

INFLUENCE OF THE THERMAL DEGRADATION ON THE DIELECTRIC PROPERTIES OF A THERMOSET*

Lisardo Núñez-Regueira[†], M. Villanueva^{**}, I. Fraga, C. A. Gracia-Fernández and S. Gómez-Barreiro

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

The thermal degradation of an epoxy system consisting of a diglycidyl ether of bisphenol A (DGEBA, $n=0$) and *m*-xylylenediamine (*m*-XDA) was studied by both thermogravimetric analysis (TG) and dielectric analysis (DEA). It has been checked a deviation of the typical behaviour in the Arrhenius plot expected for this kind of systems, owing to the thermal degradation.

Both, structural relaxation time and conductivity values, were represented as a function of the mass loss, that allow a relationship to be obtained between characteristic relaxation time and the degree of degradation at the beginning of the degradation process.

Keywords: DEA, DMA, TG, thermal degradation, thermoset

Introduction

Thermosets, and among them those originated from epoxy resins, have been widely studied both during curing and after being cured.

Moreover, due to the great number of different applications of this kind of materials, the study of their behaviour at high temperatures became a first order question [1–4].

Different Thermosets systems were previously studied in our laboratories [5–8]. One of these systems is DGEBA($n=0$)/*m*-XDA for which kinetic and lifetime studies were performed.

In the present paper, the influence of thermal degradation on the dielectric properties is reported.

Theoretical background

Dielectric Analysis (DEA) measures changes in the properties of a material as a response to the application on it of a time dependent electric field. This thermal analysis technique is a perfect complement to the other different techniques of thermal analysis [9] by identifying the transitions from the changes in the electrical properties of the materials.

An advantage of DEA over other techniques is the possibility of using a wider frequency range. Moreover, dielectric measurements are extremely sensitive to small changes in material properties. This enables detection of transitions which would not be possible through other techniques. Particularly, DEA complements DMA for characterization of the inter-

nal motions in polymers [10, 11]. Both techniques can detect many viscoelastic relaxations with the same relationship between frequency and temperature. However, DEA tends to be more sensitive to local motions that involve the reorientation of dipoles in a material as it is subjected to an oscillating electric field.

The complex dielectric constant of a material can be separated into its real and imaginary parts:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad (1)$$

where ε' is the relative permittivity (real) and ε'' is the relative loss factor (imaginary). Both are related to ε_0 the permittivity of the free space (equal to $8.85 \cdot 10^{12} \text{ F m}^{-1}$) and are functions of the measurement frequency. The ratio $\varepsilon''/\varepsilon'$ is known as the dissipation or loss tangent:

$$\tan\delta = \varepsilon''/\varepsilon' \quad (2)$$

where δ is the phase angle between the applied voltage and the current response.

As it was previously mentioned [12–17], when a sample is subjected to an applied electric field the dipoles in the material tends to orient in the direction of the electric field. The orientation process requires a characteristic time, called the dipole relaxation time and denoted by τ_d .

Experimental

Materials

Epoxy resin was diglycidyl ether of bisphenol A $n=0$, DGEBA ($n=0$), (Resin 332, Sigma Chemical Co., St. Louis, MO) with an epoxy equivalent between 172

* Presented at MEDICTA Conference 2005, Thessaloniki, peer reviewed paper.

** Author for correspondence: famariav@usc.es

and 176. Curing agent was metaxylylene diamine (*m*-XDA) (Fluka, Switzerland) 98%.

Both were used as received. Resin and diamine were carefully and homogeneously mixed at stoichiometry ratio 100:16.42. Once mixed, the sample was introduced into a frame to cure. The frame consisted of two steel plates covered by two smooth Teflon sheets and a Teflon pattern with 20 holes of 2.5·2.5 cm and 0.5 cm thick.

Curing of the systems was achieved according to a *TTT* diagram previously designed [18] for this epoxy system consisting of two steps: 20 min at 40°C followed by 2 h and 28 min at 200°C.

Methods

Dielectric analysis

Dielectric measurements were carried out using a dielectric analyser DEA 2970 from TA Instruments. The measurements assembly was the parallel plate structure.

The sensors must be calibrated for every experiment. These sensors use a geometrical value derived from the response of the electrode plate surface in mm², and value of the platinum resistance temperature detector (RTD) corresponding to the resistance at 0°C observed by the platinum thermometer in the base sensor.

The sample was under a maximum load of 250 N, to ensure a good contact between the sample and the electrodes below T_g , and the heating rate was 2°C min⁻¹. The minimum space between the top and the bottom electrodes was, according to the manual book and the maximum force, 0.501 mm, to prevent soft samples from being squeezed out of the sensor area during an experiment. All the experiments were carried out under a dry nitrogen atmosphere at a gas flow rate of 0.5 mL min⁻¹.

Thermogravimetric analysis

Thermogravimetric measurements were made using a Thermogravimetric Analyzer (TGA 7) from Perkin-Elmer controlled by a 1020 computer. All the experiments were carried under a dry nitrogen atmosphere. The heating rate used was 2°C min⁻¹.

Results and discussion

Thermogravimetric experiments

A thermogravimetric study was carried out in the temperature range from 30 to 350°C at a heating rate of 2°C min⁻¹. This same heating rate was used for dielectric and dynamic mechanical studies with the objective of making the comparisons easier.

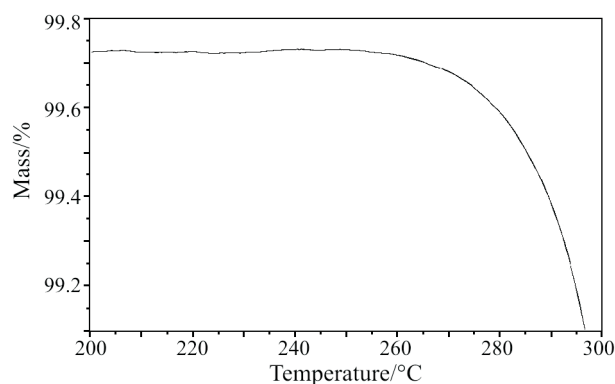


Fig. 1 TG curve corresponding to the cure of DGEBA ($n=0$)/*m*-XDA system (temperature range 200–300°C)

As dielectric measurements are very sensitive to sample changes, it is important to determine accurately the beginning of degradation. With this aim, only a temperature range from 200 to 300°C was selected from the whole experimental temperature range. This selection is shown in Fig. 1.

It can be observed that the system starts degradation between 250 and 270°C and, because of this, its composition changes.

Dielectric measurements

Dipole relaxation and ionic conductivity were followed by DEA. The experiments were carried out at a heating rate of 2°C min⁻¹. The frequency range was from 5·10⁻¹ to 10⁵ Hz and the upper temperature limit was 330°C. This limit was chosen because at temperatures above 330°C, the volatile products originated from degradation during the dielectric experiments could damage the equipment.

Figures 2a–c correspond to ϵ' – T and ϵ'' – T plots at different frequencies in the range from 5·10⁻¹ to 10⁵ Hz. The plot ϵ'' – T was divided in two parts to improve visualization of the experimental curves.

Figure 2a shows that around 240°C, low frequency permittivity undergoes a significant increase. This could be originated by electrode polarization. However, a subsequent decrease in ϵ' at about 300°C suggests the possibility of degradation of the material. Figures 2b and 2c show a decrease in ϵ'' at same high temperatures. Figure 2b shows also an increase in ϵ'' at temperatures above that corresponding to the peak of the dipole relaxation, that will be discussed further on.

Table 1 lists values of T_α (as the maximum in the ϵ'' vs. T curves), at different frequencies.

Figure 3 is an Arrhenius plot of the data recorded in this table, where ω is the angular frequency and T the temperature.

As it can be observed in Fig. 3, at low temperatures relaxation follows a Vogel type behaviour. As

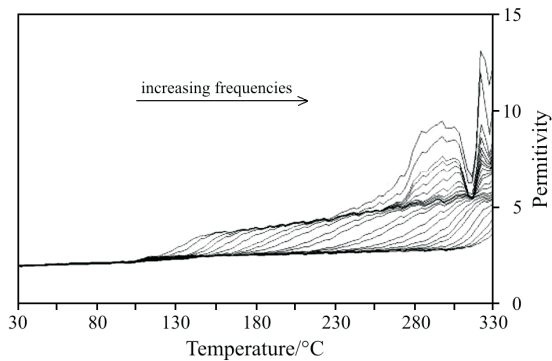


Fig. 2a ϵ' vs. T at different frequencies for the DGEBA ($n=0$)/ m -XDA system (dynamic experiment)

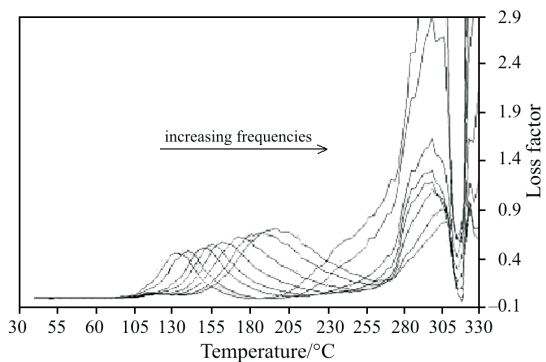


Fig. 2b ϵ'' vs. T at frequencies $5 \cdot 10^{-1}$, $1 \cdot 10^0$, $3 \cdot 10^0$, $5 \cdot 10^0$, $1 \cdot 10^1$, $2 \cdot 10^1$, $4 \cdot 10^1$ and $6 \cdot 10^1$ Hz for the DGEBA ($n=0$)/ m -XDA (dynamic experiment)

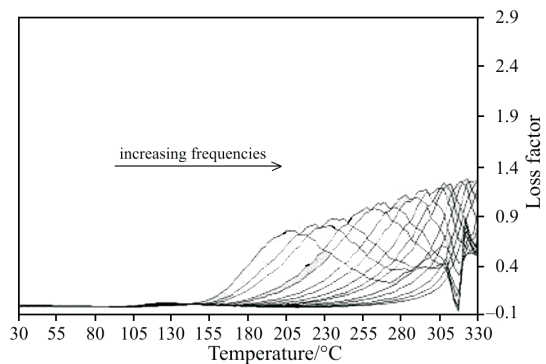


Fig. 2c ϵ'' vs. T at frequencies $1 \cdot 10^2$, $2 \cdot 10^2$, $3 \cdot 10^2$, $7 \cdot 10^2$, $1 \cdot 10^3$, $2 \cdot 10^3$, $5 \cdot 10^3$, $7.5 \cdot 10^3$, $1 \cdot 10^4$, $2 \cdot 10^4$, $5 \cdot 10^4$, $7 \cdot 10^4$ and $1 \cdot 10^5$ Hz for the DGEBA ($n=0$)/ m -XDA system (dynamic experiment)

the temperature increases, the plot becomes a straight line in accordance with an Arrhenius-like behaviour. This behaviour [19] is typical of thermosets. However, at higher temperatures, $\ln\omega$ increases considerably. This involves a significant decrease in molecular dipolar relaxation times. In other words, the response time of dipoles to the applied field decreases significantly by cause of a decrease in the restrictions

Table 1 Values of T_α at different frequencies for the system DGEBA ($n=0$)/ m -XDA

Frequency/Hz	$T_\alpha/^\circ\text{C}$
$1 \cdot 10^0$	134.33
$2 \cdot 10^0$	139.84
$6 \cdot 10^0$	148.00
$1 \cdot 10^1$	153.33
$2 \cdot 10^1$	164.40
$4 \cdot 10^1$	175.20
$8 \cdot 10^1$	186.02
$1.2 \cdot 10^2$	194.21
$2 \cdot 10^2$	207.66
$4 \cdot 10^2$	229.28
$6 \cdot 10^2$	237.38
$1.4 \cdot 10^3$	260.01
$2 \cdot 10^3$	269.55
$4 \cdot 10^3$	285.87
$6 \cdot 10^3$	293.82
$1 \cdot 10^4$	301.87
$1.5 \cdot 10^4$	307.96
$2 \cdot 10^4$	310.00
$4 \cdot 10^4$	318.19
$6 \cdot 10^4$	323.71
$1 \cdot 10^5$	326.61

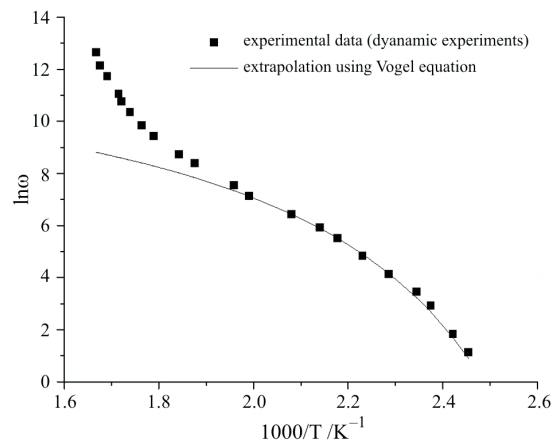


Fig. 3 Arrhenius plot of the DGEBA ($n=0$)/ m -XDA epoxy system and the extrapolation to Vogel equation

imposed on their mobility as a consequence of inter-molecular bond breaking.

The increase in $\ln\omega$ begins at approximately 260°C , a temperature within the temperature range previously reported for mass loss, thus corroborating the hypothesis of degradation.

We can check this anomalous behaviour of the Arrhenius plot by representing the data, at low temperatures, of the dynamic experiments and their ex-

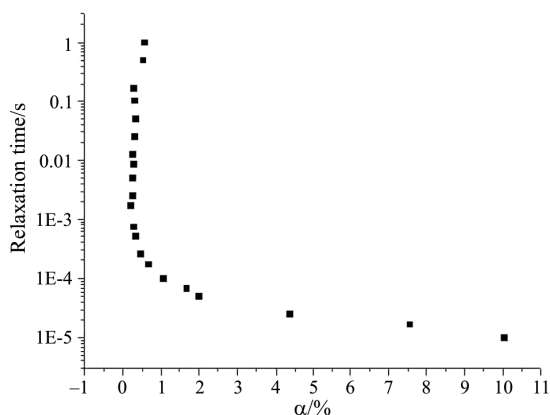


Fig. 4 Characteristic relaxation time as a function of the degree of degradation

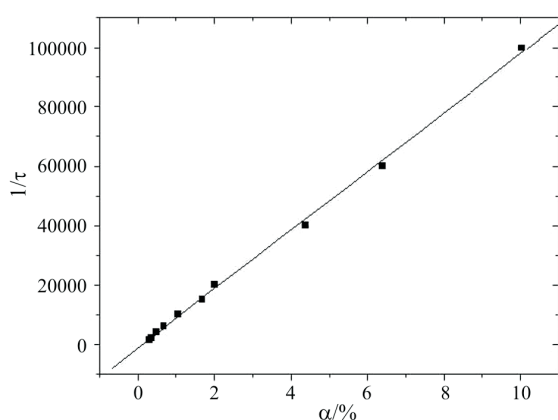


Fig. 5 $1/\tau$ vs. α plot corresponding to the early stages of degradation for the DGEBA ($n=0$)/ m -XDA system

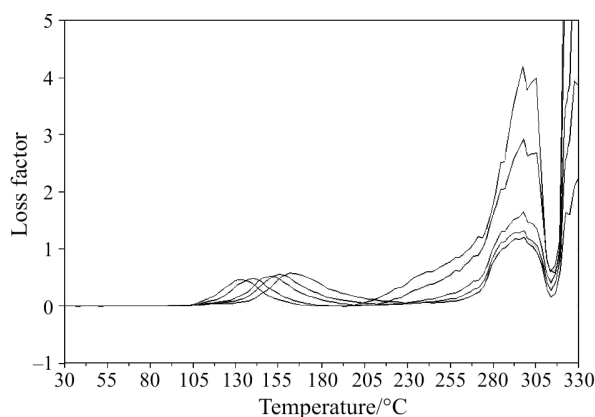


Fig. 6 ϵ'' vs. T for the DGEBA ($n=0$)/ m -XDA cured system at $5 \cdot 10^{-1}$, $1 \cdot 10^0$, $3 \cdot 10^0$, $5 \cdot 10^0$ and $1 \cdot 10^1$ Hz (dynamic experiment)

trapolation at high temperatures using the Vogel equation [13] (Fig. 3).

The knowledge of both relaxation time and mass loss as function of temperature allows the plotting of the relaxation time, τ , as function of degree of degradation α . This degree of degradation is defined as $\alpha=100 \text{ mass}\%$ where w is the actual mass per cent (Fig. 4).

As it can be seen in Fig. 4, the relaxation time for degradation is in the range from 10^{-3} to 10^{-5} s.

Considering only the temperature zone where degradation takes place, that is, above 270°C , a plot of $1/\tau$ vs. α can be defined as it is shown in Fig. 5.

From Fig. 5 it can also be observed that the inverse relaxation times vs. degradation degree values show a linear behaviour (regression coefficient R better than 0.992). This behaviour can be expressed as:

$$\tau = K/\alpha \text{ with } K=0.00017$$

Study of ionic conductivity

Figure 6 shows the dynamic experiment previously reported but only at frequencies of $5 \cdot 10^{-1}$, $1 \cdot 10^0$, $3 \cdot 10^0$, $5 \cdot 10^0$ and $1 \cdot 10^1$ Hz.

It can be observed that ϵ'' increases again after the dipole peak at a temperature of 200°C approximately. This increase is caused by the contribution of ionic conductivity to ϵ'' .

To obtain ionic conductivity [19], ϵ'' was represented vs. $\log f$. Figure 7 is one of these plots corresponding to a dynamic experiment in the temperature range from 204 to 332°C .

It can be seen in Fig. 7 that the maximum of the α -relaxation curve shifts to higher frequencies with increasing temperature. It can be observed also the appearance of a second peak at a temperature of 270°C approximately. The peaks are 2–3 decades below those corresponding to the α -relaxation and also shift to higher frequencies with the increase in temperature. Einfeldt *et al.* [20] associate this peak to electrode polarization. However, during the degradation process, a partial vitrification [21], accompanied of the corresponding dielectric relaxation associated, takes place.

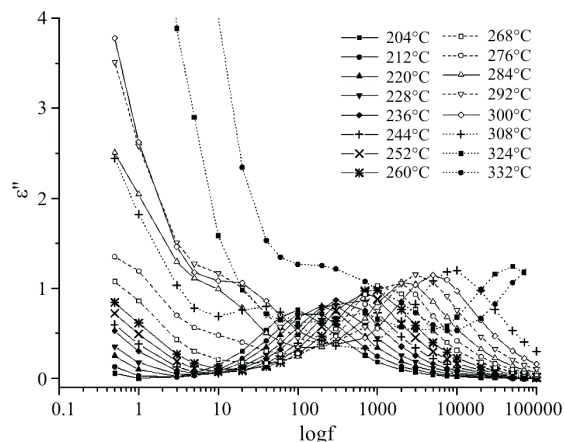


Fig. 7 ϵ'' vs. $\log f$ for the DGEBA ($n=0$)/ m -XDA system at temperatures 204, 212, 220, 228, 236, 244, 252, 260, 268, 276, 284, 292, 300, 308, 324 and 332°C

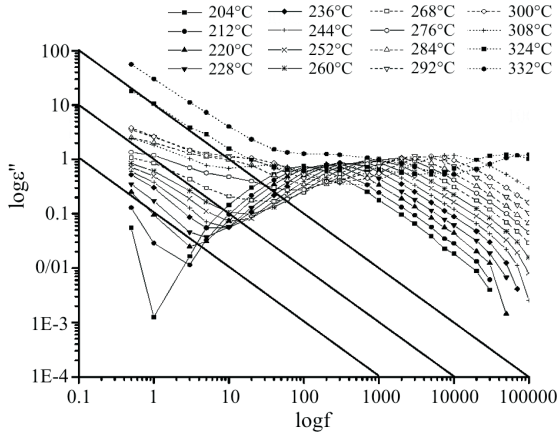


Fig. 8 $\log \epsilon''$ vs. $\log f$ for the DGEBA ($n=0$)/ m -XDA system at different temperatures

As Fig. 7 shows, at low frequencies, ϵ'' decreases with increasing $\log f$. This is a consequence of the conductive contribution, as ϵ'' is proportional to $1/w$.

For this reason, when σ is dominant:

$$\epsilon'' = \frac{\sigma}{w\epsilon_0} \quad (3)$$

taking logarithms

$$\log \epsilon'' = -\log w + \log \frac{\sigma}{\epsilon_0} \quad (4)$$

or

$$\log \epsilon'' = -\log f + \log \frac{\sigma}{2\pi\epsilon_0} \quad (4)$$

To check if σ is dominant at low frequencies; a plot of $\log \epsilon''$ vs. $\log f$ must be designed. If the plot is a straight line with a slope of exactly -1 , σ is the dominant contribution to ϵ'' and, from Eq. (4), σ can be calculated from the intercept on the y-axis. In other words, from the linear plot of $\log \epsilon''$ vs. $\log f$ and using the equation $\log \epsilon'' = m \log f + n$ where $m = -1$ when σ contribution is dominant, and $n = \log(\sigma/2\pi\epsilon_0)$, so σ can be calculated from the intercept on the y-axis.

A plot of $\log \epsilon''$ vs. $\log f$ is shown in Fig. 8, in which the straight lines have a slope -1 . These lines have been drawn as lines of sight.

Curves on Fig. 8, for low frequencies, were fitted to straight lines with slope m and intercept n on the y-axis. By doing this, it can be seen whether the slope is -1 , in which case σ could be calculated from:

$$n = \log \frac{\sigma}{2\pi\epsilon_0} \quad (5)$$

or

$$\sigma = 2\pi\epsilon_0 10^n$$

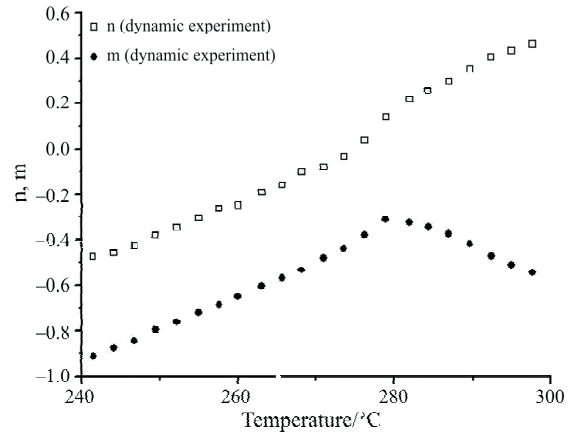


Fig. 9 Plot of n and m vs. T for the DGEBA ($n=0$)/ m -XDA system

Values of m and n , and regression coefficient (R) are recorded in Table 2.

For our study, the temperature range was chosen from 240 to 300°C because above this temperature data did not display a consistent behaviour.

To improve data interpretation, values in Table 2 were represented on 2 graphs.

Both Table 2 and Fig. 9 show that at about 240°C, the slope of the curves is approximately -1 and deviates from this value, thus, becoming less negative, as tem-

Table 2 Values of m and n , and regression coefficient (R) at different temperatures

$T/^\circ\text{C}$	n	m	R
241.5	-0.48	-0.91	0.99592
244.2	-0.46	-0.87	0.99516
246.8	-0.43	-0.84	0.9948
249.5	-0.38	-0.80	0.99434
252.2	-0.35	-0.76	0.99353
255.0	-0.30	-0.72	0.9941
257.6	-0.26	-0.69	0.99378
260.0	-0.25	-0.65	0.99217
263.0	-0.19	-0.60	0.99067
265.6	-0.16	-0.57	0.98962
268.2	-0.10	-0.53	0.98733
271.0	-0.08	-0.48	0.98597
273.6	-0.03	-0.44	0.98351
276.2	0.04	-0.38	0.97697
278.9	0.14	-0.31	0.97113
281.9	0.22	-0.32	0.98543
284.3	0.26	-0.34	0.99243
286.9	0.30	-0.37	0.99592
289.6	0.36	-0.42	0.99872
292.3	0.41	-0.47	0.99967
295.0	0.43	-0.51	0.99989
297.7	0.46	-0.55	0.99999

perature increases. This tendency changes again at around 280°C, with the slope becoming more negative thus indicating a dominant contribution to ϵ'' from conductivity. Either because of the appearance of a relaxation process or due to an experimental artefact, this change in tendency occurs within the range

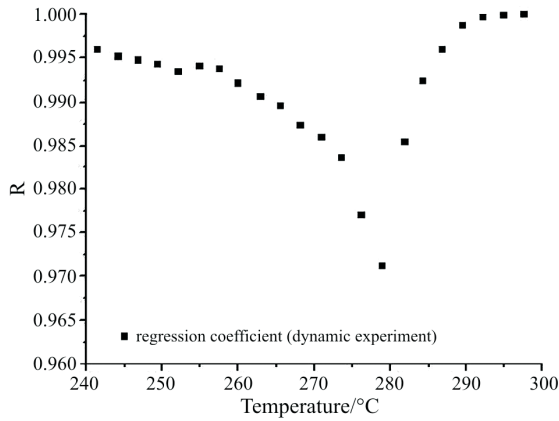


Fig. 10 Plot of the regression coefficient of Eq. (4) as a function of temperature

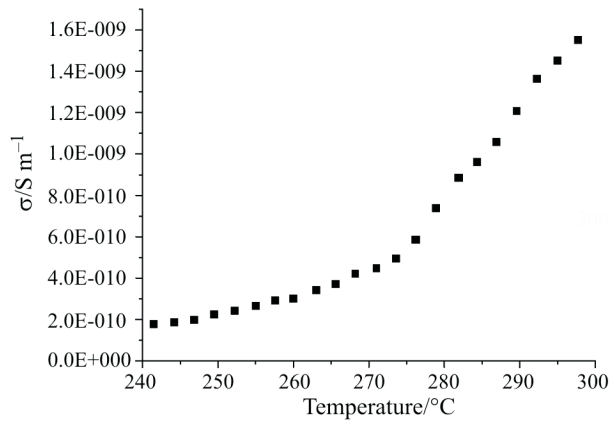


Fig. 11 σ vs. T plot of the values recorded in Table 3

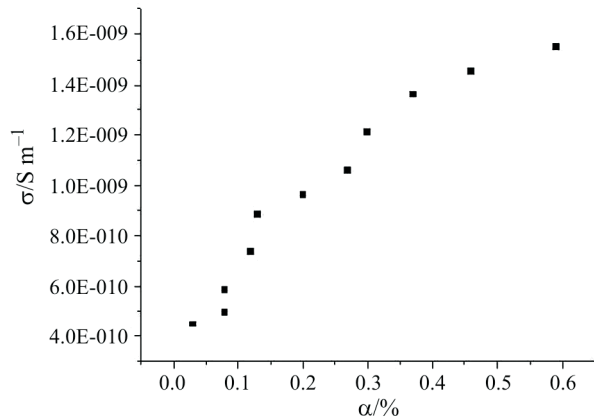


Fig. 12 Conductivity as a function of the degree of degradation at the first stages at degradation for the DGEBA ($n=0$)/ m -XDA system

where degradation takes place according to thermogravimetric experiments. Next will be the analysis of tendency of the regression (Fig. 10).

As Fig. 10 shows, it can be seen that the best fitting corresponds either to high or low temperatures. Moreover, same as previously, a change in the trend is observed at 280°C. The fact that, at certain temperatures, σ is not the dominant term in ϵ'' , involves the existence of a dipole relaxation process that can be caused either by electrodes polarization or by a partial vitrification during the degradation process of the system.

Values of σ calculated from Eq. [5], are shown in Table 3 and represented in Fig. 11. However, slope values indicate that, in the temperature range from 260 to 290°C, σ is not the dominant factor in ϵ'' , and for this reason, data in these ranges must be considered as a guide only.

Taking into account the limitations above mentioned, it can be said that approximately at 275°C, a qualitative increase in the rate of σ vs. T variation takes place. This could be a logical consequence of the bond broken caused by degradation and thus the greater mobility of free ions.

As it was done in the case of relaxation time, conductivity was represented as a function of the de-

Table 3 Values of σ calculated from the intercept n the y -axis (Fig. 9)

$T/^\circ\text{C}$	$\sigma/\text{s m}^{-1}$
241.5	1.78E-10
244.2	1.85E-10
246.8	1.99E-10
249.5	2.23E-10
252.2	2.41E-10
255.0	2.65E-10
257.6	2.91E-10
260.0	3.02E-10
263.0	3.43E-10
265.6	3.72E-10
268.2	4.22E-10
271.0	4.47E-10
273.6	4.94E-10
276.2	5.85E-10
278.9	7.38E-10
281.9	8.85E-10
284.3	9.63E-10
286.9	1.06E-9
289.6	1.21E-9
292.3	1.36E-9
295.0	1.45E-9
297.7	1.55E-9

gree of degradation, Fig. 12, within a temperature range from 260 (beginning of degradation) and 300°C, temperature above which conductivity data are not reliable.

Figure 12 shows that for degrees of degradations in the range from 0 to 1%, conductivity increases with conversion with a rate that decreases with an increase in conversion.

Conclusions

It was shown how degradation of a thermoset affects physical properties, such as dipole relaxation and conductivity. It was seen that, at high temperatures, relaxation times decrease due to possibly to a drop in restrictions of the main chains caused by chemical bonds breaking originated by the degradation process. Typical values of relaxation times at the beginning of the degradation process have been obtained and, moreover, it was found that, at this stage, relaxation time is proportional to the reciprocal of conductivity.

Dielectric curves for loss properties show a second peak that could be related either to a transition caused by the degradation or to an experimental artefact originated by the material under study.

A qualitative increase in conductivity that takes place at temperatures similar to those at which the relaxation time increases case, was also observed. It was found that it is possible to obtain information about temperatures at which conductivity becomes the dominant contribution to ϵ'' from the study of fitting parameters and regression coefficients corresponding to plots of $\log \epsilon''$ vs. $\log \omega$ as a function of temperature.

References

- 1 Y.-I. Liu, W.-L. Wei, K.-Y. Hsu and W.-H. Ho, *Thermochim. Acta*, 421 (2004) 139.
- 2 L. Núñez, C. A. Gracia-Fernández and S. Gómez-Barreiro, *J. Therm. Anal. Cal.*, 96 (2005) 2027.
- 3 M. Vinnik and V. A. Roznyanovsky, *J. Therm. Anal. Cal.*, 75 (2004) 753.
- 4 N. E. Marcovich, M. M. Reboredo and M. I. Aranguren, *Thermochim. Acta*, 372 (2001) 45.
- 5 L. Núñez, F. Fraga, M. R. Núñez, A. Castro and L. Fraga, *J. Appl. Polym. Sci.*, 74 (1999) 2997.
- 6 L. Núñez, F. Fraga, A. Castro, M. R. Núñez and M. Villanueva, *J. Appl. Polym. Sci.*, 75 (2000) 291.
- 7 L. Núñez, F. Fraga, M. R. Núñez and M. Villanueva, *J. Appl. Polym. Sci.*, 78 (2000) 1239.
- 8 M. R. Núñez, M. Villanueva, B. Rial and L. Núñez, *J. Therm. Anal. Cal.*, 66 (2001) 209.
- 9 M. E. Brown, 'Handbook of Thermal Analysis and Calorimetry', Vol. 1: Principles and Practice, Elsevier Science B. V., Amsterdam 1998.
- 10 E. A. Turi, 'Thermal Characterization of Polymeric Materials', Academic Press, Inc., San Diego 1997.
- 11 M. C. W. Coln and S. D. Senturia, 'The application of linear system theory to parametric microsensor', *Proc. Transducers* 85, 1985, p. 118.
- 12 B. J. Hunt and M. I. James, 'Polymer Characterisation', Blackie Academic and Professional., Great Britain 1993.
- 13 J. Köplinger, G. Kasper and S. Hunklinger, *J. Chem. Phys.*, 113 (2000) 4701.
- 14 J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Ed., Wiley & Sons, New York 1990.
- 15 F. N. Sheppard Jr. and S. D. Senturia, *J. Polym. Sci., Part B: Polym. Phys.*, 27 (1989) 753.
- 16 S. D. Senturia and N. F. Sheppard, Jr., 'Dielectric Analysis of Thermoset Cure', *Advances in Polymer Science*, 80, Springer-Verlag Berlin, Heidelberg 1986.
- 17 P. Debye, 'Polar Molecules', New York, Chemical Catalog Co., 1929.
- 18 L. Núñez, L. Fraga, M. R. Núñez, M. Villanueva and B. Rial, *J. Therm. Anal. Cal.*, 70 (2002) 1931.
- 19 S. Havriliak Jr. and S. J. Havriliak, 'Dielectric and Mechanical Relaxation in Materials' Hanser/Gardner Publications, Inc., Cincinnati 1996.
- 20 J. Einfeldt, D. Meissner and A. Kwasniewski, *Prog. Polym. Sci.*, 26 (2001) 1419.
- 21 R. A. Pethrick and D. Hayward, *Prog. Polym. Sci.*, 27 (2002) 1983.

Received: August 1, 2005

Accepted: October 10, 2005

OnlineFirst: May 29, 2006

DOI: 10.1007/s10973-005-7190-x