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Corresponding Author: Prof. Àngels Serra,

Corresponding Author's Institution:

First Author: Cristina Acebo

Order of Authors: Cristina Acebo; Xavier Fernandez-Francos, Dr; Silvia De la Flor, Dr; Xavier Ramis, Prof; Àngels Serra

Abstract: New dendritic modifiers have been synthesized by amidation of hyperbranched poly(ethylenimine) (PEIs) with 10-undecenoic acid to obtain hyperbranched polymers (HBPs) with different degree of modification. These HBPs have been used as toughness modifiers in a proportion of 10 and 20% in reference to the epoxy resin in diglycidyl ether of Bisphenol A (DGEBA) / methyltetrahydrophthalic anhydride (MTHPA) formulations. The curing process has been studied by dynamic scanning calorimetry and by rheometry, which allow the kinetic constants and the gel and vitrification times to be evaluated. The materials obtained have been thermally characterized and their mechanical properties have been evaluated. An increase in impact resistance has been achieved and the Tg of all thermosets prepared was higher than 100°C in spite of the flexible structure of the PEI modifiers.



UNIVERSITAT  
ROVIRA I VIRGILI

DEPARTAMENT DE QUÍMICA ANALÍTICA  
I QUÍMICA ORGÀNICA

C/ Marcel·lí Domingo s/n  
Campus Sescelades  
43007 Tarragona (Spain)  
Tel. 34 977 55 97 69  
Fax 34 977 55 84 46  
e-mail: secqaqo@urv.net

Prof. M. Piens  
Coatings Research Institute,  
Avenue P. Holoffe, 1342 Limelette,  
Belgium

Tarragona, February 9<sup>th</sup> 2015

Dear Prof. Piens:

We send our manuscript entitled: **NEW ANHYDRIDE/EPOXY THERMOSETS BASED ON DIGLYCIDYL ETHER OF BISPHENOL A AND 10-UNDECENOYL MODIFIED POLYETHYLENEIMINE WITH IMPROVED IMPACT RESISTANCE** after revision and correction of the items detailed by the reviewers for publication in Progress in Organic Coatings.

Looking forward to hearing from you, I remain.

Yours sincerely,

Prof. Angels Serra

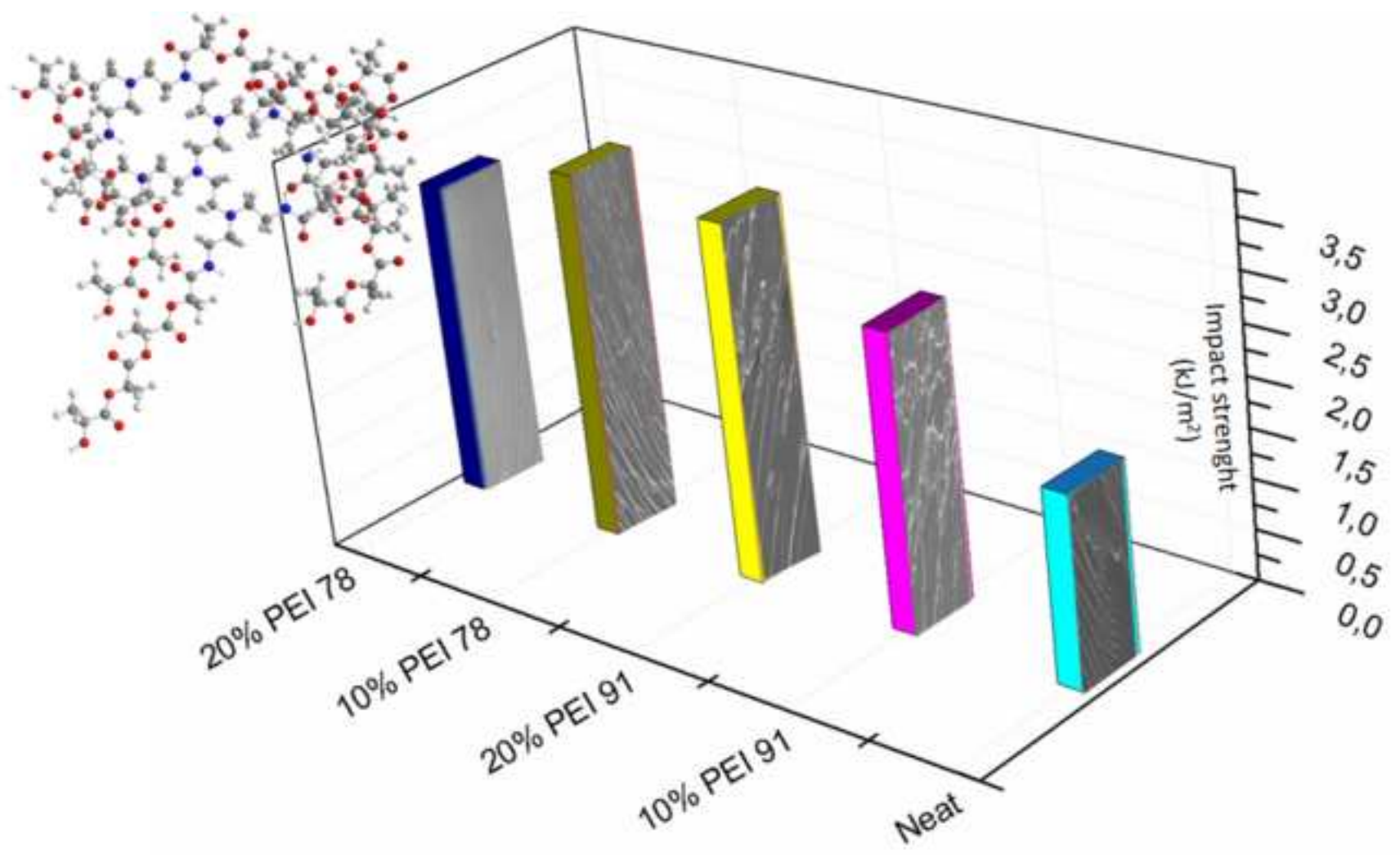


## Response to Reviewers

We thank the reviewers for their task and I would like to tell that we have corrected all the failures detailed by the reviewer 2.

We have also improved a little the grammar and we have shortened some sentences to make them more understandable.

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## Highlights

- 10-undecenoyl derivative of polyethyleneimine was obtained.
- This polymer was used as modifier in epoxy/anhydride formulations.
- The final materials were characterized thermally and mechanically.
- Impact strength was notably increased in the modified materials.

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**New anhydride/epoxy thermosets based on diglycidyl ether of bisphenol A and 10-undecenoyl modified poly(ethyleneimine) with improved impact resistance**

Cristina Acebo,<sup>1</sup> Xavier Fernández-Francos,<sup>1,2</sup> Silvia de la Flor,<sup>3</sup> Xavier Ramis,<sup>4</sup> Àngels Serra<sup>1\*</sup>

<sup>1</sup> Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, C/ Marcel·lí Domingo s/n, 43007, Tarragona, Spain.

<sup>2</sup> Centre Tecnològic de la Química de Catalunya, CTQC, C/ Marcel·lí Domingo s/n, 43007, Tarragona, Spain.

<sup>3</sup> Department of Mechanical Engineering, Universitat Rovira i Virgili, C/ Països Catalans, 26, 43007, Tarragona, Spain.

<sup>4</sup> Thermodynamics Laboratory, ETSEIB Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028, Barcelona, Spain.

\*Corresponding Author: (Angels Serra) Tel +34 977559558 FAX +34 977558446

e-mail address: [angels.serra@urv.cat](mailto:angels.serra@urv.cat)

## ABSTRACT

New dendritic modifiers have been synthesized by amidation of hyperbranched poly(ethylenimine) (PEIs) with 10-undecenoic acid to obtain hyperbranched polymers (HBPs) with different degree of modification. These HBPs have been used as toughness modifiers in a proportion of 10 and 20% in reference to the epoxy resin in diglycidyl ether of Bisphenol A (DGEBA) / methyltetrahydrophthalic anhydride (MTHPA) formulations. The curing process has been studied by dynamic scanning calorimetry and by rheometry, which allow the kinetic constants and the gel and vitrification times to be evaluated. The materials obtained have been thermally characterized and their mechanical properties have been evaluated. An increase in impact resistance has been achieved and the  $T_g$  of all thermosets prepared was higher than 100°C in spite of the flexible structure of the PEI modifiers.

## KEYWORDS

Thermosetting resins, hyperbranched, toughness, anhydride, rheology

### *1. Introduction*

Epoxy resins are ideal materials in the field of coatings, adhesives, molding compounds and polymer composites due to their excellent thermomechanical properties and chemical and environmental stability. They also present good processability before curing [1]. Their broad range of applications can be explained by the fact that they are probably one of the most versatile thermosets not only because the type of resin and the chemistry of the curing can be varied, but also a huge number of organic and inorganic modifiers and fillers can be added to improve their properties [2]. Although rigidity and strength are desired properties in engineering applications, toughness is one of the restrictions in the use of epoxy resins.

During the past decades considerable efforts have been made to improve the toughness of these materials. Toughness implies energy absorption and it is achieved through various deformation mechanisms before failure occurs. One of the most effective methods of preventing the crack from freely developing after impact is the addition of a second phase that induces the formation of particles that absorb the impact energy and deflect the crack. A combination of cavitation around the rubber particles with shear yielding in the matrix produces a cooperative effect in the energy dissipation [3]. It has been reported that the formation of micro- or nanostructures in epoxy



1 thermosets improves the overall properties without reducing crosslinking degree of the  
2 epoxy matrix and glass transition temperatures [4]. Chemically induced phase  
3 separation (CIPS) is one of the methodologies in which the morphology develops  
4 during curing. It starts from an initial homogenous mixture composed of the resin,  
5 curing agent and modifiers [5,6]. On curing, a blend of epoxy matrix filled with rubber  
6 or thermoplastic microspheres is formed, with a final size of these particles controlled  
7 by the viscosity of the reacting mixture during curing.  
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12 The first attempts to improve toughness were based on the addition of liquid rubbers  
13 or thermoplastics. However, these additives usually compromise the modulus and  
14 thermomechanical characteristics of the thermosets and the processability of the  
15 formulation [7]. Some years ago the use of hyperbranched polymers (HBPs) was  
16 proposed to overcome the limitations of traditional modifiers [8] and since then a  
17 significant number of research groups have adopted this strategy [9-12]. The dendritic  
18 structure of HBPs makes these modifiers very promising in terms of processability  
19 because of the low entanglement that leads to low viscosities in comparison to rubbers  
20 or linear polymers [13]. By partial or total modification of their reactive terminal  
21 groups, it is possible to tune their interaction or covalent linkage with the epoxy matrix.  
22 This can lead to phase separated or homogenous morphologies.  
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33 In previous papers we demonstrated that the addition of HBPs to a curing system  
34 improves mechanical properties [14-16]. In these cases, the chemical incorporation of  
35 hydroxyl ended HBPs to the epoxy matrix led to materials with homogenous  
36 appearances without any phase separation.  
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40 We reported the use of partially modified Boltorn type polyesters with 10-  
41 undecenoyl moieties in DGEBA thermosets cured with anhydrides, resulting in a  
42 significant increase in impact strength, up to 400% with respect to the neat formulation,  
43 without sacrificing thermal and mechanical properties [17]. Efficient toughening was  
44 obtained because of the CIPS process leading to well dispersed hyperbranched particles  
45 covalently attached to the thermosetting matrix by the unmodified hydroxyl groups of  
46 the HBP. Following the same approach, we synthesized end-capped multiarm star  
47 polymers as modifiers in the curing of DGEBA with anhydride and a significant  
48 increase in impact strength was also achieved, attributed to the nanophase separation  
49 observed [18].  
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58 In the present work, we propose the use of a series of partially modified  
59 poly(ethyleneimine) (PEI) with 10-undecenoyl chains as modifier of DGEBA  
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thermosets cured with anhydride in the presence of a tertiary amine as a catalyst. Our interest is to investigate the influence of the degree of modification of the PEI structure with 10-undecenoyl groups and the proportion of this modifier in the formulation on the curing evolution and on the mechanical and thermal characteristics of the materials obtained, emphasizing toughness improvement.

## 2. Experimental section

### 2.1 Materials

Poly(ethyleneimine) (PEI) (Lupasol<sup>®</sup>FG, 800 g/mol, BASF) was used after drying under vacuum. From the molecular weight of the polymer and of the repeating unit an average degree of polymerization of 18.6 was calculated. According to the data sheet, the relationship (NH<sub>2</sub>/NH/N) was (1/0.82/0.53) and thus by calculations the equivalent number of primary, secondary and tertiary amines resulted to be 0.010, 0.00837, and 0.0053 eq/g. 10-Undecenoic acid was purchased from Fluka and 1,1-carbonyldiimidazole (CDI) was purchased from Sigma-Aldrich. Chloroform (CHCl<sub>3</sub>) was dried under CaCl<sub>2</sub> and distilled before used. Diglycidylether of bisphenol A (DGEBA, Araldite GY 240, Huntsman, 182 g/eq) and methyl tetrahydrophthalic anhydride (MTHPA, Aradur HY 918, Huntsman) (166 g/mol) were used as received. Benzyl dimethylamine (BDMA, DY 062, Huntsman) was used as catalyst.

### 2.2 Amidation of hyperbranched polyethylenimines

The amidation of PEIs was performed according to a reported procedure [19,20]. The modified PEIs were achieved by reaction of the PEI with different ratio of 10-undecenoic acid and the degree of modification was calculated by means of <sup>1</sup>H-NMR spectroscopy. The synthesis of amidated PEIs were exemplified for the polymer PEI<sub>91</sub>: 8.49 g (52 mmol) of CDI were slowly added to a solution of 9.66 g (52 mmol) of 10-undecenoic acid in 40 mL of chloroform. The solution was stirred at room temperature for 1h, and then 3 g (3.75 mmol) of PEI in 10 mL of chloroform were added. The mixture was stirred at room temperature for 4h, and then at 50°C overnight. After cooling down, the mixture was washed several times with NaCl aqueous solution. The organic phase was dried by anhydrous MgSO<sub>4</sub> and after filtration and removal of the volatiles, the residue was kept at 40°C in vacuum oven overnight and a honey-like polymer was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 1.20-1.36 (-CH<sub>2</sub>-, **4-8**),

1.59 (-CH<sub>2</sub>-CH<sub>2</sub>-CO-, **3**), 2.04 (-CH<sub>2</sub>-CH=CH<sub>2</sub>, **9**), 2.15 (-CH<sub>2</sub>-CO-NH, **2**), 4.77 (-NH-, **1**), 4.95 (CH<sub>2</sub>=CH-, **11**), 5.80 (CH<sub>2</sub>=CH-, **10**) and 3.46-2.55 (PEI core) (Figure 1).

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

**Table 1.** Characteristics of the modified HBPs synthesized

<i>Notation</i>	<i>DA (%)<sup>a</sup></i>	<i>M<sub>n</sub><sup>b</sup> (g/mol)</i>	<i>T<sub>g</sub><sup>c</sup> (°C)</i>	<i>T<sub>5%</sub><sup>d</sup> (°C)</i>
PEI <sub>91</sub>	91	2925	-56	204
PEI <sub>78</sub>	78	2626	-49	196

<sup>a</sup> Degree of amidation calculated by <sup>1</sup>H-NMR.

<sup>b</sup> Determined by <sup>1</sup>H-NMR spectroscopy.

<sup>c</sup> Determined by DSC.

<sup>d</sup> Temperature of 5% of weight loss determined by TGA under N<sub>2</sub> atmosphere.

### 2.3 Preparation of mixtures

Neat formulations were prepared by mixing the DGEBA with the stoichiometric amount of MTHPA. Then, the selected proportion of BDMA was added and the mixture was homogenized by mechanical stirring. The formulations containing 10-20% wt of PEIs (by weight of DGEBA) were prepared by first adding the required amount of PEIs to the epoxy resin and gently heating until they were dissolved and subsequently mixing with MTHPA and BDMA by mechanical stirring. For all the formulations, the quantity of MTHPA was calculated taking into account that 1 mol of anhydride reacts with 1 mol of epoxide group and the amount of BDMA was always 1 phr (1 part per hundred) with respect to the anhydride. The samples were kept at -20°C before use to prevent polymerization.

### 2.4 Characterization

#### 2.4.1 NMR characterization

<sup>1</sup>H NMR measurements were carried out at 400 MHz and in a Varian Gemini 400 spectrometer. CDCl<sub>3</sub> was used as the solvent. For internal calibration, the middle solvent signal corresponding to CDCl<sub>3</sub> was taken as δ (<sup>1</sup>H) = 7.26 ppm.

#### 2.4.2 Differential Scanning Calorimetry (DSC)

Calorimetric analyses were carried out on Mettler DSC 822e and Mettler DSC 821e calorimeter with a TSO01RO robotic arm. The kinetic studies were performed at heating rates of 2, 5, 7.5, 10°C/min to determine the kinetic parameters and the reaction

1 heat. The glass transition temperatures ( $T_g$ ) of the HBPs were determined from a  
 2 dynamic scan from -100°C to 200°C at 10°C/min. The glass transition temperatures of  
 3 the completely cured materials ( $T_g^\infty$ ) were determined by means of a heating scan at  
 4 10°C/min, after isothermal curing process performed during 3h at 100°C and 1h at  
 5 150°C.  
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 9 The curing kinetics of non-isothermal DSC experiments was analyzed by means of  
 10 isoconversional and model-fitting procedures applied to non-isothermal DSC  
 11 data [21].  
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14 The isoconversional activation energy at different degrees of conversion  $x$  was  
 15 determined from multiple heating rate experiments using the Kissinger-Akahira-Sunose  
 16 method:  
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$$19 \ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A \cdot R}{g(x) \cdot E}\right) - \frac{E}{R \cdot T} \quad (1)$$

20 where  $\beta$  is the heating rate,  $A$  is the pre-exponential factor,  $E$  is the activation energy  
 21 and  $g(x)$  is an integral function corresponding to the kinetic model. The time needed to  
 22 reach a given conversion in an isothermal experiment can be determined from the  
 23 results of the isoconversional analysis of non-isothermal experiments using the  
 24 following expression:  
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$$27 \ln t = \ln\left(\frac{g(x)}{A}\right) + \frac{E}{R \cdot T} \quad (2)$$

28 The kinetic model was determined using a 2<sup>nd</sup> order autocatalytic kinetic model with  
 29  $g(x) = (1/(n-1)) \cdot ((1-x)/x)^{1-n}$  and rearranging the above expressions as  
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$$33 \ln\left(\frac{g(x) \cdot \beta}{T^2}\right) = \ln\left(\frac{A \cdot R}{E}\right) - \frac{E}{R \cdot T} \quad (3)$$

### 34 2.4.3 Thermogravimetric analysis (TGA)

35 Thermogravimetric analyses were carried out in a nitrogen atmosphere with a Mettler  
 36 TGA/SDTA 851e thermobalance. Samples with an approximate mass of 8 mg were  
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1 degraded between 40 and 800 °C at a heating rate of 10 °C/min in N<sub>2</sub> (100 cm<sup>3</sup>/min  
2 measured in normal conditions).

#### 3 2.4.4 Rheological characterization 4

5 Rheological measurements were carried out in the parallel plates (diameter of 25  
6 mm) mode with an ARG2 rheometer (TA Instruments, UK, equipped with an  
7 electrically heated plates system, EHP). The curing of the mixtures was monitored in an  
8 isothermal experiment at 100 °C by means of a multiwave frequency sweep (1, 3 and 5  
9 Hz). The frequency independent crossover of  $\tan\delta$  was used to determine the gel time  
10 [22]. The vitrification time was taken as the maximum of  $\tan\delta$  at 5 Hz. The conversion  
11 at gelation ( $x_{gel}$ ) was determined by stopping the rheology experiment at gelation and  
12 performing a subsequent dynamic DSC scan of the gelled sample to measure the  
13 remnant heat of curing. The degree of curing achieved in gelation was determined using  
14 the following equation:  
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$$24 \quad x_{gel} = 1 - \frac{\Delta H_{t,gel}}{\Delta H_{dyn}} \quad (4)$$

25 where  $\Delta H_{t,gel}$  is the heat of the sample obtained by rheological experiment at gelation  
26 and  $\Delta H_{dyn}$  is the total reaction heat.  
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#### 29 2.4.5 Dynamic mechanical thermal analysis (DMTA) 30 31 32

33 Dynamic mechanical thermal analyses were carried out with a TA Instruments DMA  
34 Q800. The samples were cured isothermally in a mold (5 mm width and 3 mm thick) at  
35 100 °C for 3 h and then post-cured for 1 h at 150 °C. Single cantilever bending at 1 Hz  
36 and deformation of 0.05% was performed at 3°C/min, from 30°C to 230°C on prismatic  
37 rectangular samples (10x10x1 mm<sup>3</sup>).  
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#### 45 2.4.6 Impact test 46

47 Impact tests were performed at room temperature by means of a Zwick 5110 impact  
48 tester according to ASTM D 4508-05 (2008) standard using rectangular samples (25 x  
49 12 x 2.5 mm<sup>3</sup>) cured by the same thermal process scheduled for DMTA samples. The  
50 pendulum employed had a kinetic energy of 0.5 J. For each material 9 determinations  
51 were made. The impact strength (IS) was calculated from the energy absorbed by the  
52 sample upon fracture as:  
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$$IS = \frac{E - E_0}{S} \quad (5)$$

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.

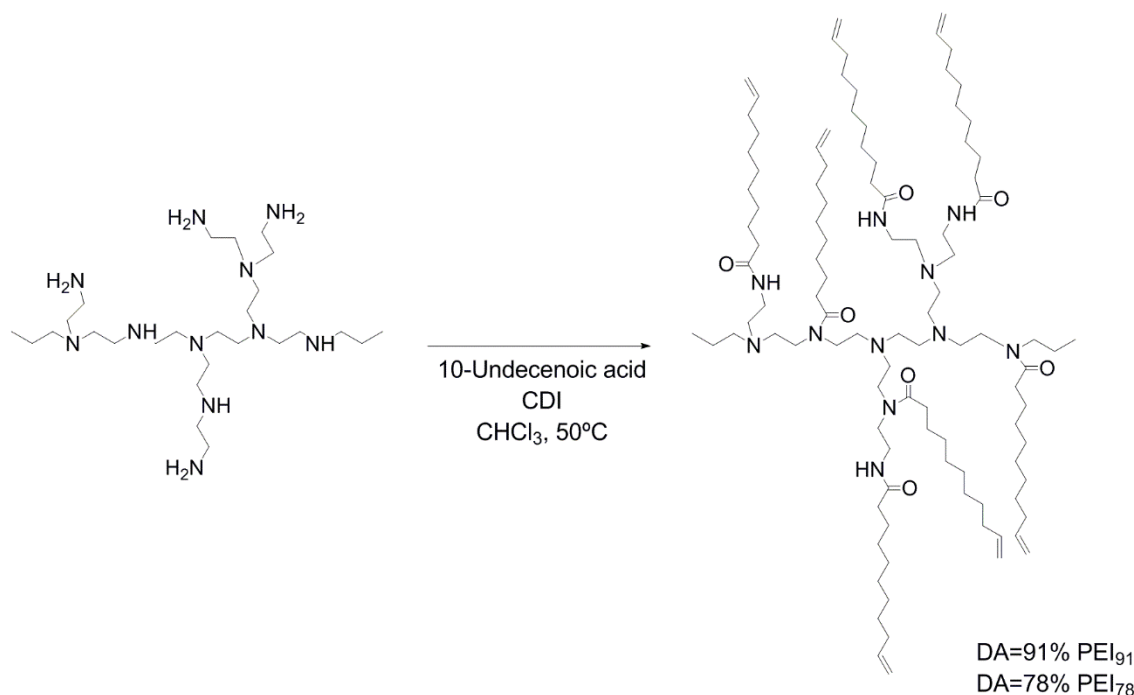
#### 2.4.7 SEM

The fracture area of impacted samples was metalized with gold and observed with a scanning electron microscope (SEM) Jeol JSM 6400 with a resolution of 3.5 nm.

### 3. Results and discussion

#### 3.1 Synthesis and characterization of 10-undecenoyl modified PEI

Poly(ethyleneimine) possesses high number of reactive amines as end groups that can be modified to different extents. In the present study, total and partial modifications with 10-undecenoyl chains of this polymer were attempted. From the degree of polymerization of PEI, the proportion of  $\text{NH}_2/\text{NH}/\text{N}$  and the equivalent number of primary and secondary amines by molecule we calculated the number of reactive groups capable of being modified ( $\text{NH}_2$  and  $\text{NH}$ ), which resulted to be 14 per PEI molecule. From this number and desired degree of modification the quantity of 10-undecenoic acid and CDI used in the chemical modification was calculated. In the notation of the modified polymers, the subscript indicates the percentage of modification attained. The idealized structure and the synthetic procedure are represented in Scheme 1.



**Scheme 1.** Synthetic route to the modified PEIs

In previous studies [17,23] the modification of hydroxyl ended HBPs with 10-undecenoyl groups was performed by reaction with 10-undecenoyl chloride in the presence of 4-(N,N-dimethylamino) pyridine (DMAP) as hydrochloric acid acceptor. However, when we used PEI as HBP the elimination of DMAP by acidic extraction was impossible because the basic character of the modified polymer. Therefore, as the alternative synthetic procedure we selected the one proposed by Antonietti et al. [19] for the modification of PEI with palmitic acid which consists in two steps: the first one is the activation of 10-undecenoic acid by reaction with CDI in chloroform. The second step is the nucleophilic substitution of imidazole group in the CDI derivative by amines of the PEI structure. By selecting the proper amount of CDI derivative in reference to the active amine groups in the PEI core, different degrees of modification were reached, 91% and 78%. No complete modification could be reached similarly to that described in PEI modification with long-chain aliphatic acids [19,20].

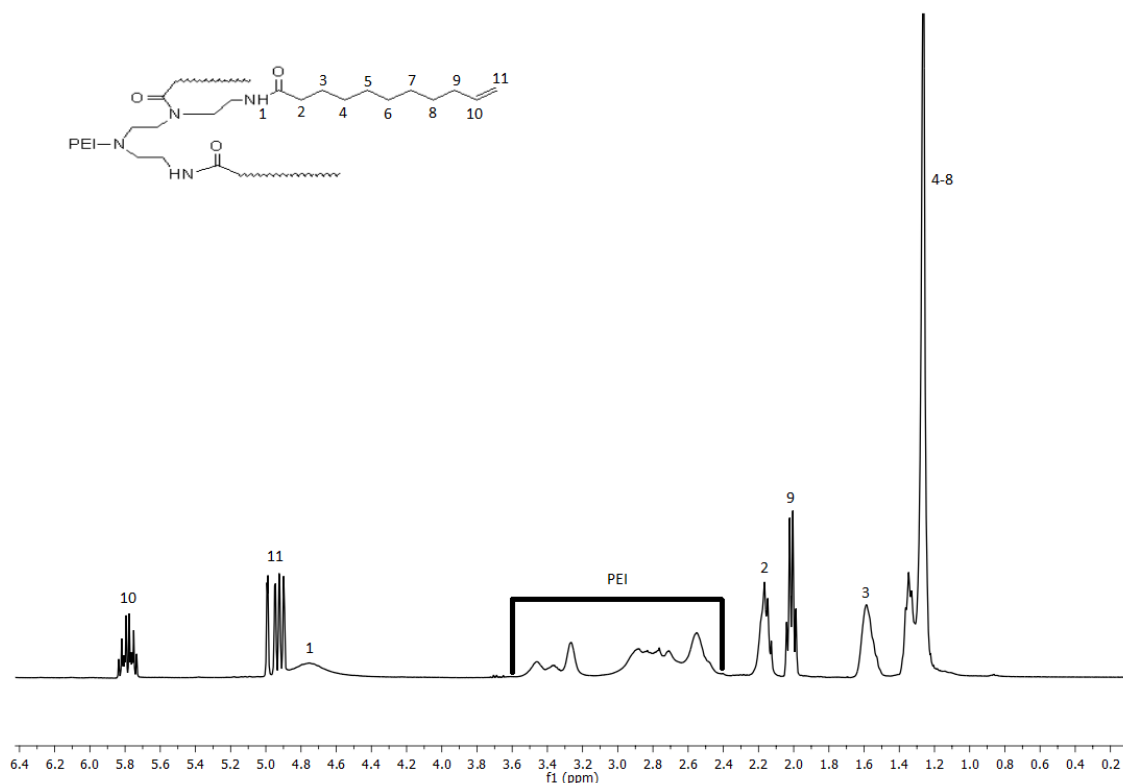
The degree of modification was calculated by <sup>1</sup>H-NMR, following a previously reported method [19]. Figure 1 shows the spectrum for the partially modified polymer with the signal assignments. From the intensities of signal 2, corresponding to methylene protons directly attached to amide group divided by two (*A*) and the area in the region between 3.6 and 2.4 ppm which corresponds to the core of PEI (*P*), we determined the value of *x*. This value corresponds to the ratio of alkyl chains introduced

per amine moiety in the starting PEI, which includes tertiary, secondary and primary amines. From  $x$  and the values of the primary amine end groups (T), secondary amine linear units (L), and tertiary amine branched units (D) it is possible to calculate the degree of amidation (DA) by using the following equations:

$$x = A / \left[ \frac{P}{(5-x)} \right] \quad (6)$$

$$DA = x(L+T+D)/(L+T) \quad (7)$$

The values of  $DA$  were slightly lower than expected. In the case of adding the stoichiometric amount of CDI derivative to PEI, an only 91% of the total reactive amines could be modified, whereas the difference between the expected and the reached degree of modification is lower for lower degrees of modification. Probably the aliphatic shell formed in the modification of PEI hinders the possibility of nucleophilic attack of amine groups to the carbonyl group of the CDI derivative.



**Figure 1.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of the  $\text{PEI}_{78}$

From the thermogravimetric data shown in Table 1 it was observed that the higher the degree of modification the higher the temperature of initial degradation. However, there is a decrease in their  $T_g$  as the degree of modification increases. This is a feature



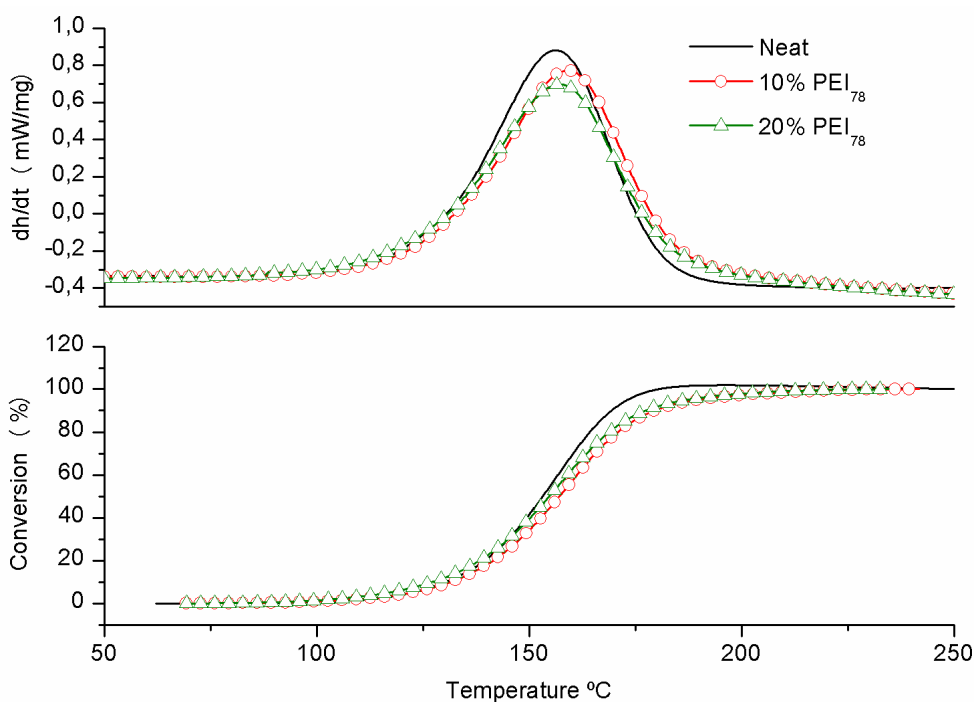
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that was observed in modified hyperbranched poly(glycidol) with 10-undecenoyl chains [23] caused by both the decrease in the intensity of inter- and intra-molecular H-bonding interactions and the increased in free volume associated with the presence of the 10-undecenoyl chains [24,25].

### 3.2 Effect of the 10-undecenoyl modified PEI on the curing kinetics

Figure 2 represents the curing thermograms and conversion evolution of the DGEBA neat formulation and the formulations containing 10% and 20% of the PEI<sub>78</sub> cured with MTHPA in the presence of BDMA. Table 3 summarizes the most relevant data obtained from the curing of the formulations.

If we observe the shape of the crosslinking exotherm, it seems that there is no much influence on adding the PEI<sub>78</sub> to the reactive mixture. The curing exotherms for formulations with PEI<sub>91</sub>, although not shown in the figure, had similar appearance, without differences in the temperature of the maximum of the peak.



**Figure 2.** DSC scanning curves (top) and degree of conversion (bottom) against temperature of the curing of the neat and the modified formulations with 10% and 20% of the PEI<sub>79</sub> at a heating rate of 10°C/min.

**Table 3.** Calorimetric data of the curing of the different formulations studied

Formulation	$T_{peak}^a$ (°C)	$E_a^b$ (kJ/mol)	$k_{150°C} \cdot 10^{3c}$ (s <sup>-1</sup> )	$k_{100°C} \cdot 10^{3c}$ (s <sup>-1</sup> )	$\Delta h^d$ (J/g)	$\Delta h^e$ (kJ/ee)	$T_g^f$ (°C)
Neat	158	78.8	0.759	0.038	290	101	123
10% PEI <sub>91</sub>	158	75.7	0.659	0.036	291	106	110
20% PEI <sub>91</sub>	157	69.7	0.653	0.046	304	107	101
10% PEI <sub>78</sub>	159	72.3	0.582	0.037	304	111	117
20% PEI <sub>78</sub>	158	65.5	0.655	0.054	282	109	103

a Temperature of the maximum of the exothermic DSC curve

b Activation energy at 0.5 of conversion evaluated by isoconversional non-isothermal integral procedure.

c Rate constants at 150°C and 100°C calculated using the 2nd order autocatalytic kinetic model with  $n=1.6$ , determined using eq (3) and the Arrhenius expression for the kinetic constant  $k=A \cdot \exp(-E/R \cdot T)$ .

d Reaction heat per gram determined by DSC.

e Reaction heat per epoxy equivalent determined by DSC.

f Glass transition temperature of thermosetting samples prepared for DMTA analysis

The calculated activation energy decreases proportionally to the amount of PEI in the formulation, being the lower the one calculated for the curing of the formulation containing 20% of PEI<sub>78</sub>. Following the procedure described in a previous paper [18], we determined the constant rates of the curing processes at 150 °C and observed that the addition of PEI modifier retarded the curing. At 100 °C, the kinetic constants indicate that the curing process is only slightly retarded in the presence of 10 % of the PEI modifiers and even significantly accelerated when 20% of the modifiers are used. This change in trend is caused by the lowering of the overall activation energy when the PEI modifiers are used. Curing processes of epoxy-anhydride formulations are complex and involve a number of competitive reactions [26] that may have different temperature dependence. The remaining unreacted amine groups in the PEI modifiers may react with either epoxy or anhydride groups, leading to hydroxyl or carboxyl chain ends that can participate actively in the curing process and even have a catalytic effect [27,28].

We can see in Table 3 that the average reaction heat released per epoxy equivalent is around 100-110 kJ for all formulations and within the reported literature values for analogue epoxy-anhydride systems [29,30,31]. The addition of the PEI modifiers to the formulation slightly decreases the value of the  $T_g$  but temperatures higher than 100°C were determined for all the materials.

### 3.3 Rheological studies of the curing of the formulations

Gelation and vitrification processes are important phenomenological issues taking place during curing and processing of epoxy formulations. Gelation corresponds to the formation of a giant macromolecular structure that percolates the reaction medium. Then, the gel fraction extends and increases crosslinking as the curing advances leading to an insoluble, fully three-dimensional network at the end of the curing process. Macroscopically, a change from a liquid to a solid mass can be observed (the sample viscosity tends to infinite). The material ceases to flow and starts to build-up mechanical properties [22]. As a consequence, internal stresses can appear after gelation owing to curing shrinkage. The knowledge of the conversion and gelation time is also of the main importance from the processing point of view. Vitrification may occur if the  $T_g$  of the system equals and becomes higher than the reaction temperature, decreasing the mobility of the reactive species because of the reduction of the free volume. Thus, the curing dramatically slows down and the reaction stops, preventing the curing from reaching completion and producing materials with lower crosslinking density than expected. Therefore, vitrification should be surpassed in order to get complete cure by increasing the curing temperature above the  $T_g$  of the fully cured material. Rheometric monitoring of curing processes is a methodology used to determine accurately the gel point and vitrification because it is highly sensitive to the dramatic changes in the viscoelastic properties that occur [32,33,34].

The values of gelation and vitrification times and conversion at the gel point are collected in Table 4.

**Table 4.** Data obtained from rheometric monitoring of the curing of the formulations at 100 °C.

Formulation	$t_{gel}^a$ (min)	$x_{gel}^b$	$t_{vit}^c$ (min)
Neat	33	31	103
10% PEI <sub>91</sub>	32	40	90
20% PEI <sub>91</sub>	34	44	67
10% PEI <sub>78</sub>	31	43	100
20% PEI <sub>78</sub>	35	49	71

a. Gel time determined from the frequency independent crossover of  $\tan \delta$ .

b. Determined as the conversion reached by rheometry and DSC tests at 10°C/min.

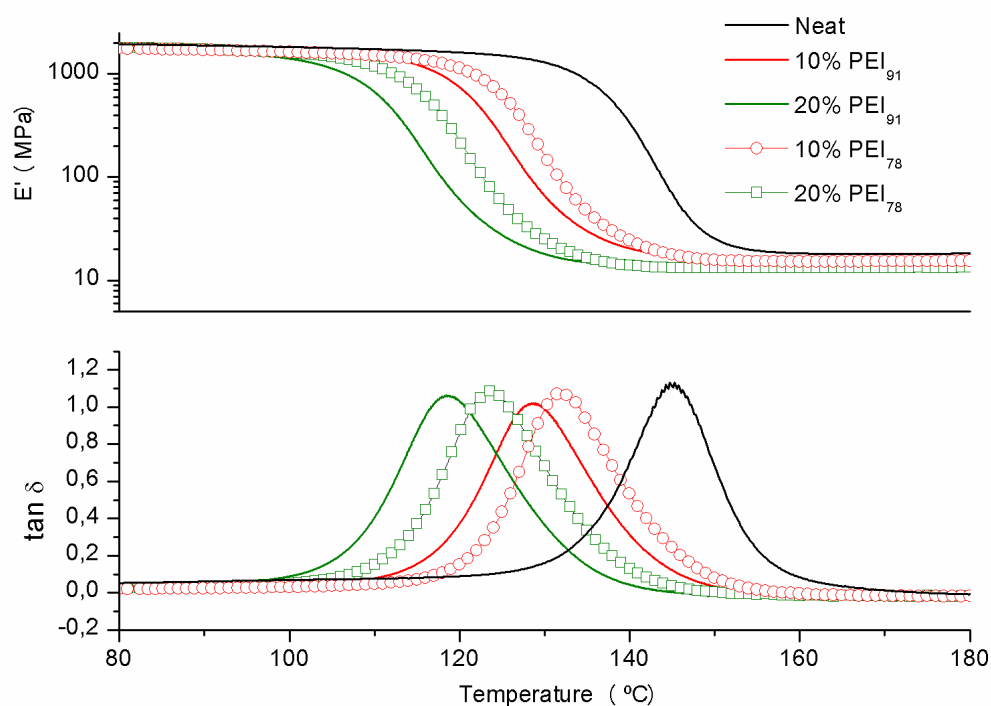
c. Vitrification time determined as the  $\tan \delta$  peak time at the frequency of 5 Hz.

1 As can be seen, there is a small effect of the addition on the gelation time. However,  
2 the conversion at gelation increases notably, and this should have a positive effect in  
3 terms of internal stresses because of the reduced curing shrinkage after gelation,  
4 assuming that curing shrinkage is proportional to conversion [35]. The conversion at  
5 gelation is higher than in the curing of DGEBA/MTHPA mixtures modified with  
6 poly( $\epsilon$ -caprolactone) multiarm stars [18] possibly due to the participation of unreacted  
7 amine groups of the modified PEI in the curing process. Thus, the higher the proportion  
8 of PEI in the formulation or the lower the modification degree, the higher the  
9 conversion at the gelation is. Because of the faster curing kinetics at 100 °C when PEI  
10 modifiers are added, gelation times are comparable in spite of the higher degree of  
11 conversion at the gel point.  
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21 On comparing the vitrification times of the formulations studied it can be seen that  
22 on increasing the proportion of modifier this value is reduced. Possibly the network  
23 build-up process during curing of the modified formulations is affected by the presence  
24 of the modified PEI, leading to a faster increase in the  $T_g$  of the curing formulation, but  
25 the trend is consistent with the overall positive effect of PEI modifiers on the curing  
26 kinetics at 100 °C, especially when a proportion of 20% is used.  
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### 32 *3.4 Thermal and thermomechanical properties of the thermosets obtained*

34 The thermosets prepared were studied by DMTA Figure 3 represents the  
35 mechanical spectra of the thermosets and the main parameters determined are collected  
36 in Table 5.  
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**Figure 3.** Storage modulus and  $\tan \delta$  against temperature at 1Hz for neat DGEBA and the thermosets containing different amounts of PEIs.

As we can see in the figure, the  $\tan \delta$  curves are unimodal as correspond to homogeneous material although relaxations corresponding to the PEI modifier added could appear under ambient temperature. On increasing the proportion of PEI modifier, the transitions are shifted toward lower temperature which indicates partial or total compatibility of the modifier with the epoxy network. On the other hand, on decreasing the degree of 10-undecenoyl modification in the PEI structure the decrease is reduced. This can be due to the plasticizing effect of the flexible 10-undecenoyl moieties of the PEI structure, which is predominant for PEI<sub>91</sub> formulations. However, this effect is not as evident in the modulus in the rubbery state, parameter which is more affected by the molecular weight between crosslinks, which does not change significantly.

**Table 5.** Thermomechanical and thermogravimetric data of the thermosets prepared

Formulation	DMTA		TGA	
	$T_{\tan\delta}$ <sup>a</sup> (°C)	$E_r$ <sup>c</sup> (MPa)	$T_{5\%}$ <sup>d</sup> (°C)	$T_{\max}$ <sup>e</sup> (°C)
Neat	146	20	348	401
10% PEI <sub>91</sub>	129	17	345	406
20% PEI <sub>91</sub>	119	14	328	401
10% PEI <sub>78</sub>	134	16	352	409
20% PEI <sub>78</sub>	123	14	326	393

a. Temperature of maximum of  $\tan \delta$ .

b. Storage modulus in the glassy state determined at 40°C.

c. Storage modulus in the rubbery state determined at  $\tan \delta$  peak + 50°C

d. Temperature of the onset decomposition on TGA data at 10°C/min calculated for a 5% weight loss.

e. Temperature of the maximum decomposition rate based on the TGA data at 10°C/min

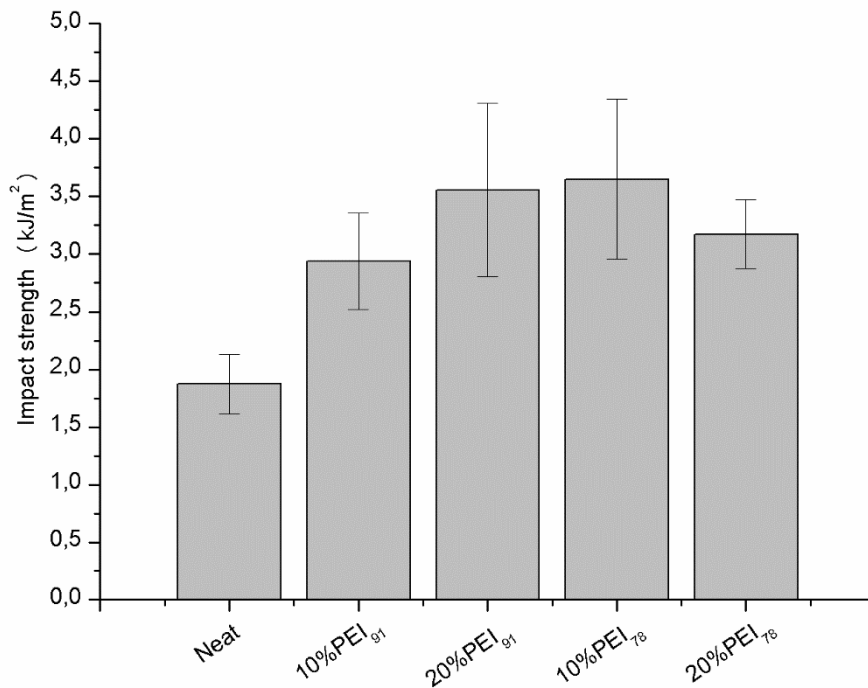
From the values of the table we can observe that the addition of the 10-undecenoyl modified PEI to the formulations reduces the temperature of the maximum of the  $\alpha$ -relaxation, as seen with DSC. The reduction in this temperature is more notable than in thermosets with 10-undecenoyl modified hyperbranched polyesters previously reported [17]. The highly flexible structure of the PEI core and the higher compatibility between the matrix and the modifier can explain the differences in the behavior.

The modified materials have a slightly lower modulus in the rubbery state than the neat thermoset, which indicates a less crosslinked network, due to the presence of the modifier. As discussed in the preceding sections, the remaining amine groups of the PEI modifier may react with epoxy and anhydride groups leading to species that can participate in the epoxy-anhydride curing mechanism and can catalyze the process. In previous works it was observed that the crosslinking density in epoxy-anhydride thermosets decreased upon addition of reactive hyperbranched [27]. This could be rationalized by the participation of the reactive hydroxyl groups of the hyperbranched modifier in the complex reaction mechanism during curing of epoxy-anhydride thermosets, in spite of the presence of internal branching points in the hyperbranched structure. It is hypothesized that the effect should be similar in the present case, especially taking into account the small number of available unmodified amine groups. The trend in crosslinking density and decrease in  $T_g$ , reflecting a loosening of the network structure, is also consistent with the increasing conversion at gelation upon addition of the modifiers.

1 The thermal stability of these materials was rated by thermogravimetry. The  
2 shape of the thermogravimetric curves was unimodal indicating a single degradative  
3 process or overlapping processes with comparable thermal dependence. From the values  
4 of the table we can state that a proportion of 10% of PEIs does not compromise the  
5 stability of the material, since the temperature of the initial degradation ( $T_{5\%}$ ) is  
6 maintained. However, this temperature is reduced on adding a 20% of the modifier in  
7 the formulation. The presence of 20% of PEI<sub>79</sub> in the material produces a reduction in  
8 the temperature of the maximum rate of degradation.  
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### 14 3.5 Mechanical characterization and morphology

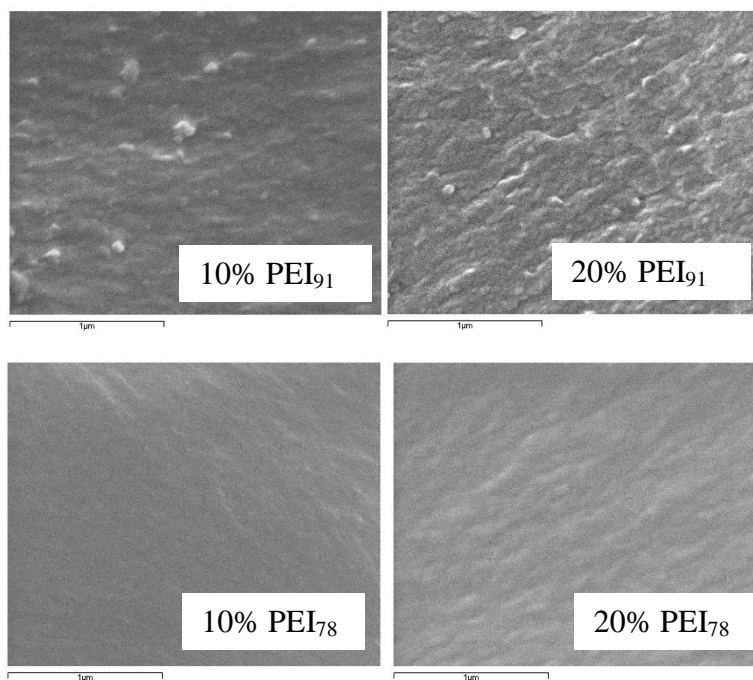
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17 Toughness is one the weakest properties of epoxy resins and for that reason a lot  
18 of efforts have been made to improve it. The addition of flexible structures in a  
19 thermoset helps to dissipate the energy of impact, increasing toughness. Thus, the  
20 structure of the modifiers studied in the present work, seems to be good candidates to  
21 dissipate impact energies, taking also into account that they can be mixed easily to  
22 prepare the DGEBA/MTHPA formulation and that  $T_g$ s are not much influenced by the  
23 addition of this modifier. As it can be seen in Figure 4, the addition of modified PEI  
24 improves the impact resistance of the resulting thermosets in comparison with the neat  
25 material.  
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**Figure 4.** Impact strength values for thermosets prepared

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In the case of using PEI<sub>91</sub> as modifier, on increasing its proportion impact resistance is improved. This fact can be explained in terms of the morphology of samples observed by SEM. The fracture surfaces after impact tests were investigated by this technique and all micrographs are shown in Figure 5. In the micrographs of the formulations with PEI<sub>91</sub> it can be observed the presence of a nanograined morphology more evident on increasing the proportion of modifier. When 10% of PEI<sub>78</sub> was used as modifier, the increase in impact strength was higher than with any proportion of PEI<sub>91</sub>, but further addition decreased the impact strength. The inspection of the impacted surfaces of these samples by SEM does not show any clear phase separation or nanograined morphology and both surfaces are quite smooth at this magnification.



**Figure 5.** SEM micrographs of the surface of fracture of the modified thermosets

From the surface inspection of all the samples, no clear phase separation was put in evidence, in contrast with our previous report on epoxy/anhydride thermosets modified with 10-undecenoyl terminated hyperbranched polyesters [17]. In that work, an increase in the impact resistance higher than 400% was achieved and it was explained by a cavitation mechanism, based in the phase separation and in the covalent linkage of the remaining hydroxyl terminal groups of the HBP to the epoxy matrix. As



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it has been commented, cavitation around rubber particles in combination with shear yielding in the matrix produces a cooperative effect in the energy dissipation. In the present study, improvements below 200% were reached and fracture mechanisms of *in situ* reinforcing or plasticization of the matrix can be considered as responsible. The higher reactivity of unreacted amine groups towards anhydrides and epoxy than hydroxyl groups and the lower molecular weight of the PEI structures in comparison to the modified polyesters can explain the final compatibility of PEIs with the epoxy matrix. Thus, PEI<sub>78</sub>, with a higher proportion of unreacted amines leads to the smoother surfaces observable in Figure 5. Although the modification of poly(ethyleneimine) with higher molecular weight (Lupasol WF<sup>®</sup>, 25000 g/mol) with 10-undecenoyl moieties was performed, there was a lack of compatibility with the DGEBA/MTHPA mixture that hindered the preparation of homogeneous samples to make mechanical and thermomechanical tests.

#### 4. Conclusions

Amine groups of poly(ethyleneimine) could be amidated by using a synthetic procedure consisting in the previous activation of 10-undecenoic acid with carbonyldiimidazole and further reaction of this derivative with PEI. However, the complete modification of all amine groups could be not achieved reaching a 91% of maximum modification degree. The degree of modification was determined by <sup>1</sup>H-NMR spectroscopy.

The curing kinetics was accelerated by the presence of the PEI modifiers at moderate curing temperatures. However, rheological measurements showed that gelation time was hardly affected because of the increasing degree of conversion at gelation. The addition of the PEI modifiers to the DGEBA/MTHPA formulation slightly decreased the value of *T<sub>g</sub>* but they were higher than 100°C for all the thermosets.

Thermosets containing modified PEI showed improved impact resistance in reference to the neat material. Nanograined morphology was observed by SEM for materials containing PEI<sub>91</sub>, whereas materials with PEI<sub>78</sub>, because of the chemical bonding of remaining amine groups to the epoxy matrix, showed a smoother surface of impact.

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