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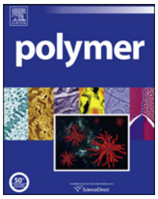

New improved thermosets obtained from DGEBA and a hyperbranched poly(ester-amide)

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ABSTRACT

The influence on the curing process of a commercial hydroxy-functionalized hyperbranched poly(ester-amide) (HBP) Hybrane® S1200 on diglycidylether of bisphenol A (DGEBA) was studied. By Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) the curing reaction was studied 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 S1200 proportion was observed. The incorporation of S1200 increased the glass transition temperature (T_g) and reduced the overall shrinkage, specially after gelation. The modified materials were more thermally degradable than neat DGEBA thermosets. Thermal expansion coefficient, Young's modulus, impact strength and microhardness were improved without compromising the thermomechanical characteristics. The water uptake behaviour was also evaluated.

1. Introduction

In some epoxy resins applications such as coatings for electronic encapsulations, properties such as toughness and low shrinkage are necessary [1,2]. During the curing process the volume is usually reduced, which tends to originate deformations and cracks, decreasing the adhesion and consequently the protective capacity of the coating. Degradability is required when the reworkability of the electronic devices is desired. The improvement on this property could be achieved with the introduction of labile groups such as esters of secondary or tertiary alkyl groups in the network [3,4]. It is well known, that thermosetting materials cannot be recycled but they can be broken down under controlled conditions to remove them from the substrate, enabling the repairing or recycling of electronic devices assembled with such materials [5].

Toughness is also needed to prevent the loss of adhesion and the damage of the electronic devices caused by brittle fractures. During the past decades considerable efforts have been made to improve it. One of the most successful approaches to decrease the brittleness of epoxy resins is to blend them with rubbers or elastomers able to stand energy absorption mechanisms [6,7]. However, using these modifiers, some thermomechanical properties can be strongly affected and some problems arise in terms of processing.

Hyperbranched polymers (HBP)s, dendritic macromolecules with a large number of functional groups at the end of the branches, are a new class of modifiers for epoxy resins, which have the advantage of reducing the viscosity of the reactive mixture and can improve the mechanical properties [8,9]. Most of the commercial HBPs used have hydroxyl groups at the end of the branches, but up till now, there are few reports concerning the role of these HBPs on the toughness of epoxy resins [10,11]. Although some improvements on this property were observed, the covalent incorporation of the HBP in the matrix was not completely clarified.

Anhydrides are common curing agents for epoxy resins, but they have been scarcely employed in the modification of diglycidylether of bisphenol A (DGEBA) with hydroxyl HBPs (Boltorn® H30) [11,12]. Anhydrides can react with both epoxy and hydroxyl groups forming ester linkages, which is advantageous to increase reworkability.

In the present work, we selected as HBP the hydroxyl ended commercial hyperbranched poly(ester-amide) Hybrane® S1200 as a reactive modifier of DGEBA and methyltetrahydrophthalic anhydride (MTHPA) with a tertiary amine as curing agent. The addition of S1200 to this curing system should allow improving the thermal reworkability through the presence of secondary ester groups. It was also expected a reduction of the shrinkage after gelation as we

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saw in previous studies [12,13]. In addition, the flexibility of the HBP structure can improve the toughness of the thermosets.

2. Experimental

2.1. Materials

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*-dimethylbenzylamine (BDMA) (Aldrich) were used as-received. The hydroxyl terminated hyperbranched poly(ester-amide) Hybrane® S1200 (DSM) was used as modifier. The average molecular weight, as reported on data sheet, is about 1200 g/mol, and the theoretical number of OH groups/molecule is 8. T_g value is 45 °C.

2.2. Preparation of DGEBA/MTHPA/HBP mixtures

The mixtures were prepared by adding the required amount of S1200 into the epoxy resin. The initial mixture with the selected proportion of DGEBA and S1200 was heated until the HBP was dissolved and the solution became clear. Then, MTHPA was added and the resulting solution was stirred and degassed under vacuum for 15 min at 70 °C. Finally, BDMA was added and the mixture was stirred and cooled down to −10 °C maintaining it at this temperature until use to prevent polymerization. The mixtures containing 0–20%$_{wt}$ (by weight) of HBP 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.

2.3. Characterization techniques

Calorimetric analyses were carried out on a Mettler DSC-821e thermal analyzer. Samples of approximately 5 mg in weight were cured in aluminium 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:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}} \tag{1}$$

where ΔH_T is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to this temperature, and ΔH_{dyn} is the total reaction heat associated with the complete conversion of all reactive groups.

The 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 under N_2 atmosphere.

An 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 from the normalized changes of absorbance at 913 and 1777 cm^{-1}:

$$\alpha(t)_{epoxy} = 1 - \left(\frac{\overline{A}^t_{913}}{\overline{A}^0_{913}}\right) \tag{2}$$

$$\alpha(t)_{anhydride} = 1 - \left(\frac{\overline{A}^t_{1777}}{\overline{A}^0_{1777}}\right) \tag{3}$$

where $\overline{A}^0$ and $\overline{A}^t$ are respectively the normalized absorbance of the reactive group before curing and after a reaction time t.

From these conversions and taken into account the equivalent formulation of the mixtures, the equivalent evolution of the reactive groups which participates in the curing can be obtained:

$$\mathrm{eq}(t)_{epoxy} = \mathrm{eq}_{initial} \cdot \alpha(t)_{epoxy} \tag{4}$$

$$\mathrm{eq}(t)_{anhydride} = \mathrm{eq}_{initial} \cdot \alpha(t)_{anhydride} \tag{5}$$

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 ($\alpha_{shrinkage}$) can be calculated as follows:

$$\alpha_{shrinkage} = \frac{L_t - L_0}{L_\infty - L_0} \tag{6}$$

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 change (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 gelled in TMA in a non-isothermal experiment.

Table 1

Compositions of the formulations with different weight percentages of S1200: in equivalent ratio, (Xeq) and in percentage by total weight (wt%).

Formulation	DGEBA		MTHPA		BDMA		OH from HBP	
	Xeq	wt%	Xeq	wt%	Xeq	wt%	Xeq	wt%
DGEBA/MTHPA	1	50	1	50	0.0065	0.53	–	–
DGEBA/MTHPA/5%	0.93	48.1	1.07	46.9	0.0061	0.50	0.14	5
DGEBA/MTHPA/10%	0.88	44.2	1.14	45.8	0.0061	0.50	0.26	10
DGEBA/MTHPA/15%	0.83	40.3	1.21	44.4	0.0061	0.50	0.38	15
DGEBA/MTHPA/20%	0.75	36.2	1.33	42.8	0.0061	0.50	0.58	20

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 coefficient of thermal expansion (CTE) can be determined as:

$$\mathrm{CTE} = \frac{1}{L_0}\frac{\mathrm{d}L}{\mathrm{d}T} = \frac{1}{L_0}\frac{\mathrm{d}L/\mathrm{d}t}{\mathrm{d}T/\mathrm{d}t} \tag{7}$$

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

The glass transition temperatures (T_gs) of the cured samples were also determined by non-isothermal TMA experiment as the cross of the tangents between the glassy and rubbery states.

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 in 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 °C to 200 °C on prismatic rectangular samples ($2 \times 0.5 \times 0.15$ cm^3).

Young's modulus was measured with the Universal Testing Machine Hounsfield 10-KS. Tensile tests were performed on cylindrical samples of 8 mm of diameter. The gauge length was 50 mm and the test cross-head speedy was 1 mm/min. For each material 6 determinations were made with a confidence level of 95%.

The impact test was performed at 23 °C by means of an Izod 5110 impact tester, according to ASTM 256-05a using V-notched rectangular samples. The pendulum employed had a kinetic energy of 1 J. The fracture area of the specimens for impact tests was observed with scanning electron microscope (SEM). The samples were metalized with gold and observed with a Jeol JSM 6400 with a 3.5 nm resolution.

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:

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

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, 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 ($1 \times 1 \times 0.1$ 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:

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

2.4. Diffusion coefficient determination

Water uptake has been modeled by Fick's second law: [14,15]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{10}$$

where D is the diffusion coefficient. If the material has a uniform initial diffusant concentration (C_0) and the surface kept at a constant concentration $C_{\max}$ the solution of Eq. (10) is:

$$\frac{C-C_0}{C_{\max}-C_0}=1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[-D(2n+1)^2\pi^2t/L^2\right]\cdot\cos\frac{(2n+1)\pi x}{L} \tag{11}$$

The total amount of substance diffusing in the polymeric material (M) as a function of time is given by the integral of Eq. (11) across the thickness (L):

$$\frac{M}{M_{\max}} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-D(2n+1)^2\pi^2t/L^2\right] \tag{12}$$

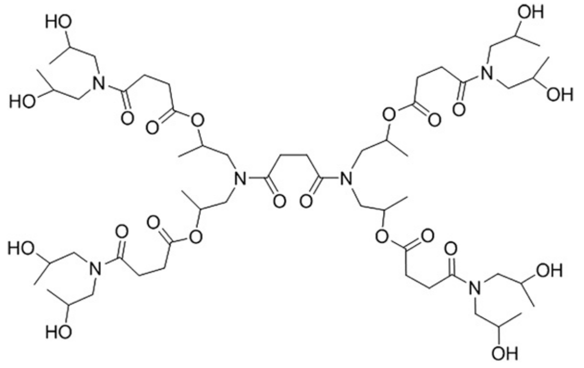
where $M_{\max}$ is the maximum quantity of the diffusing substance at infinite time. A simplified form of Eq. (12) for values $M/M_{\max}$ lower than 0.6 has the form:

$$\frac{M}{M_{\max}} = \frac{4}{L\sqrt{\pi}}\sqrt{Dt} \tag{13}$$

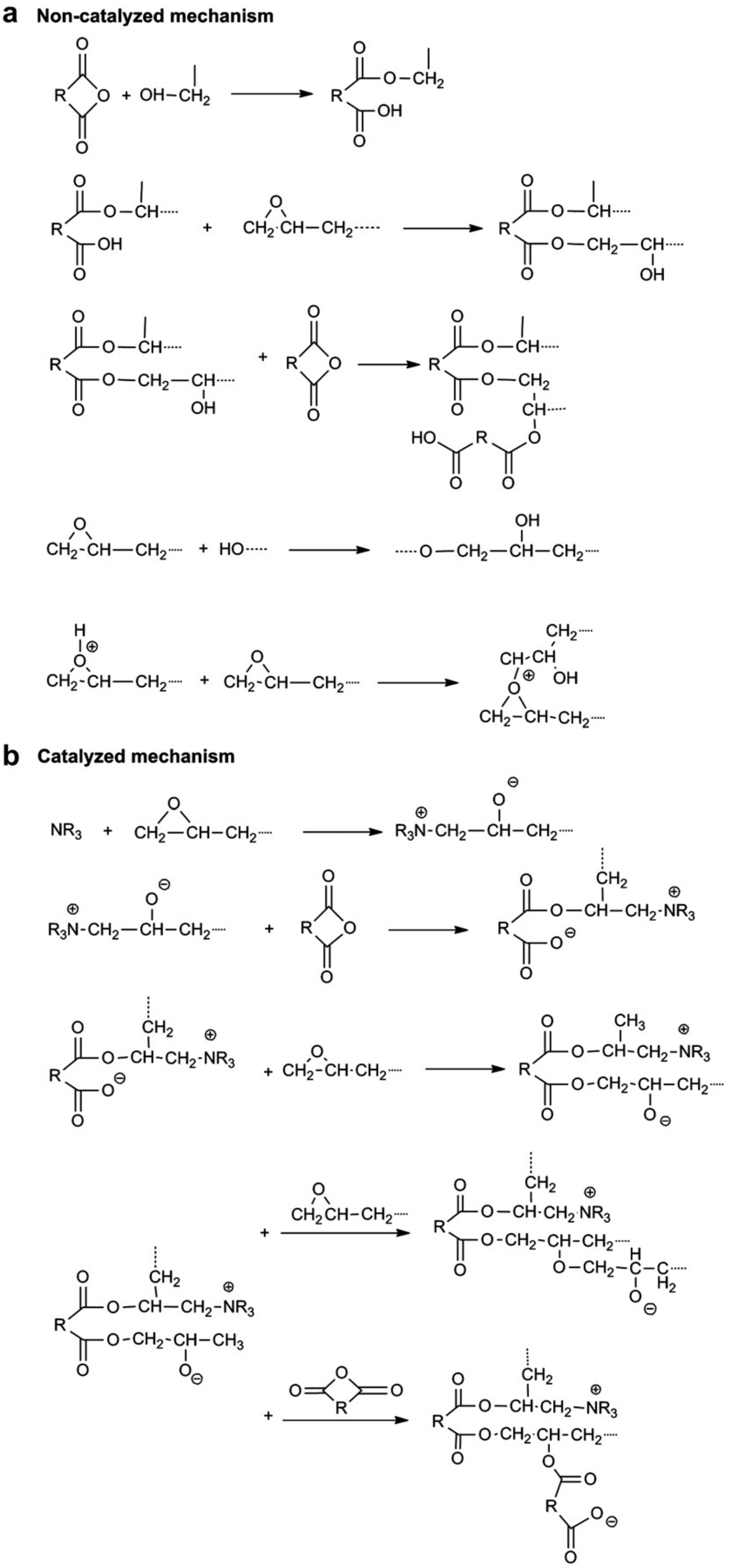
Representing $M/M_{\max}$ for values lower than 0.6 in front of $\sqrt{t}/L$ enables D to be determined from the slope.

3. Results and discussion

Amongst the hyperbranched polymers used as thermoset toughners the aliphatic polyesters based on bis-hydroxymethyl propionic acid, commercially available from Perstorp polyols (Boltorn®) are the most reported [8,9,11,16,17]. However there are some other commercially available hyperbranched polymers which can be employed to improve the properties of an epoxy thermoset. Concretely, in this study an aliphatic poly(ester-amide) hyperbranched polymer (HBP) Hybrane® S1200 has been used to modify DGEBA. The idealized chemical structure of this modifier is shown in Scheme 1. The structure of S1200 presents some advantages: the hydroxylic groups at the chain ends allow the covalent bonding of the HBP to the matrix, the aliphatic structure can flexibilize the



Scheme 1.



Scheme 2.

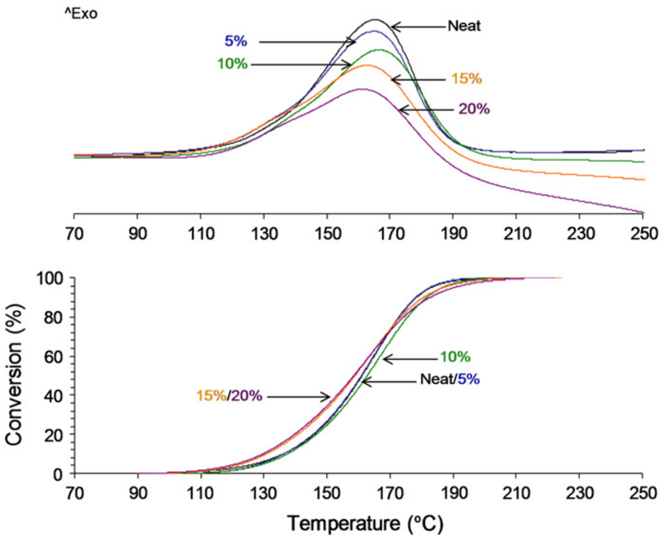


Fig. 1. DSC scanning curves and conversion degrees against temperature of the curing of DGEBA/MTHPA and DGEBA/MTHPA mixtures containing different weight percentages of S1200 at a heating rate of 10 °C/min.

network while maintaining the T_g value by the high functionality of the HBP, and the presence of secondary alkyl esters can help to increase the thermal degradability of the materials.

The reaction of DGEBA with anhydrides as curing agents has been broadly studied in terms of its reactivity and mechanism [1,18,19]. The reactive process is complex and it involves higher temperatures with several competing reactions capable to taking place; particularly etherification takes an important role in non-catalyzed systems. The most significant reaction mechanisms are shown in Scheme 2 (a), which corresponds to a polycondensation initiated by hydroxyl groups.

Because of the epoxy/anhydride reaction is slow, an accelerator is often used to initiate the process at lower temperatures. This catalyzed mechanism is represented in Scheme 2 (b) and follows a ring-opening pathway. It is important to note that the introduction of the HBP in an epoxy/anhydride system can contribute to the non-catalyzed mechanism favouring the polycondensation mechanism. 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. *Calorimetric studies of DGEBA/MTHPA/BDMA with several S1200 proportions*

In a previous work [12] 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 and a 0.5 wt% BDMA was employed in all the formulations prepared. This optimal formulation has been selected to prepare the formulations studied, which are collected in Table 1.

Fig. 1 shows the DSC exotherms and the conversion degrees against temperature recorded at 10 °C/min of neat DGEBA/MTHPA and DGEBA/S1200/MTHPA formulations. It can be observed, that there is no much influence on the shape of the crosslinking exotherm on changing the proportion of S1200 in the reactive mixture, since all of them exhibit a unimodal curve. The addition of little percentages of HBP does not accelerate the curing process but the addition of 15 wt% or 20 wt% produces an accelerative effect in the first stages of curing. This fact could be attributed to the high proportion of hydroxyl groups in S1200 which can favor the non-catalyzed mechanism at the beginning of the curing process. These mixtures show a delay at higher temperatures and higher conversions due to the concurrence of the different reactive processes. A similar behaviour was observed in a previous study on the curing of DGEBA/Boltorn® H30/anhydride/BDMA mixtures [12].

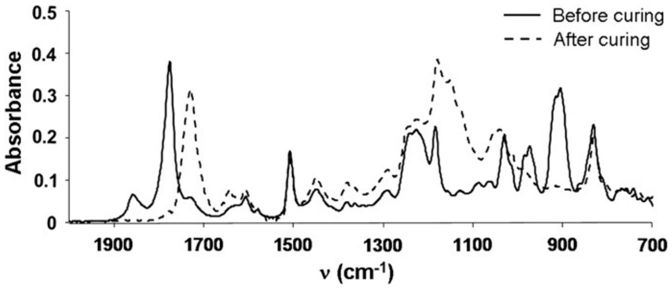


Fig. 2. ATR-FTIR spectra of the mixture DGEBA/MTHPA with 20 wt% of S1200 and 0.5 wt% of BDMA before and after curing at 120 °C.

In Table 2 the calorimetric data of the curing process of the formulations studied are collected. The reaction enthalpy is mainly due to the opening of epoxy group because of the strained ring. For that reason, it is shown that the enthalpy is decreased as the amount of HBP is increased, since the proportion of DGEBA in the formulation is going down. It can be also commented that there are not many differences on the maximum of the curing exotherm on adding HBP to the epoxy resin. The presence of S1200 in the material leads to an increase in the T_g, but this value is not affected by the percentage of modifier in the material. This can be explained by the opposite effects arising from the flexibility of the structure and its high functionality.

3.2. *FTIR studies of DGEBA/MTHPA/BDMA with 20 wt% of S1200*

By FTIR the evolution of the characteristic functional groups taking part in the curing process was followed. Fig. 2 shows the initial and final spectra of the 20 wt% S1200 DGEBA/MTHPA mixture with 0.5 wt% of BDMA at 120 °C. In the initial spectrum, we can observe two main carbonyl bands at 1777 and 1859 cm^{-1} attributable to the unsymmetrical and the symmetrical stretching vibration of the cyclic anhydride, respectively. Moreover, the shoulder at 1729 cm^{-1} can be attributed to the ester groups of the S1200 structure. In the region between 950 and 850 cm^{-1} the deformation of the C–O–C bond of epoxy group at 913 cm^{-1} can be observed. The disappearance of the absorptions of the anhydride and epoxide indicates the complete consumption of these groups. During curing the ester band at 1729 cm^{-1} increases because of the reaction of anhydride with epoxides and hydroxyl groups.

To monitor the disappearance of the hydroxyl groups during curing we followed the different consumption of anhydride and epoxy groups in terms of equivalents, which are represented in

Table 2
Calorimetric data of DGEBA/MTHPA/BDMA mixtures with different percentages of S1200.

Formulation (% S1200)	ΔH (J/g)	T_{max}[a] (°C)	T_g[b] (°C)
DGEBA/MTHPA/0%	245	165	92
DGEBA/MTHPA/5%	220	165	97
DGEBA/MTHPA/10%	216	167	97
DGEBA/MTHPA/15%	210	163	97
DGEBA/MTHPA/20%	190	162	95

[a] Temperature of the maximum of the curing exotherm.

[b] Glass transition temperature obtained by DSC in a second scan after dynamic curing.

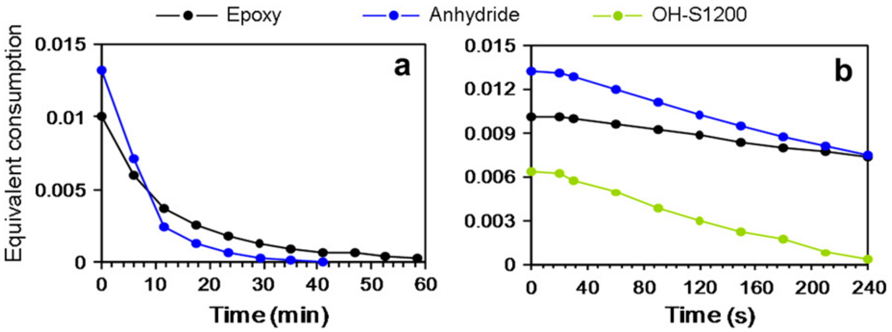


Fig. 3. a) Epoxy (913 cm^{-1}) and anhydride (1777 cm^{-1}) equivalent evolution versus time for the mixture DGEBA/MTHPA with 20 wt% of S1200 and 0.5 wt% of BDMA during all the curing process at 120 °C by ATR-FTIR (b) Epoxy, anhydride and OH-HBP equivalent evolution versus time for the same mixture during the 4 first minutes of curing at 120 °C by ATR-FTIR.

Fig. 3(a). We can observe that anhydride groups disappear faster than epoxide in the first stages of the curing, which implies an initial reaction of hydroxyl groups with anhydride. The different evolution can be emphasized by representing the equivalent consumption of epoxy, anhydride and hydroxyl groups in a 20 wt% S1200 formulation during the first minutes of curing, which is shown in Fig. 3(b). Thus, epoxides and anhydrides can react by both mechanisms represented in Scheme 2, but hydroxyl group only participates in the polycondensation mechanism, Scheme 2 (a). These results indicate that S1200 becomes covalently linked to the growing network from the very beginning of its formation, acting as a true reactive modifier.

3.3. *Study of the gelation process and shrinkage of the formulations*

It is known that internal stresses in thermosets mainly appear when the network loss its mobility. For this reason it is desirable to advance the gelation until higher conversions. Experimentally, one can determine the gelation point by using TMA starting at a region in which contraction is not observed between two contraction steps in the sample. When the material reaches sufficient mechanical stability (gelation) the TMA measuring probe deforms less the sample and the amplitude of the oscillations is reduced. The gel conversion, α_{gel}, can be determined as the DSC conversion at the temperature gelled in TMA in a non-isothermal experiment. Fig. 4 shows the signal derivative from which the conversion at the gelation can be determined.

By isothermal TMA the degree of shrinkage, $\alpha_{\mathrm{shrinkage}}$, 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 previous papers [20,21] we demonstrated, by solubility test and DMTA essays at different forces, how this point can be associated with the gel point.

Fig. 5 shows the plot of the shrinkage evolution during the curing at 120 °C against time for all the formulations studied, obtained by isothermal TMA. The first stage of contraction, before gelation, increases with the percentage of S1200, but this is not detrimental because of the materials have enough mobility to stand deformations. The higher shrinkage before gelation can be explained by the polycondensation mechanism, with a high shrinkage, which takes place between the hydroxyl groups of the HBP and the anhydride. After gelation shrinkage clearly decreases with the addition of S1200, which is beneficial from the point of view of the appearance of internal stresses. TMA only allows determining the relative contraction before and after gelation during the curing process but it does not allow quantifying the global shrinkage. We evaluate it by determining the density of all the formulations before and after curing by gas pycnometry.

In Table 3 the values for the conversion at the gelation (α_{gel}), gelation time (t_{gel}), global shrinkage, and shrinkage before and after gelation of DGEBA/MTHPA with different proportions of S1200 are collected. From the values of the table we can observe that there is not an obvious tendency of the evolution of the conversion at the gelation but there is a little reduction of the gelation time when the modifier is incorporated, in accordance to the accelerative effect at low temperatures observed by DSC studies. In a previous work [13],

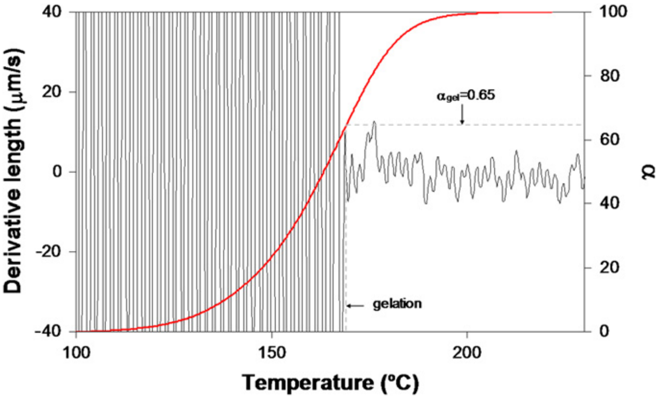


Fig. 4. Gel point determination using combined TMA and DSC for the mixture DGEBA/MTHPA with 20 wt% of S1200 and 0.5 wt% of BDMA.

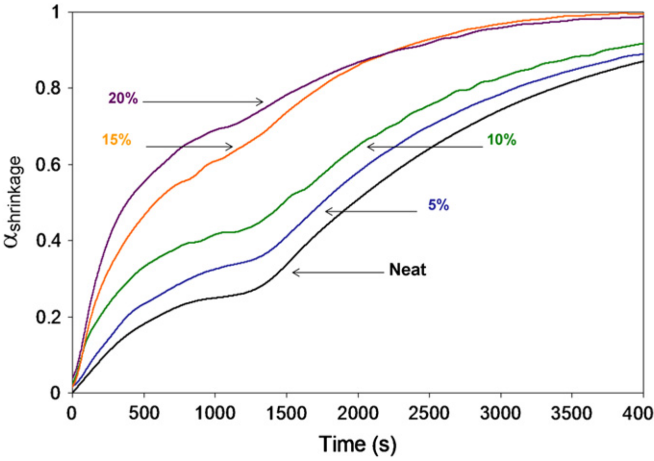


Fig. 5. Degree of shrinkage, $\alpha_{\mathrm{shrinkage}}$, versus time of the curing in TMA at 120 °C of mixtures DGEBA/MTHPA and DGEBA/MTHPA/S1200 in different weight percentages.

Table 3
Gelation data, densities and shrinkage of the systems studied.

Formulation (% S1200)	α_{gel}[a]	t_{gel}[b] (min)	$\alpha_{shrinkage}$[c]	ρ_{mon} (g/cm^3)	ρ_{pol} (g/cm^3)	Shrinkage[d] (%)	Shrinkage[e] after gel.
DGEBA/MTHPA/0%	0.64	21.5	0.27	1.182	1.214	2.64	1.93
DGEBA/MTHPA/5%	0.59	21.9	0.36	1.182	1.214	2.64	1.69
DGEBA/MTHPA/10%	0.65	19.8	0.43	1.186	1.214	2.35	1.34
DGEBA/MTHPA/15%	0.61	17.8	0.62	1.188	1.213	2.13	0.81
DGEBA/MTHPA/20%	0.59	18.4	0.70	1.194	1.213	1.54	0.46

[a] Determined as the conversion reached by non-isothermal TMA and DSC tests at 10 °C/min.
[b] Determined by TMA at 120 °C.
[c] Degree of shrinkage before gelation determined by TMA at 120 °C.
[d] Shrinkage determined as $[(\rho_{polymer} - \rho_{monomer})/\rho_{polymer}]$.
[e] Degree of shrinkage after gelation determined as $[\text{shrinkage}\cdot(1 - \alpha_{shrinkage})]$.

we could prove that the addition of a HBP to a DGEBA cationic curing system greatly increased the conversion at the gelation, which can be explained in the basis of a decrease in the global functionality of the system on adding HBP ($f \approx 4$ for the DGEBA and $f \approx 3$ for the HBP obtained from an AB_2 type monomer). In the present work, the average functionality of a DGEBA/MTHPA system is 3 similarly to that of S1200, and for this reason the conversion at the gelation should not be influenced by the presence of S1200. In contrast, there is a big variation of the contraction after gelation on increasing the proportion of HBP from 0.73 to 0.30. The mixture densities increase with the percentage of HBP, whereas the densities of the cured materials slightly decrease in comparison to the neat formulation. As the result, global shrinkage decreases with the incorporation of the modifier, showing the lowest shrinkage the material containing 20 wt% of S1200. From the degree of shrinkage and the global shrinkage we can estimate the contraction after gelation, which is notably reduced on increasing the proportion of S1200. These results can be explained if we consider that the use of this kind of modifiers increases the free volume due to the expandable effect that occurs during the chemical incorporation of these macromolecules into the matrix, such as was previously described [12,13,22]. Some authors [23] reported that the addition of HBP to epoxy systems leads to more dense thermosets with less free volume, but these differences can be attributed to the structure of epoxy resin and HBP and also to the curing mechanism selected.

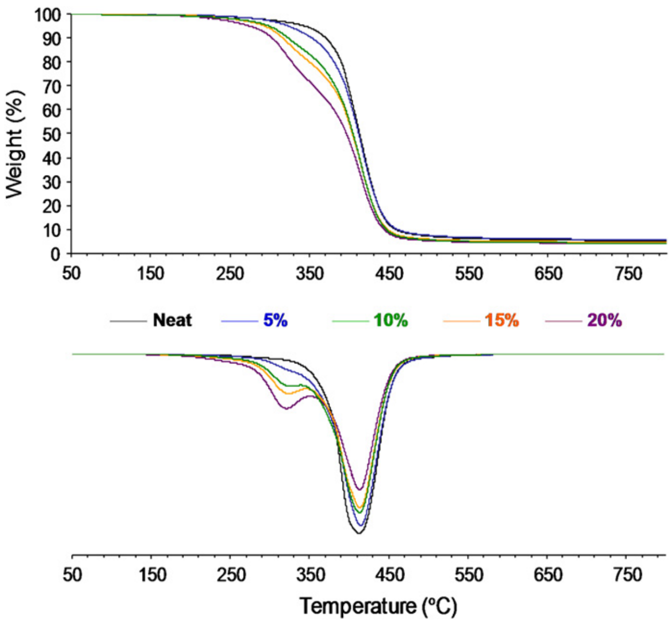


Fig. 6. TG and DTG curves at 10 °C/min in N_2 atmosphere of thermosetting materials obtained from DGEBA/MTHPA containing different proportions of S1200.

3.4. *Study of the thermal degradability*

To test if our modification procedure leads to more reworkable thermosets, our materials were analyzed by TGA. Fig. 6 shows the TGA and DTG curves for the cured materials. In Table 4 the thermogravimetric parameters are collected. DTG curves show that the addition of HBP leads to the appearance of a small peak at 325 °C, which increases with the proportion of HBP and therefore can be attributed to the rupture of the secondary ester bonds of the S1200, because of they turn into little fragments which can be lost at this temperature. The main peak corresponds to the degradation of the crosslinked network and it remains similar for all materials. From TGA data it is observed that the onset of degradation is notably reduced when the proportion of S1200 is increased. It was reported, that the optimal temperatures for safe rework operations are in the range 230–250 °C in nitrogen atmosphere, therefore, materials containing 15 wt%–20 wt% of S1200 are able to be classified as reworkable thermosets [24].

3.5. *Determination of thermal expansion coefficient*

One of the most common causes of internal stresses in coatings is due to the mismatch in the thermal expansion coefficients (CTEs) between the coating and the substrate. Table 4 collects the CTE values determined in the glassy and rubbery states of the materials prepared and the T_g determined as the cross of the tangents between both regions. It is interesting to note that on increasing the proportion of HBP the CTEs decrease. Usually, the introduction of flexible structures and the reduction of the crosslinking density increase this coefficient [25]. In these materials, flexible structures are introduced in the network and therefore the reduction of CTE should be attributed to a higher degree of crosslinking, due to the high number of functional groups in the HBP. It should be commented that the T_g has a major influence on the apparition of the internal stresses after curing. At the T_g the CTE changes from ~60 in the rubbery state to ~200 ppm/K in the glassy state and therefore the nearer the T_g to the curing temperature the less stresses are originated, when the coating is applied on the substrate.

3.6. *Study of the thermomechanical properties*

It has been observed by some authors [11,26], that the use of aliphatic hyperbranched polyesters as modifiers in epoxy resins leads to less densely crosslinked networks with an increased distance between crosslinks and therefore, mechanical properties of the material were affected in terms of strength. Figs. 7 and 8 show the mechanical relaxation spectra and the tan δ plot of the different thermosets obtained. The tan δ curves are unimodal,

Table 4
TGA, TMA and DMTA data of the materials prepared.

Formulation (% S1200)	$T_{2\%}$[a] (°C)	T_{max} (°C)	%Char ($T = 800$ °C)	$CTE_{glass} \cdot 10^6$ (K^{-1})	$CTE_{rubber} \cdot 10^6$ (K^{-1})	T_g[b] (°C)	Tan δ[c] (°C)	E'[d] (MPa)
DGEBA/MTHPA/0%	319	408	7	64.3	201.5	116	118	11.7
DGEBA/MTHPA/5%	282	415	6	64.1	201.4	119	132	17.8
DGEBA/MTHPA/10%	252	415	5	62.9	193.2	119	122	12.0
DGEBA/MTHPA/15%	250	414	4	62.1	191.5	119	116	8.8
DGEBA/MTHPA/20%	222	414	4	–	–	–	117	7.2

[a] Temperature of a 2% of weight loss calculated by thermogravimetry.
[b] Glass transition temperature obtained by TMA.
[c] Temperature of the maximum of the tan δ determined by DMTA.
[d] Storage modulus of material at the rubbery region at a temperature of tan $\delta + 40$ °C.

which indicates that the materials are homogeneous, although the material containing 20 wt% of S1200 shows a broader peak. The characteristic parameters associated to these spectra are shown in Table 4. As can be seen, the addition of a 5 wt% of S1200 leads to the highest tan δ temperature. A further addition of S1200 slightly reduces this value. Tan δ temperatures correlate with T_g values determined by DSC.

The value of the relaxed modulus (E') reaches also a maximum for the material with a 5 wt% of S1200. Again, further addition of HBP reduces this parameter.

From these studies we can state that the addition of percentages of S1200 until 10 wt% increases the T_g and relaxed modulus in comparison to the neat epoxy, which can be explained by the higher density of crosslinking achieved by the addition of the HBP, which can be considered as a whole as a multifunctional crosslinker.

3.7. Mechanical characterization

Boogh and colleagues [8] studied the effect of HBP as tougheners in epoxy resins. Their system was based in the curing of an epoxy resin and epoxy functionalized HBPs with isophoronediamine. They could demonstrate that the addition of 10 wt% of HBP to the material allows increasing 10-fold the toughness with a drop of the modulus of 10%. The HBPs used were epoxy modified polyesters based in Boltorn®, which originated microphase separation. Yang et al. [11] observed a 20% of improvement in impact strength by adding 10 wt% of Boltorn® H30 to an epoxy resin/anhydride system with a high reduction of the Young modulus from 3.9 to 1.3 GPa. These materials did not show phase separation by SEM observation. Fu et al. [27] observed that the maximum impact strength was achieved by addition of 5–15 wt% of a very flexible HBP to the DGEBA and in this way improvements of about 2–7 times in toughness were observed, although with a decrease in the T_g value. From these different results, it can be extracted that the structure of the components of the formulation and the mechanism selected are of capital importance in the mechanical behaviour.

The obtained values of Young's modulus, impact strength (I.S.) and Knoop microhardness (M.H.) for all the materials prepared are collected in Table 5. It is observed that, in general, the addition of S1200 slightly increases Young's modulus, reaching the maximum value for the material containing 10 wt% of modifier (a 10% of increase).

Impact resistance is a useful measure to evaluate the toughness or brittleness of a material. The addition of S1200 leads to a slight improvement on impact strength, also reaching the highest value for the thermoset containing 10 wt% of HBP (60% of improvement). Higher proportions of this modifier are detrimental, but in all cases the impact strength measured was higher than in the unmodified epoxy thermoset. This increase in toughness can be explained by the more flexible structure of S1200 introduced in the network [28].

Microhardness measurements are very useful in rating coatings on rigid substrates for their resistance to mechanical abuse, such as that produced by blows, gouging and scratching. This technique is used in the 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, the addition of HBP slightly increases the microhardness in reference to pure cured DGEBA. This property, generally, is related with the final mechanical properties of the material: elongation at break and strength at break. In materials presenting higher values for these properties, the microhardness should be also higher.

In previous studies of our research group on the copolymerization of DGEBA with lactones [25,29] it was observed that the flexibilization of the network structure led to a decrease of the microhardness, modulus and T_g values. The use of S1200 in epoxy/anhydride systems leads to improvements of all the mechanical properties studied while maintaining the thermomechanical characteristics.

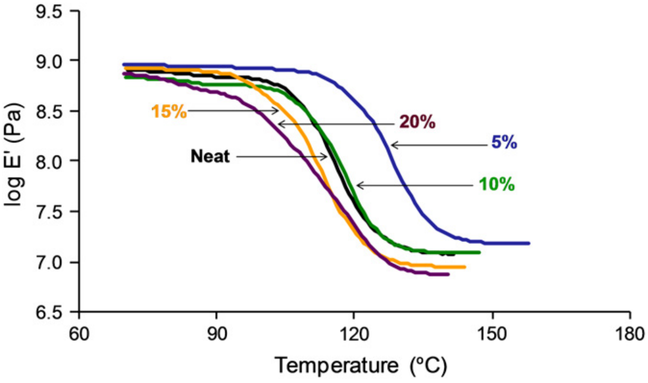


Fig. 7. Storage modulus (E') against temperature for the materials obtained.

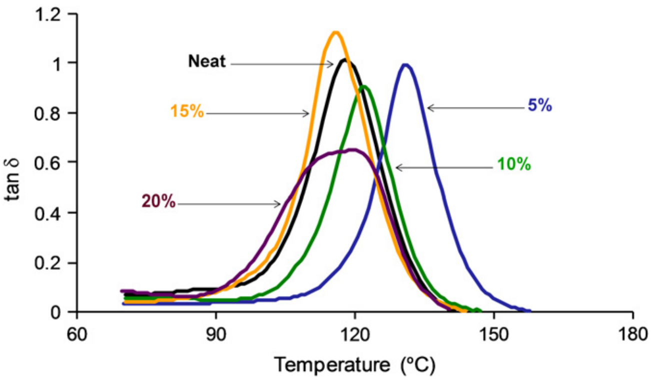


Fig. 8. Tan δ against temperature for the materials obtained.

Table 5
Mechanical properties and water uptake parameters evaluated of the materials prepared.

Formulation (% S1200)	Young's modulus (GPa)	I.S. (kJ/m^2)	M.H. HK0	M_{max} (%)	$D \times 10^{-8}$ (cm^2/s)
DGEBA/MTHPA/0%	3.8 (0.1)	1.3 (0.1)	19.7 (0.1)	1.0 ($2 \cdot 10^{-4}$)	4.3 (0.2)
DGEBA/MTHPA/5%	3.7 (0.2)	1.7 (0.1)	20.6 (0.1)	1.2 ($4 \cdot 10^{-4}$)	3.6 (0.0)
DGEBA/MTHPA/10%	4.3 (0.1)	2.1 (0.1)	20.4 (0.1)	1.7 ($7 \cdot 10^{-4}$)	2.9 (0.2)
DGEBA/MTHPA/15%	4.1 (0.3)	1.4 (0.1)	24.7 (0.2)	2.1 ($3 \cdot 10^{-4}$)	2.2 (0.1)
DGEBA/MTHPA/20%	4.0 (0.1)	1.5 (0.2)	21.3 (0.2)	2.6 ($6 \cdot 10^{-4}$)	1.7 (0.1)

The standard deviations are shown in parentheses.

3.8. Morphology analysis by SEM

The toughness behaviour of DGEBA/MTHPA and the S1200 modified thermosets can be explained in terms of morphology observed by SEM. The fracture surfaces after impact tests were investigated by this technique and the most representative micrographs are shown in Fig. 9.

All the micrographs present a homogeneous appearance without any phase separation, although S1200 is a hydrophilic polymer and the epoxy matrix is hydrophobic. This homogeneity can be due to the fact that the particle size is too small to observe, which is attributed to the covalent bonding of the reactive groups of S1200 to anhydrides in the matrix. The smooth glassy fractured surface with little cracks in the unmodified material can be observed in Fig. 9(a), without any sign of deformation, which accounts for its poor impact strength. In contrast, the fracture surface of the material with a 5–10 wt% of S1200 Fig. 9(b) and (c) is rougher than that of the unmodified material with more striations, suggesting that the impact specimens break more yieldingly. When the proportion of S1200 is increased again a brittle fracture is observed as a smooth surface. All these observations agree with the impact strength values measured (Table 5).

3.9. Water uptake behaviour

Epoxy resins are considered to be hardy polymers capable of stand deleterious conditions for considerable times. However, extended exposure to water can lead to damage. The main consequence of exposure to water is plasticisation, leading in turn to reduction of elastic modulus, strength and lowering the glass transition temperature [30]. Thus, the water absorption of the materials prepared is an important task to be studied.

The water absorption curves against time and the relative water gained against the root square of time at 50 °C are shown in Fig. 10 for the thermosets obtained. 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 aliphatic poly(ester-amide) HBP compared with neat DGEBA/MTHPA system and to the increase in the free volume [31]. The equilibrium water uptake (M_{max}) was taken as the maximum values reached of the water absorption curves. The obtained values of this parameter and the corresponding diffusion coefficients determined for each material are collected in Table 5. The diffusion coefficient, calculated by the equations given in Experimental part, on the contrary than the water uptake, decreases on adding HBP. This indicates that

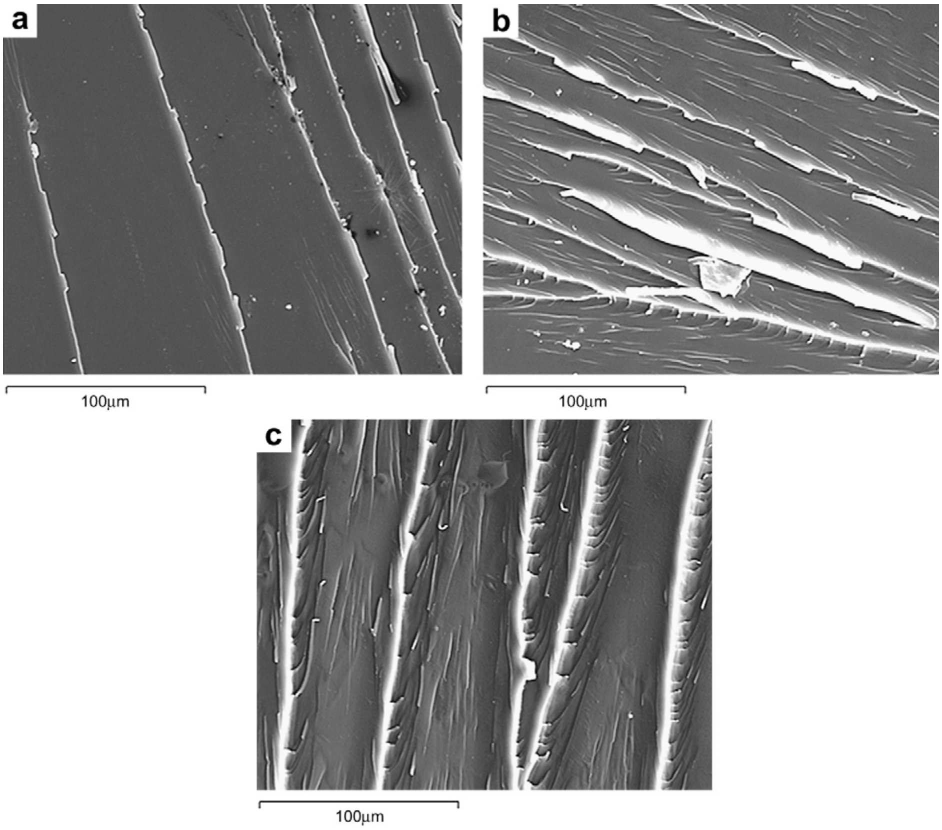


Fig. 9. SEM micrographs for fracture surfaces of the following materials cured at 150 °C: (a) neat DGEBA/MTHPA; (b) 5 wt% S1200/DGEBA/MTHPA; (c) 10 wt% S1200/DGEBA/MTHPA.

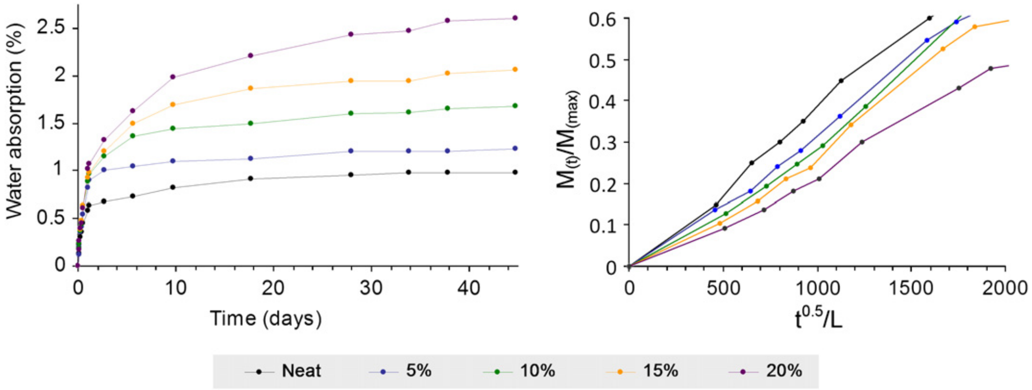


Fig. 10. Water absorption curves against time and relative water weight gained as a function of root square of time at 50 °C for DGEBA/MTHPA and DGEBA/MTHPA modified with different percentages of S1200.

on adding S1200 the rate of absorption initially decreases but the equilibrium saturation percentages increases.

4. Conclusions

The addition of a hydroxyl ended HBP to epoxy/anhydride systems, in the presence of a tertiary amine as catalyst, affects the mechanism of the curing process, favouring the non-catalyzed mechanism, which 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.

Shrinkage after gelation is notably reduced on adding S1200. On increasing the proportion of modifier a progressive decrease of the global shrinkage is observed, which implies an increase in the free volume.

The thermal reworkability of the thermosets increases on adding a higher proportion of HBP.

By DMTA and SEM the homogeneous character of the materials prepared has been demonstrated. The tan δ value reaches a maximum for the material with a 5 wt% of S1200. The addition of S1200 to DGEBA/MHTPA system increases the T_gs evaluated by DSC and TMA.

Thermal expansion coefficients in the glassy and rubbery states are slightly reduced on adding S1200 to the formulations.

Mechanical properties (Young's modulus, impact strength and microhardness) show little improvements on adding the HBPs tested to the material formulations. The proportion of 10 wt% is the optimum one in order to achieve the best characteristics.

The presence of S1200 in the materials increases the water uptake, proportionally to the amount added, but decreases the diffusion coefficients.

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