied. The reaction enthalpy is mainly due to the opening of epoxy group because of the strained ring. For that reason, it can be seen that the enthalpy is decreased as the amount of HBP or its molecular weight is increased, since the proportion of DGEBA in the formulation is going down. As it is seen, the temperature of the maximum of the curing exotherm on adding HBP to the epoxy resin is maintained.

The T_gs of the materials are slightly higher when the proportion of HBP is limited to a 10 wt% and higher proportions of HBP reduce this parameter. The high functionality and the stiffness which is conferred by the cycloaliphatic units of the HBP structure lead to higher values than those determined for S1200 modified materials reported previously [20].

3.2. Study of the gelation and shrinkage during curing

The irreversible transformation of a viscous liquid to an elastic gel is called gel point. At this point, the formation of a crosslinked network begins and gelation defines the upper limit in which the material can be applied. In the curing process, the loss of mobility after the gelation leads to the appearance of internal stresses, which originate voids and cracks in the thermoset and therefore it is desirable to advance the gelation until higher conversions.

Molecular gelation takes place at a defined conversion of the crosslinking reaction (α_{gel}) and it depends on the reactivity, stoichiometry and functionality of the reactants. The conversion at the gelation can be calculated if the chemical process is well known. In the present case, the concurrence between several chemical reactions prevents the conversion at the gelation to be calculated.



Scheme 2. Individual reactions taken place during curing.

To experimentally determine the gelation point we used thermomechanical analysis (TMA), in which the gelation is seen as a reduction in the oscillation amplitude because the gelled material is less deformable. This reduction is better observed in the signal derivative (Fig. 2) where the effect of volume change is eliminated. When the material

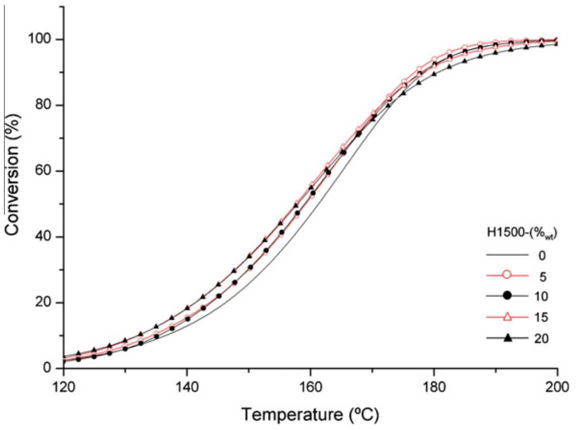


Fig. 1. Conversion degrees as determined by DSC against temperature of the curing of DGEBA/MTHPA and DGEBA/MTHPA mixtures containing different weight percentages of H1500 at a heating rate of 10 °C/min.

reaches sufficient mechanical stability (gelation) the TMA measuring probe deforms less the sample and the amplitude of the oscillations is reduced [23]. The gel conversion, α_{gel}, can be determined as the DSC conversion at the temperature gelled in TMA in a non-isothermal experiment. The figure shows the calculation method applied to the formulation containing a 10 wt% of H30000, which led to an $\alpha_{gel} = 0.69$. In Table 3 the conversion at the gelation is shown for all the formulations studied. As can be seen, the addition of HBP produces a progressive slightly increase of this parameter. However, the gelation time does not show any regular tendency due to the combination of the kinetics of the curing and the variation of the conversion at the gelation. The conversions at the gelation are similar to those reported previously in formulations containing Boltorn® H30 [15], but the gelation time is a little longer for H1500 modified materials, which can be advantageous for application.

By isothermal TMA, the degree of shrinkage ($\alpha_{shrinkage}$) during curing at 120 °C has been determined. Experimentally, one can detect the gelation point by using TMA starting at a region in which contraction is not observed between two contraction steps in the sample. In a previous study [24] we proved, by solubility test and DMTA essays, how this point can be associated to the gelation. Fig. 3 shows the plot of the shrinkage evolution during the curing

Table 2
Calorimetric data of DGEBA/MTHPA/BDMA mixtures with different percentages of H1500 or H30000.

Formulation	DSC				DMTA		TGA	
	ΔH (J/g)	ΔH^{a} (kJ/ee)	$T_{max}{}^{b}$ (°C)	$T_{g}{}^{c}$ (°C)	$T_{\tan\delta}{}^{d}$ (°C)	E'^{e} (MPa)	$T_{2\%}{}^{f}$ (°C)	T_{max} (°C)
DGEBA/MTHPA/0%	245	90	165	92	118	11.5	283	413
	H1500							
DGEBA/MTHPA/5%	238	90	164	103	129	20.9	268	411
DGEBA/MTHPA/10%	232	95	162	103	130	14.1	252	415
DGEBA/MTHPA/15%	228	98	161	94	125	11.2	254	409
DGEBA/MTHPA/20%	204	89	160	90	127	8.3	259	413
	H30000							
DGEBA/MTHPA/5%	230	93	165	100	128	13.8	265	412
DGEBA/MTHPA/10%	220	98	165	106	122	11.5	237	414

[a] Enthalpies per equivalent of epoxy group.
[b] Temperature of the maximum of the curing exotherm.
[c] Glass transition temperature obtained by DSC. Second scan after dynamic curing.
[d] Temperature of the maximum of the tan δ.
[e] Storage modulus of material at the rubbery region at tan δ + 50 °C.
[f] Temperature of a 2% of weight loss calculated by thermogravimetry.

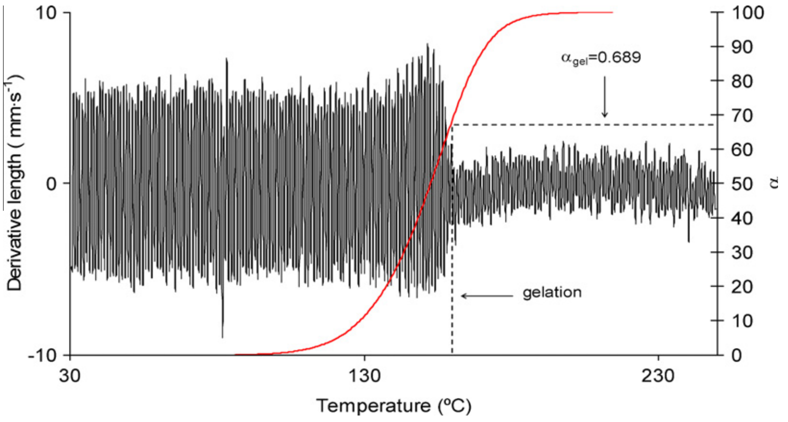


Fig. 2. Gel point determination using combined TMA and DSC for the mixture DGEBA/MTHPA with 10 wt% of H30000 and 0.5 wt% of BDMA.

Table 3
Gelation data, densities, shrinkage, CTEs and gravimetric water diffusion coefficients of the systems studied.

Formulation	α_{gel}[a]	t_{gel}[b] (min)	α_{shrink}[c]	ρ_{mon} (g/cm^3)	ρ_{pol} (g/cm^3)	Shrink.[d] (%)	Shrink.[e] after gel. (%)	CTE$_{glass}$ × 10^6 (K^{-1})	CTE$_{rubber}$ × 10^6 (K^{-1})	$D \times 10^8$ [f] (cm^2/s)
DGEBA/MTHPA/0%	0.64	21.5	0.27	1.182	1.214	2.64	1.93	64.3	201.5	4.3 (0.2)
H1500										
DGEBA/MTHPA/5%	0.65	24.0	0.37	1.181	1.209	2.38	1.50	62.1	193.8	3.4 (0.3)
DGEBA/MTHPA/10%	0.67	20.6	0.43	1.180	1.208	2.32	1.32	61.7	190.1	2.4 (0.2)
DGEBA/MTHPA/15%	0.70	23.7	0.64	1.180	1.205	2.08	0.75	58.6	188.3	1.2 (0.2)
DGEBA/MTHPA/20%	0.73	23.9	0.69	1.182	1.204	1.81	0.56	50.4	185.8	0.8 (0.0)
H30000										
DGEBA/MTHPA/5%	0.65	18.7	0.33	1.177	1.200	1.92	1.29	44.5	187.9	1.0 (0.0)
DGEBA/MTHPA/10%	0.69	22.1	0.46	1.184	1.198	1.10	0.59	28.0	178.4	0.9 (0.0)

[a] Degree of conversion at the gelation determined as the conversion reached by non-isothermal TMA and DSC tests at 10 °C/min.
[b] Gelation time determined by TMA at 120 °C.
[c] Degree of shrinkage before gelation determined by TMA at 120 °C.
[d] Global shrinkage on curing determined as $[(\rho_{polymer} - \rho_{monomer})/\rho_{polymer}]$.
[e] Degree of shrinkage after gelation determined as $[\text{shrinkage} \times (1 - \alpha_{TMA})]$.
[f] Water diffusion coefficient with the standard deviations shown in parentheses.

at 120 °C against time for the formulations containing different proportions of H1500. The first stage of contraction, before gelation, increases steadily with the percentage of HBP, and this is beneficial because at this stage the materials have enough mobility to withstand deformations. The increase in the shrinkage before gelation can be explained by the polycondensation mechanism (Scheme 2(a)) which takes place between hydroxyl groups of the HBP and anhydrides. After gelation, the shrinkage decreases with increasing the amount of HBP. This can be also related to the curing mechanism, which at the final stages takes mainly place the ring-opening mechanism (represented in Scheme 2(b)), which leads to less contraction.

Because TMA allows determining the relative contraction before and after gelation during the curing process, but not to quantify the global shrinkage, we evaluated it by determining the densities of all the formulations before and after curing by means of gas pycnometry. From the densities the shrinkage was calculated. These values are collected in Table 3, where we can observe that on increasing the proportion of HBP in the formulation the shrinkage is reduced. This is more pronounced when H30000 was used as a modifier. From the degree of shrinkage at the gelation and the global shrinkage we can estimate the contraction after gelation, which is notably reduced on increasing the HBP proportion and values of ~0.5–0.6% have been reached. From this point of view, the addition of high molecular weight HBP seems to be more beneficial, since the addition of 10 wt% of H30000 but of 20 wt% of H1500 led to similar values for shrinkage.

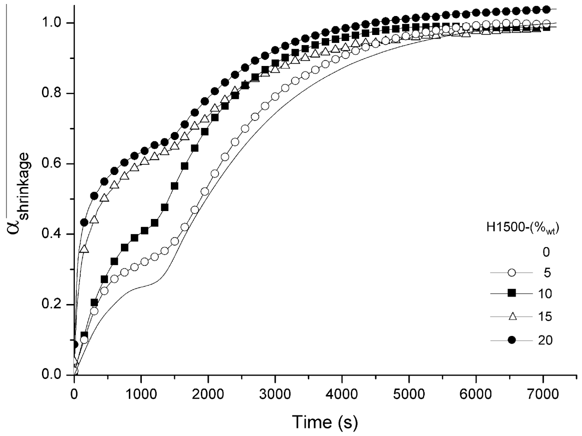


Fig. 3. Degree of shrinkage, $\alpha_{shrinkage}$, versus time of the curing determined by TMA at 120 °C of mixtures DGEBA/MTHPA and DGEBA/MTHPA/H1500 in different weight percentages.

3.3. Study of the thermal degradability

To confirm that our modification procedure increases the reworkability of thermosets, our materials were analyzed by TGA. Fig. 4 shows the DTG curves for the H1500 modified materials and the main data for all the materials studied are collected in Table 2. DTG curves show that the addition of HBP leads to the appearance of a shoulder at 325 °C, which increases with the proportion of HBP. This peak can be due to the rupture of the secondary ester bonds of the HBP, which leads to the formation of small fragments able to be volatilized. The main peak corresponds to the degradation of the crosslinked network and it remains similar for all materials.

A valuable TGA data is the $T_{2\%}$ because when the material looses 2% in weight the mechanical properties of the materials go down and the coatings can be removed from the substrate. From the values of the table, we can see that the addition of H1500 increases the reworkability, but a further addition does no increase it. On increasing the molecular weight of the modifier the $T_{2\%}$ is going down, because of the higher proportion of ester linkages in the material. It was reported [25] that the optimal temperatures for safe rework operations are in the range 230–250 °C in N_2 atmosphere, and thus the materials containing proportions of 10 wt% of HBP are able to be classified as reworkable thermosets.

On comparing the materials prepared from H1500 with those obtained from S1200 with a comparable molecular weight, we can state that S1200 led to higher improvements on the reworkability [20]. This fact can be rational-

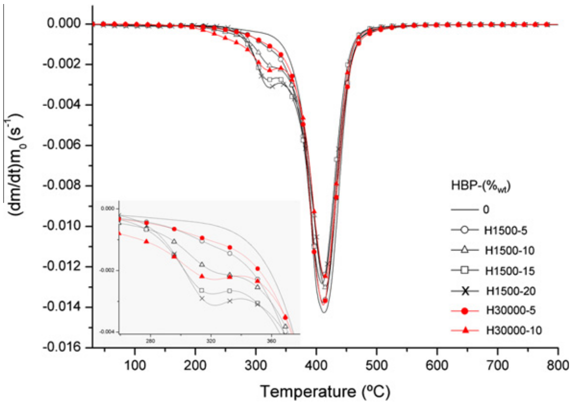


Fig. 4. DTG curves at 10 °C/min in N_2 atmosphere of thermosetting materials obtained from DGEBA/MTHPA containing different proportions of H1500 or H30000.

ized by the less flexible structure of the cycloaliphatic HBPs which makes the formation of the six-membered cycles, adopted in the transition state of the pyrolytic β-elimination process, difficult [26].

3.4. Determination of thermal expansion coefficient

One of the most common causes of internal stresses in coatings is produced by the mismatch in the thermal expansion coefficients (CTEs) between the coating and the substrate. Table 3 collects the CTE values determined by TMA in the glassy and rubbery states. It is worth to note that CTEs decrease on increasing the proportion of H1500. This decrease is more evident than the one observed for S1200 modified materials [20] and it can be explained on the basis of the more rigid structure of the cycloaliphatic HBP and on the degree of crosslinking achieved. On increasing the molecular weight of the HBP there is also a decrease in the CTE values.

It was reported that by adding Boltorn® E1, an epoxy functionalized hyperbranched aliphatic polyester, to an epoxy system the CTE in the glassy state does not change, but it increases in the rubbery state from 185 to 260 K^{-1}. This observation was rationalized by the phase-separated particles, which appear in the thermoset. Thus, the CTE below T_g was dominated by the neat epoxy resin and above T_g by the HBP domains. In our case, the CTE decreases in both regions which is due to the homogeneous character of the material.

3.5. Study of the thermomechanical properties

The mechanical relaxation spectra and the tan δ plot of all the materials prepared were registered. The tan δ curves were unimodal with a similar sharpness, which accounts for the homogeneity of these materials. The characteristic parameters associated to these spectra are shown in Table 2. As can be seen, the addition of HBPs increases the tan δ temperature but it does not change appreciably on increasing the proportion. Relaxed modulus increased on adding 5 wt% of H1500 or H30000 but further addition reduces this value. This could indicate that in our materials there is no complete reaction of hydroxyl groups when high proportions of HBP were added to the formulation. It has been reported that the increase in the molecular weight of a hydroxyl-ended HBP leads to a partial fold back into the HBP molecule, thus leaving less hydroxyl groups able to react with anhydrides [18].

Many authors observed that the incorporation of HBPs to epoxy resins leads to a decrease of the tan δ value, which was attributed to a higher free volume inside the network caused by the HBP [18,22]. Moreover, the modification with HBP reduces the relaxed modulus in systems in which hydroxyl terminal groups remained not-covalently linked to the matrix [18]. Thus, the covalent linkage of the HBP to the epoxy matrix is necessary to maintain the thermomechanical characteristics.

3.6. Mechanical characterization

Several authors [5–7,22] studied the effect of HBPs as tougheners in epoxy resins and they could demonstrate their beneficial effect on this property, but the maximum effect was obtained in phase separated materials forming globular micro-particles in a continuous epoxy matrix. Fu et al. [27] observed a maximum improvement when they added a 5–15 wt% of an aliphatic–aromatic hyperbranched polyester to the DGEBA matrix and in this way improvements of about 2–7 times in toughness were observed, although with a decrease in the T_g value, because of the flexibility of the HBP structure.

The effect of adding our poly(ester-amide) HBPs to the formulations in the impact strength is shown in Fig. 5, since it is a useful measure for the evaluation of the toughness or brittleness. It can be seen that only the materials containing 5 wt% of H1500 and 10 wt% of H30000 have higher impact strength. The addition of 10 wt% of higher molecular weight HBP leads to the highest improvement in toughness. In our previous study [20], the addition of S1200 in percentages between 10 and 20 wt% led to a slight improvement on impact strength, reaching the highest value for the thermoset containing 10 wt% of HBP. The superior increase in toughness, obtained in the latter study, can be explained by the more flexible structure of S1200 introduced in the network.

Flexural moduli of elasticity were determined for all the materials prepared in a three point bending assembly. The values are represented in Fig. 6. In general, the addition of HBP increases the rigidity of the material, but the influence is higher when the molecular weight of the HBP increases. Although the addition of H1500 leads to a regular increase with the proportion, on adding H30000 there is not a clear tendency. The maximum modulus was reached for the material containing 10 wt% of H30000.

An increase in the rigidity of the material on increasing the proportion of HBP was also observed on adding S1200 to a DGEBA/MTHPA formulation [20], but there was no relationship between this property and the proportion of HBP, since 10 wt% of HBP led to the maximum value. Other authors [8,22] described a loss of this modulus on adding HBP, but the structure of the HBP in these cases was much more flexible than that of H1500 and H30000.

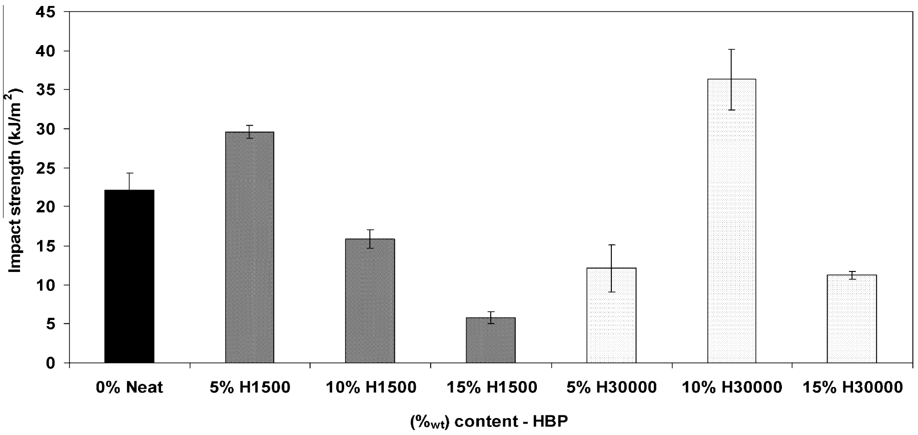


Fig. 5. Dependence of impact strength of DGEBA/MTHPA thermosets containing different weight percentages of H1500 or H30000.

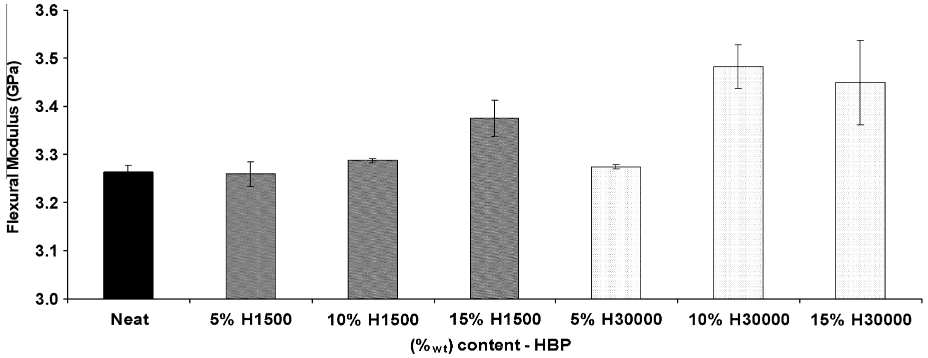


Fig. 6. Dependence of flexural modulus of DGEBA/MTHPA thermosets containing different weight percentages of H1500 or H30000.

Microhardness is a measure of the resistance that one body offers against penetration by another. This technique is used in the coating industry to characterize the mechanical properties related to resistance and hardness of materials and it measures their capability to resist static loads or applied at low rates. As we can see in Fig. 7, only the addition of H30000 increases the microhardness in reference to pure cured DGEBA.

From all the mechanical tests performed we can state that the more beneficial effect was reached when 10 wt% of H30000 were added to the formulation.

3.7. Morphology analysis of the fractures by ESEM

The toughness behavior of DGEBA/MTHPA and the HBPs modified thermosets can be explained in terms of morphology observed by ESEM. The fracture surfaces after impact tests were investigated by this technique and representative micrographs are shown in Fig. 8.

All the micrographs presented a homogeneous appearance without any phase separation, similarly to S1200 modified materials, in spite of their different hydrophilic/hydrophobic character [20]. This homogeneity can be

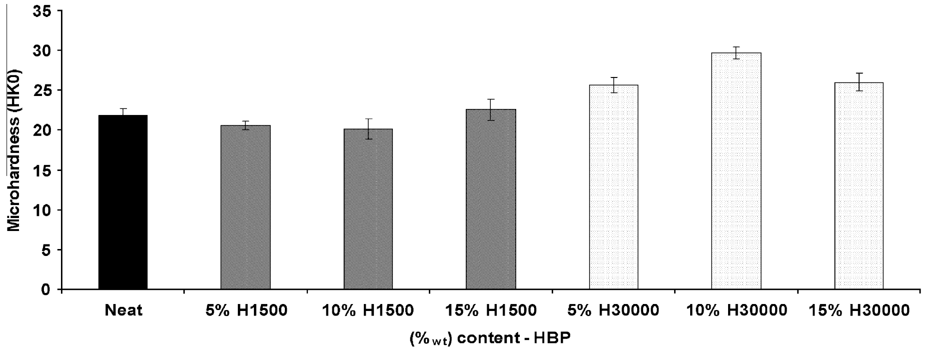


Fig. 7. Dependence of microhardness of DGEBA/MTHPA thermosets containing different weight percentages of H1500 or H30000.

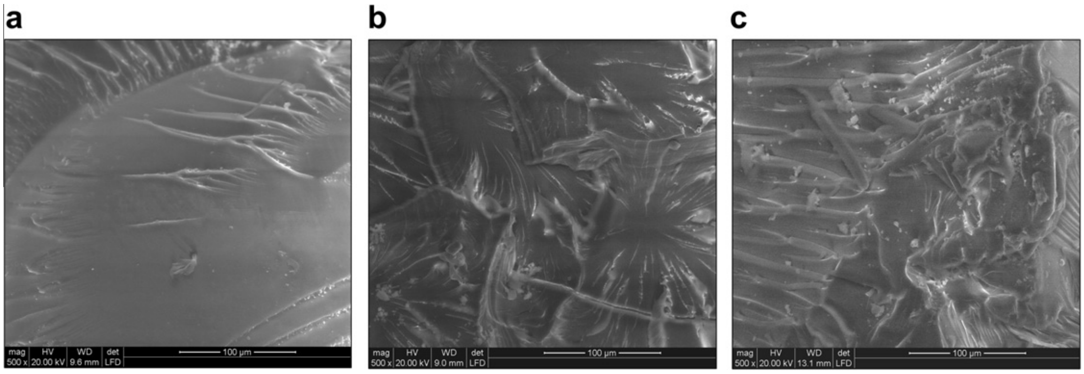


Fig. 8. ESEM micrographs for fracture surfaces of the following materials cured at 150 °C: (a) neat DGEBA/MTHPA; (b) 5 wt% H1500/DGEBA/MTHPA; (c) 10 wt% H30000/DGEBA/MTHPA.

attributed to the covalent bonding of the reactive groups of HBPs to anhydrides in the matrix. The smooth glassy fractured surface with little cracks in the unmodified material observed in Fig. 8(a) accounts for its poor impact strength. In contrast, the fracture surface of the materials with 5 wt% of H1500 Fig. 8(b) or with 10 wt% of H30000 Fig. 8(c) are rougher than that of the unmodified, suggesting that the impact specimens break more yieldingly. The observations of the fractured surfaces agree with the impact strength values measured (Fig. 5).

Accordingly to Fu et al. [27] it seems that there is an optimum toughness value versus the generation number and content of the HBP, which can be explained as synergism combination among the plastic deformation and “in situ” toughening mechanisms.

3.8. Water uptake behavior

The water absorption curves against time for the thermosets obtained are shown in Fig. 9. It is clear that HBP incorporation leads to an increase in the amount of absorbed water ($M_{\max}$) due to the higher polarity of the thermosets containing the hydroxyl-ended cycloaliphatic poly(ester-amide), compared with the neat DGEBA/MTHPA material. The water uptake increases with the proportion of HBP and reaches the highest values for H30000 modified thermosets. The equilibrium water uptake ($M_{\max}$) was taken as the maximum values reached of the water absorption curves and were used to calculate the corresponding diffusion coefficients, which are collected in Table 3. However the diffusion coefficient, calculated by the equations given in the experimental part, decreases with the amount of HBP. This indicates that with the addition of HBPs, the rate of absorption initially decreases whereas the equilibrium saturation percentages increase.

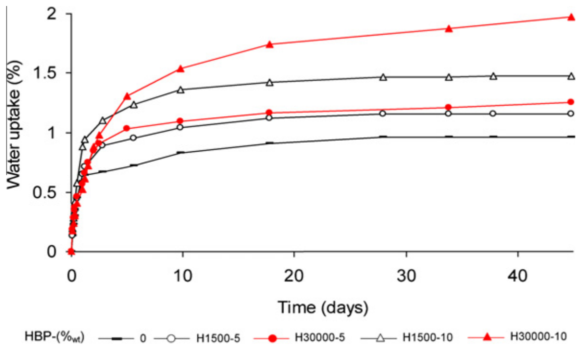


Fig. 9. Water absorption curves against time at 50 °C for DGEBA/MTHPA and DGEBA/MTHPA modified with different weight percentages of H1500 or H30000.

The hydrophobic character of H1500 and H30000 in comparison to the more hydrophilic S1200 [20] leads to a lower water uptake for the materials prepared in the present study.

4. Conclusions

The addition of hydroxyl terminated cycloaliphatic hyperbranched poly(ester-amides) to epoxy/anhydride systems, in the presence of a tertiary amine as catalyst, affects the mechanism of the curing process favoring the non-catalyzed mechanism. This implies the reaction of hydroxyl and epoxy groups with anhydrides by a polycondensation process leading to the covalent incorporation of the HBP to the network from the very beginning of the curing process.

On increasing the proportion of HBP a progressive decrease of the global shrinkage is observed. This reduction is more pronounced for the HBP with high molecular weight. Moreover, the contraction after gelation is also notably reduced and low values of ~0.5–0.6% have been reached.

The thermal reworkability of the thermosets increases on adding HBP due an earlier start of the thermal degradation. Thus, materials containing 10 wt% of HBP are able to be classified as reworkable thermosets.

By DMTA and ESEM the homogeneous character of the materials prepared has been demonstrated. The addition of HBPs increases the tan δ temperature and the relaxed modulus increased only on adding 5 wt% of H1500 or H30000 because further HBP content reduces this parameter.

Thermal expansion coefficients in the glassy and rubbery states decrease on increasing the proportion of H1500. These coefficients are even more reduced when the modifier H30000 is used.

Mechanical properties (elastic modulus, impact strength and microhardness) show a maximum value when 10 wt% of H30000 were added to the formulation.

The presence of HBPs in the materials increases the water uptake, proportionally to the amount added, but decreases the diffusion coefficients. The water uptake is higher when H30000 is added in the formulation.

In summary, hyperbranched poly(ester-amide)s of the Hybrane® H1500 type are also very suitable for increasing the toughness and for reducing the shrinkage in epoxy thermosets. Significantly high molar mass samples of HBP (of 30,000 g/mol) and an addition of 10 wt% seem to be the most favorable conditions for achieving optimized thermosets which can be reworked.

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