

# EFFECT OF A REACTIVE DILUENT ON THE CURING AND DYNAMOMECHANICAL PROPERTIES OF AN EPOXY-DIAMINE SYSTEM\*

Lisardo Núñez-Regueira<sup>†</sup>, M. Villanueva<sup>\*\*</sup> and I. Fraga-Rivas

Research Group TERBIPROMAT, Departamento de Física Aplicada, Universidade de Santiago de Compostela, Campus Sur, 15782 Santiago de Compostela, Spain

Differential scanning calorimetry was used to study the influence of an epoxy reactive diluent, vinylcyclohexane dioxide, on the curing reaction of a polymeric system composed of diglycidyl ether of bisphenol A ( $n=0$ ) and 1,2-diaminecyclohexane (DCH). Heat evolution and glass transition temperature, were measured in terms of the added diluent percentage. Experimental results show that both the curing degree and the glass transition temperature of the polymeric system decrease with an increase in the diluent percentage.

Dynamic mechanical analysis of several samples also showed that  $T_g$  decreases with the increase of diluent percentage, thus corroborating DSC measurements.

**Keywords:** DMA, DSC, epoxy-diamine system, glass transition temperature, reactive diluent

## Introduction

A key factor when formulating a coating is to achieve a viscosity that will permit proper coating application and flow. One of the components in a coating formulation is commonly an epoxy material. The ‘standard’ epoxy resin (DGEBA) has a very high viscosity that makes very difficult its application without any modification. One of the possible solutions is the introduction of a diluent. There are many different kinds of diluents, depending on their reactive or non-reactive nature. Within the reactive group, epoxy reactive diluents play an important role because owing to the epoxy groups of the diluent, the alteration of some important properties of the original system (such as conversion, glass transition temperature, lifetime...) will not be as affected as they are with the introduction of a non epoxy diluent. Epoxy-based reactive diluents can participate, together with a resin and a curing agent, in polymerization and crosslinking reactions thus permitting the diluent to become chemically bound into the cross-linked network. The extent to which properties are reduced is a function of both diluent type and concentration. In an attempt to preserve physico-mechanical properties at elevated temperatures, the use of a polyfunctional epoxy diluent was considered [1, 2].

The objective of this work was to study the curing of the neat system DGEBA ( $n=0$ )/1,2-DCH modified with different concentrations of the multifunctional epoxy reactive diluent vinylcyclohexane dioxide (named hereafter as VCHD). In previous works, the influence of this reactive diluent on the thermal stability of the DGEBA ( $n=0$ )/1,2-DCH system was studied [3].

## Experimental

### Materials

The epoxy resin was a commercial DGEBA ( $n=0$ ) (Resin 332, Sigma Chemical Co., San Louis, USA) with an equivalent molecular mass of 173.6 g/eq, as determined by wet analysis [4, 5]. The curing agent was 1,2-DCH (Fluka, Switzerland) with an amine hydrogen equivalent mass of 28.5. The epoxy reactive diluent was VCHD (Fluka, Switzerland).

### Sample preparation

For calorimetric experiments, epoxy resin and reactive diluent were carefully and homogeneously mixed, at different proportions of 5, 10, 15, 20, 25 and 30% in mass of the total mass of the original system (epoxy, diamine), before being added an amount of curing agent which corresponds to the stoichiometric amount for the system DGEBA/1,2-DCH. The order of mixing was to prevent the start of reaction before the addition of the three components. In every case bulk samples of 200 mg were prepared. The experiments were carried out using 4–6 mg in size samples that were taken from these bulk samples, that were sealed in pans, using a press, before introducing them into the calorimeter.

For DMA studies, similar samples were introduced in a cylindrical frame. The curing reaction was programmed according to a TTT diagram calculated for the system DGEBA/1,2-DCH [6]. It consists of two stages: a first step of 24 h at 23°C and a second one of 16 h at 70°C in an oven. After curing, the sam-

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\*\* Author for correspondence: famariav@usc.es

ples were removed from the frame and cut in the form of 15–25 mg in mass and 6 mm in diameter discs and 20 mm in length.

### Methods

#### Calorimetric analysis (DSC)

Experimental data reported in this work were obtained from DSC studies using a PerkinElmer DSC-7 unit under the control of a 1020 system controller. The calorimeter was employed to measure the heat evolved during the curing reaction (first scan of samples) and final glass transition temperatures (second scan of samples).

DSC experiments were carried out in the dynamic mode, in a temperature range from  $-40$  to  $250^{\circ}\text{C}$ , at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . Owing to the low temperature necessary for the performance of measurements, a cooling device (Intercooler II supplied by PerkinElmer) was adapted to the DSC-7 equipment. The calorimeter was calibrated following the procedure given in the PerkinElmer DSC-7 Manual [7]. Two standards, indium and bidistilled water obtained by the Millipore method (Millipore, Bedford, MA), were used.

#### Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured using a PerkinElmer DMA-7 operated in the three-point-bending horizontal measuring system. The DMA equipment was calibrated using indium as a standard. Experiments were conducted in a temperature range from  $30$  to  $250^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . Experimental conditions were: dynamic force ( $700$  mN), static force ( $750$  mN), and heating rate ( $10^{\circ}\text{C min}^{-1}$ ). The frequency value used in all the experiments was  $1$  Hz.

## Results and discussion

### Calorimetric analysis (DSC)

Table 1 shows the heat evolved during the dynamic cure reaction of the system DGEBA ( $n=0$ )/1,2-DCH with different percentages of diluent. This heat was calculated as the area of the peak, and is related to the energy evolved during cure. It can be seen that the curing heat decreases with the increase of diluent. As it is known, DSC technique is very useful to check the differences introduced through very small changes in the composition of an epoxy system [8, 9]. Taking the curing heat value for the system without diluent (named as neat system or 0% VCHD) as a reference and assuming a 100% final conversion for this system, relative changes in the final conversion of the different systems respect to the conversion value of the neat system were

**Table 1** Values corresponding to the different percentages of diluent in the DGEBA ( $n=0$ )/1,2-DCH

VCHD/%	$\Delta H/\text{J g}^{-1}$	$\Delta\alpha/\%$	$T_g/^{\circ}\text{C}$	$\Delta T_g/\%$
0	-414	–	131.9	–
5	-404	-2.42	132.7	0.6
10	-385	-7.00	124.8	-5.4
15	-366	-11.59	125.3	-5.0
20	-340	-17.87	112.9	-14.4
25	-323	-21.98	109.0	-17.4
30	-261	-36.96	95.3	-27.7

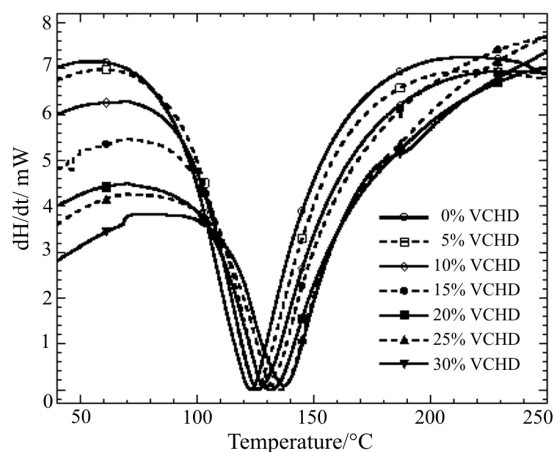
obtained. These values are also shown in Table 1. Obviously, a similar trend as that observed for the heating values was detected. The decrease in the final conversion was not important for the systems with concentrations up to 15%, but beyond this percentage of diluent, conversion decreased considerably, being 37% lower for the system with 30% of diluent.

From second DSC scans, glass transition temperatures were calculated as the inflection point of the DSC curves. Values for the different systems are shown in Table 1. The values of  $T_g$  were not very affected when the percentages of diluent were lower than 15% (relative differences respect to the neat system are 5.4% or less), but for systems with 20–30% of diluent, the values of  $T_g$  decreased in a range between 19 and  $37^{\circ}\text{C}$ , corresponding to a 14–28% of change respectively. Therefore, it can be concluded that the introduction of the reactive diluent does not affect considerably the final conversion and glass transition temperature values if the percentage of diluent is lower than 15%, but beyond this concentration, appreciable and not desired decreases in these properties were observed.

Figure 1 shows the curves obtained from the dynamic experiments carried out with samples of different concentrations of diluent. Table 2 shows the temperature values corresponding to the onset and peak of first DSC scans. From this table and Fig. 1, it can be seen that increasing the percentage of diluent shifts the beginning and also the peak of the cure reaction to higher temperatures. As in the case of  $T_g$  and  $\Delta H$  values, this change is more pronounced for systems with contents of diluent

**Table 2** Onset and peak temperatures of DSC dynamic curing experiments for different reactive diluent contents

VCHD/%	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$
0	91.67	122.58
5	95.72	125.25
10	95.99	125.92
15	101.9	128.61
20	103.17	132.28
25	107.48	135.96
30	114.12	137.33



**Fig. 1** DSC curves from dynamic experiments of the system DGEBA ( $n=0$ )/1,2-DCH with different concentration of reactive diluent

higher than 15%. The reason can be that the plasticizer effect is not too strong at low concentrations of reactive diluent, but beyond a critical value the extension of linear chains during the initial step of curing provokes that the heat detection starts later and that the final conversion and the  $T_g$  are lower. An increase in the percentage of diluent can be considered as a decrease in the curing agent (diamine) ratio (or an epoxy excess) because of the two epoxy groups introduced through the addition of diluent that have not been compensated with an additional amount of diamine. So, as the concentration of diluent increases, the shortage of diamine increases. The later detection of heat during dynamic cure can be due to the fact that, as the percentage of diluent increases, there are less activated molecules to begin the reaction, shifting the peak to higher temperatures. For this reason, it is necessary to reach a higher temperature to activate the reaction (higher activation energy). The shortage of curing agent is also the responsible for the decrease of the maximum conversion attained during these dynamic experiments. This same reasoning was reported by some other authors for similar systems [10]. A decrease on  $T_g$  values was also observed by other authors using non-stoichiometric mixtures of epoxy systems [11].

#### Dynamic mechanical analysis (DMA)

In dynamic mechanical analysis [12] samples were under a variable sinusoidal stress of frequency  $\omega$ . For a viscoelastic material the resulting strain is also sinusoidal but out of phase with stress an angle  $\delta$  because of the energy dissipated as heat. Young's modulus is defined as the quotient between the applied stress and the resulting strain per unit length. It is usually convenient to express the sinusoidal varying stress as a complex quantity. Then, Young's modulus is also complex, the real part is named the storage modulus  $E'$ , and the imaginary part is the loss modulus  $E''$ :

$$\frac{\sigma(t)}{\varepsilon(t)} = E^* = E' + iE'' \quad (1)$$

The quotient  $E''/E'$  is termed the loss tangent ( $\tan\delta$ ), which is the ratio of the energy dissipated per cycle to the maximum potential energy stored during a cycle:

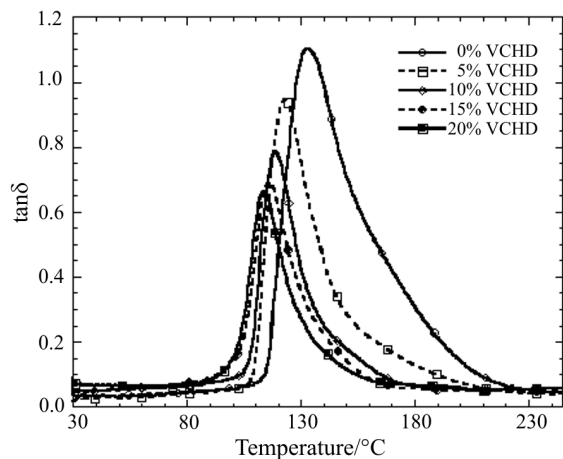
$$\tan\delta = \frac{E''}{E'} \quad (2)$$

For a DMA study,  $T_g$  can be taken a) as that corresponding to the maximum of the curve  $\tan\delta$  vs. temperature, b) as the midpoint corresponding to  $\log E'$  transition, c) as the intersect of the tangents to  $\log E'$  curve before the transition and the decrease characterizing the transition.

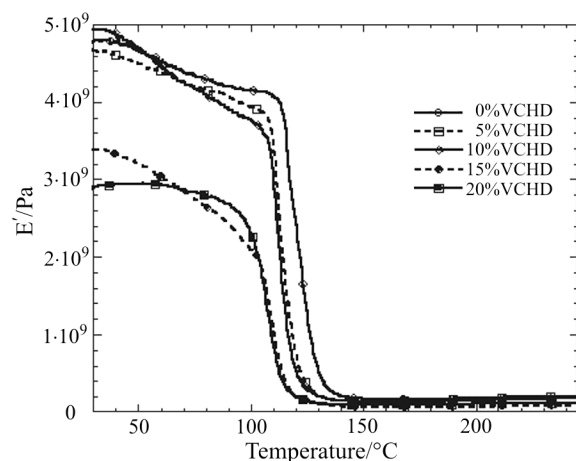
Several authors have studied the characteristics of the different assignments of the glass transition temperature. The most commonly used is that corresponding to the peak in a  $\tan\delta$  vs.  $T$  plot, but it is also taken as the peak temperature in a  $E''$  vs.  $T$  plot; however, this temperature is 20–30°C lower than that corresponding to the  $\tan\delta$  peak. This last temperature is very close to that of the  $E'$  inflection point decrease, while the temperature of the  $E''$  peak is closer to that based on the intersect of the tangents criterion [13]. In this work the first criterion mentioned above was used to determine  $T_g$  value.

Figures 2a to c show DMA curves ( $\tan\delta$ , storage modulus  $E'$  and loss modulus  $E''$ , respectively) obtained during first scans for the systems DGEBA–1,2-DCH and DGEBA–1,2-DCH–VCHD with concentrations in mass of reactive diluent 5, 10, 15 and 20%. Values corresponding to higher percentages were not measured because at higher concentrations of diluent, samples were extremely stiff and cracked and even broke during the experiment, being the analysis impossible.

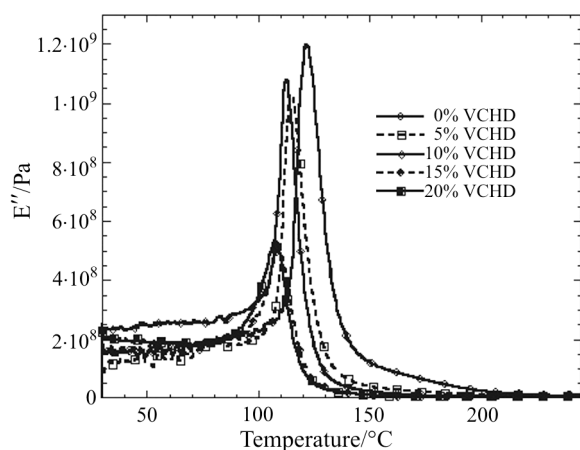
From Fig. 2a it can be observed that the  $\tan\delta$  peak shifts to lower temperatures as the concentration of diluent increases. This is in concordance with the behaviour observed in calorimetric analysis and with the expected plasticizing effect [12, 15]. In Table 3 the glass transition temperatures obtained from the peak of  $\tan\delta$  are shown. The diluent acts as a plasticizer because it enlarges the linear chains, thus reducing the energy necessary to cause rotations around molecular bonds, and because of this, originating a glass transition shift to lower temperatures. From the first scans, it can be observed a decrease in  $T_g$  as the diluent content increases. This decrease is more pronounced with the  $T_g$  values obtained from second scans, as it can be seen in Table 3. It can also be observed that the increase in second  $T_g$  values respect to first scans is higher for low contents in reactive diluent. The lack of diamine does not permit a



**Fig. 2a**  $\tan\delta$  curves from DMA experiments for the system DGEBA ( $n=0$ )/1,2-DCH with different reactive diluent content



**Fig. 2b** Curves  $E'$ - $T$  recorded from DMA experiments carried out on the system DGEBA ( $n=0$ )/1,2-DCH with different reactive diluent content



**Fig. 2c** Curves  $E''$ - $T$  recorded from DMA experiments carried out on the system DGEBA ( $n=0$ )/1,2-DCH with different reactive diluent content

**Table 3**  $T_g$  values calculated from  $\tan\delta$  curves of first and second DMA scans

VCHD/%	$T_g/^\circ\text{C}$	
	1 <sup>st</sup> DMA scan	2 <sup>nd</sup> DMA scan
0	132.6	192.3
5	124.2	183.8
10	122.8	157.3
15	116.0	130.5
20	113.7	125.6

complete postcure, even with a second scan; therefore the increase in  $T_g$  values respect to first scan diminishes as the reactive diluent content increases. As the percentage of VCHD decreases,  $T_g$  final values approaches to the  $T_g$  values corresponding to the neat system (system without diluent) obtained through DMA and DSC techniques.

From Fig. 2a it can be observed that not only the glass transition temperature, but also the peak intensity, decreases with the reactive diluent content. According to Matsuoka [16], an increase in the number of crosslinking points causes: (1) a decrease of the chain mobility, (2) a loss of a certain amount of free volume, and (3) an increase in  $T_g$ . The greater the motion associated with the transition, the greater the intensity of  $\tan\delta$  peaks. Because of this, the epoxy groups not reacting can restrict the molecular motion, caused by an increase in the diluent content, thus causing a decrease in the  $\tan\delta$  peak intensity.

In Table 4 values of the area under  $\tan\delta$  vs.  $T$  curves for different contents of reactive diluent are shown. As it can be seen, this area decreases with an increase in the diluent content, that causes an increase in damping. This decrease in the peak implies a greater energy absorption by the material.

From Fig. 2b, it can be seen that the storage modulus presents 3 different transition zones. At VCHD contents in the range 15–20%, the glass transition takes place at short times that increase in the range 5–10% and later for the neat system (0% VCHD). In the glassy region, the storage modulus of the system containing 5–10% slightly decreases, while the decrease is more pronounced for the system

**Table 4** Area values of the  $\tan\delta$  vs.  $T$  curves recorded from DMA experiments at different reactive diluent content

VCHD/%	Tan $\delta$	
	1 <sup>st</sup> scan area	2 <sup>nd</sup> scan area
0	45.55	17.85
5	28.26	15.42
10	17.03	15.19
15	13.76	15.54
20	13.37	12.97

with 15–20% VCHD. This means that the energy stored during the strain cycle is practically constant for low values of diluent. In the elastic region, the lowest  $E'$  values correspond to the systems with high diluent content, as it was expected to happen with a plasticizer. In this way, high content of diluent makes the system to store less energy per cycle, what means that the system shows less recovery before strain, being this effect more significant for systems with high content in diluent.

In Figs 3a to e,  $\tan\delta$  curves corresponding to first and second scan for the different studied systems are shown. As it can be seen, second scans give smaller area peaks. The broadness of the peaks depends on the % considered. For the neat, 5 and 10% VCHD systems, second scans gave narrower  $\tan\delta$  peaks, corresponding this feature to a postcuring effect [17]. But for 15 and 20% VCHD systems,  $\tan\delta$  peaks of second scans are broader than those of first scans, and present small shoulders. This characteristic can be associated to an incomplete curing and also to a non-homogeneous network. This can be possible because of the defect of

diamine. At high diluent contents, many of the epoxy groups do not react, even with a second scan, because there is no enough diamine. It is also possible the presence of different regions with different conversions or degree of entanglement. This can explain the broader

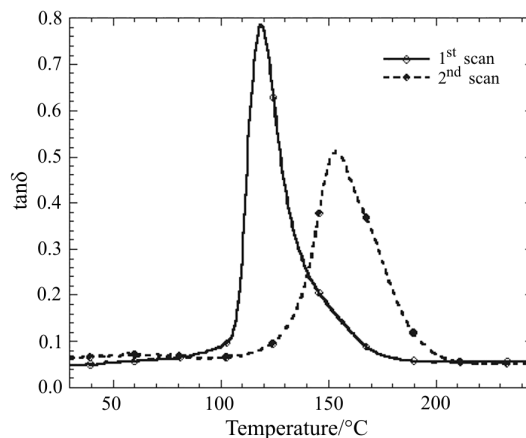


Fig. 3c  $\tan\delta$  vs.  $T$  curves recorded for the first and second scan performed on the 10% VCHD system

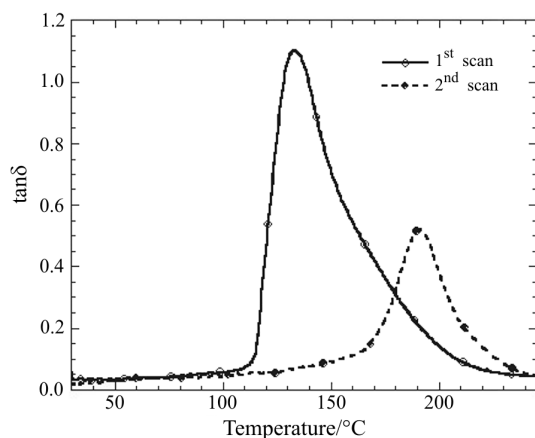


Fig. 3a  $\tan\delta$  vs.  $T$  curves recorded for the first and second scan performed on the neat system

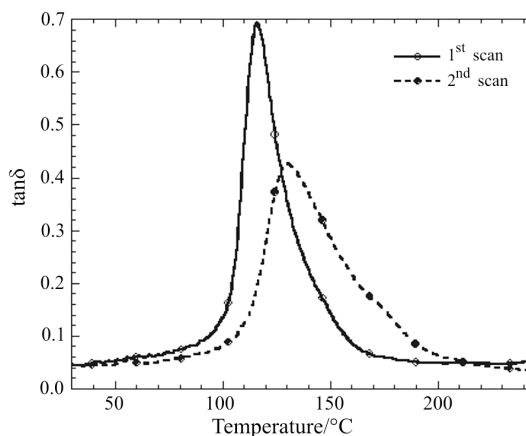


Fig. 3d  $\tan\delta$  vs.  $T$  curves recorded for the first and second scan performed on the 15% VCHD system

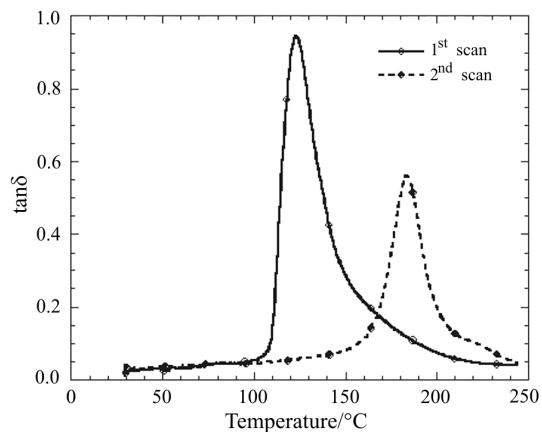


Fig. 3b  $\tan\delta$  vs.  $T$  curves recorded for the first and second scan performed on the 5% VCHD system

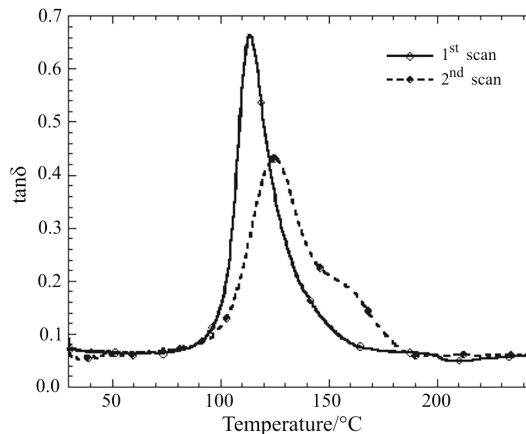


Fig. 3e  $\tan\delta$  vs.  $T$  curves recorded for the first and second scan performed on the 20% VCHD system

peak corresponding to a broader glass transition region (there is not only one glass transition temperature but also an interval of temperatures associated to the different crosslinked regions). It can also be observed that second  $\tan\delta$  curves give for all diluent percentages, peaks with lower intensities than first scans. This can be associated with an increase of the extent of curing during the first scan [18].

As a comment, it can be mentioned the poor mechanical resistance of the samples containing 20% of reactive diluent, as some of them get broken during DMA experiments.

## Conclusions

The influence of the addition of an epoxy reactive diluent on the curing and dynamomechanical properties of the epoxy system DGEBA ( $n=0$ )/1,2-DCH have been studied.

From the first DSC scans of the uncured samples, a shift to higher temperatures of the curing peaks as the reactive diluent concentration increased was observed. This behaviour was attributed to the higher activation energy associated to the curing reaction. Maximum conversion values decreased with an increasing RD content.

From the second DSC scan, a decrease in  $T_g$  values with an increase of the diluent content was detected. Nevertheless, low diluent contents do not affect considerably the dynamic curing of the system.

A similar behaviour for  $T_g$  values was observed from DMA experiments carried out on samples cured following a sequence selected from a *TTT* diagram constructed for the neat system. Owing to a shortage in the diamine content respect to the stoichiometric ratio, increasing the diluent content implies a non-complete curing, even after a second DMA scan. There is also evidence of regions with different crosslinking degrees in the  $\tan\delta$  peaks. Second scans of samples at high diluent contents gave broader and even with shoulders  $\tan\delta$  peaks. Differences between  $T_g$  values corresponding to first and second scans increased with an increase in the diluent content, being these differences appreciable for systems with 15 and 20% of diluent. The storage modulus decrease as the reactive diluent content increases, as it was expected.

It can be concluded that the effect of addition of the reactive diluent selected is not important at low

concentration values (below 15%) but beyond 15%, very important properties as  $T_g$ , degree of crosslinking, storage modulus... are seriously affected. This means that the reactive diluent here studied can be used up to 15% concentrations but not beyond this value.

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