Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1025-1032

THERMAL DEGRADATION OF TETRAFUNCTIONAL/ PHENOL NOVALAC EPOXY MIXTURE CURED WITH A DIAMINE

L. Barral, J. Cano, J. López, I. López-Bueno, P. Nogueira, C. Ramirez, A. Torres and M. J. Abad

Departamento de Fisica, E. U. P. Ferrol, Universidad de A Coruña. Cra. Aneiros s/n
15405 Ferrol, Spain

Abstract

The effect of thermal degradation on the mechanical behaviour of a system containing both tetraglycidyl-4-4'-diaminodiphenylmethane (TGDDM) and a multifunctional novolac glycidyl ether (EPN) resins, cured with 4,4'-diaminodiphenylsulphone (DDS) has been studied using dynamic mechanical analysis (DMA) and tensile tests. Different curing paths using the isothermal time-temperature-transformation (TTT) diagram for this system were designed, obtaining thermosetting materials with different conversions. The influences of the degree of cure and of the aging temperature were also studied. The results showed different trends in the dynamic mechanical properties and an increase in the stiffness of the material with increasing aging time. Changes were faster and more intense with the higher temperature.

Keywords: dynamic mechanical tests, epoxy resin, tensile tests, thermal degradation

Introduction

The ultimate criterion of the durability of a polymer component is the length of time it continues to perform satisfactorily under service conditions. Aging tests are intended to accelerate those elements of the environment that are destructive to the polymer. A commonly used accelerated test for oxidative stability is the air oven test. The change in the mechanical properties is measured on samples removed from the oven at intervals until the specimen is deemed to have failed. The failure point of course depends on the purpose for which the polymer is intended [1].

Controlling degradation requires understanding of many different phenomena, including the diverse chemical mechanisms underlying structural changes in macromolecules or the influence of polymer morphology. Finally, comes the difficulty of understanding the relationship between the numerous changes in material composition that occur upon aging and the observed changes in the physical properties and/or failure mechanisms of interest for the material [2].

The thermosetting system of this work is a mixture of the epoxy prepolymers tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), from Ciba-Geigy MY720, and a multifunctional novolac glycidyl ether resin (EPN), from Ciba-Geigy EPN 1138, cured with an aromatic amine hardener, the 4,4'-diaminodiphenylsulphone (DDS), from Fluka Chemie.

1418–2874/99/ $ 5.00
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Kluwer Academic Publishers, Dordrecht

The cure kinetics and the construction of the isothermal time-temperature-transformation (TTT) diagram, using DSC, as well as the kinetics of the thermal decomposition of this system, using TG, have been reported in previous papers of our group [3–5]. The aim of this article was to investigate the effect of thermal degradation on the mechanical and dynamic mechanical properties and to get interrelations between the structure and the behaviour of the system with the aid of the TTT diagram. We have employed aging tests, dynamic mechanical analysis (DMA), and mechanical techniques.

Experimental

Materials and curing schedules

All the components of the TGDDM/EPN/DDS epoxy system were commercial products, and were used as received without purification, so the masses per epoxy equivalent for TGDDM and EPN were determined in our laboratory [6]. The composition of the system to obtain rich in epoxy formulation was the same one as in the previous works.

The thermosetting material was prepared by mixing the components at 120°C with continuous mechanical stirring, until a homogeneous liquid was obtained, and then poured into a rectangular stainless steel mould of 250x350 mm, which was preheated at the same temperature and placed into a forced air convection oven, where the curing schedules were finally applied.

In this way, we attained sheets of the material with slightly smaller dimensions than of the mould due to shrinkage, and about 4 mm thick. These sheets were properly mechanised to obtain the samples for the different tests.

The knowledge of the cure kinetics and the TTT diagram were used to design curing processes in order to obtain glassy solids which achieved different degrees of conversion supplying a system with a range of variation in its properties [7].

Table 1 Curing paths and crosslinking of the material

Path	Curing time and temperature	T_g/°C	M_c/g mol^{-1}
1	2 h at 180°C	211	196
2	2 h at 160°C and 2 h at 220°C	251	163

In this work, two different curing paths were applied. Table 1 summarises these paths, and gives the values of the glass transition temperatures, T_g, measured on the maximum of tanδ peaks, and of the molecular mass between crosslinks, M_c, obtained from a previous work [7], and calculated according to the empirical relationship by Nielsen [8].

The material cured with the two-step-path 2 has reached a major conversion, near $\alpha=0.92$, and higher crosslinks densities than the one under path 1. Also, as a result of the high temperature of cure, etherification reactions became significant [3, 4].

We have aged the samples of the material with the cure path 1 at 200°C, a temperature near T_g, and the samples of the material with the cure path 2 at 280°C, a temperature well above its T_g. The selection of two different temperatures and cures will allow us to examine the influence of the temperature and the degree of cure on the degradation behaviour of this system.

Dynamic mechanical tests

DMA measurements were made with a Perkin Elmer dynamic mechanical analyser series 7 equipped with a liquid nitrogen-cooling accessory CCA7. The temperature scan mode at a constant heating rate of 5°C min^{-1} was used. A constant dynamic stress at the standard frequency of 1 Hz with the three-point bending measuring system, under a helium flow of 40 cm^3 min^{-1} was applied to the samples.

Stress strain tests

Tensile stress strain tests were performed using an Instron universal-testing machine 5566, according to the general specifications of ASTM D638M and ISO 527 [9, 10]. All tests were made at room temperature and at a crosshead speed previously selected of 1 mm min^{-1}. The samples were M-II type and a minimum of five of them was tested for each aging time. The data reported are averages of the tests.

Results and discussion

DMA tests

Figure 1 shows the tanδ curves and Fig. 2 the storage modulus E' for the material cured following the path 1, and with 0, 24, 96, and 240 h of aging time at 200°C.

In a similar way, Figs 3 and 4 show the curves for the material cured with the path 2 after 0, 0.5, 1, 2, 12 and 24 h of thermal degradation at 280°C.

Figure 5 gives the values of the dynamic mechanical properties and their variations with the degradation time at 200°C in row (a), and at 280°C in row (b), mea-

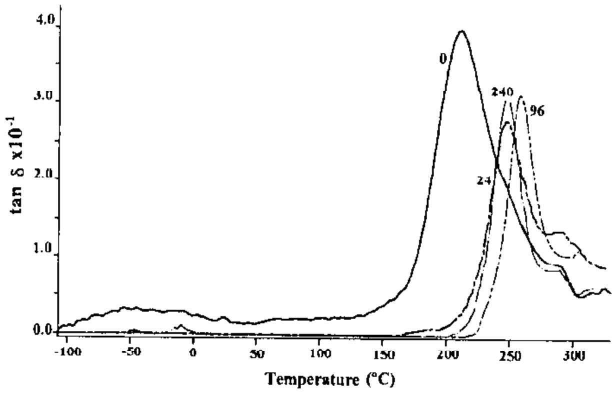


Fig. 1 Plots of tanδ as a function of aging time at 200°C

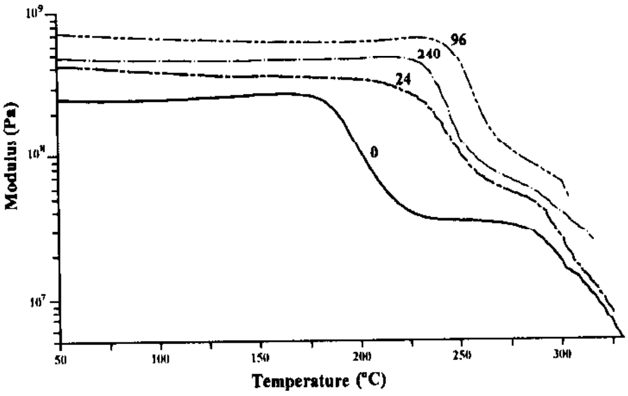


Fig. 2 Plots of E' as a function of aging time at 200°C

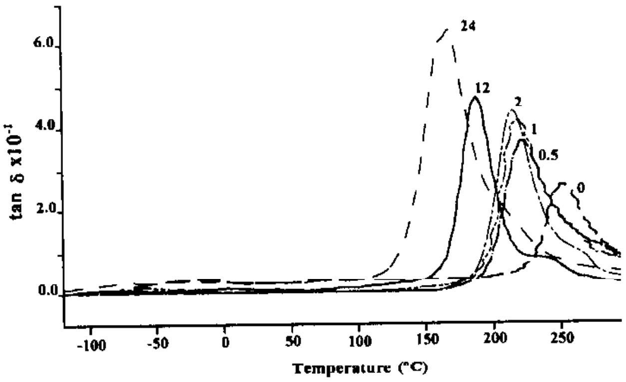


Fig. 3 Plots of tanδ as a function of aging time at 280°C

sured on the previous curves. The properties showed are T_g, the storage modulus in the rubbery plateau region, E'_r, and the maximum of tanδ.

The material with cure 1 showed a shift of the glass transition to higher temperatures and an increase in E'_r values during the first 96 h of degradation, while tanδ maxima were reduced. The length of the rubbery plateau decreased accordingly T_g was approaching the temperature of the intense degradation of the material. TG results [5] exhibited the onset of the severe loss of mass near 330°C.

The trends observed in the T_g, E'_r and tanδ values can be explained in terms of a reactivation of the curing reactions during the initial aging times, which caused a further crosslinking and a decrease in the segmental mobility of the macromolecular chains. Larger periods of aging times led to structural changes in the material, with breakdown of crosslinking points and losses of dangling chains which diminished

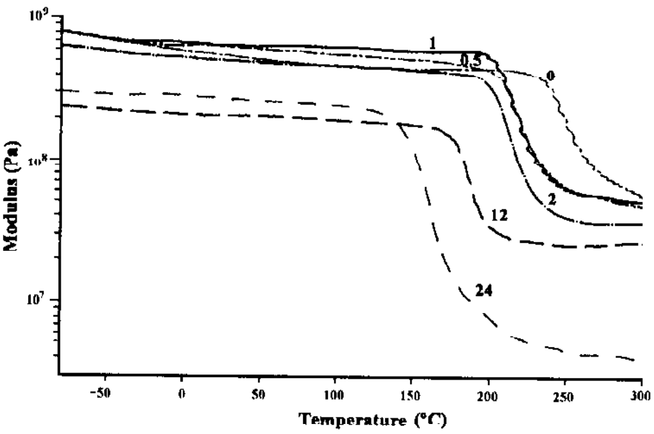


Fig. 4 Plots of E' as a function of aging time at 280°C

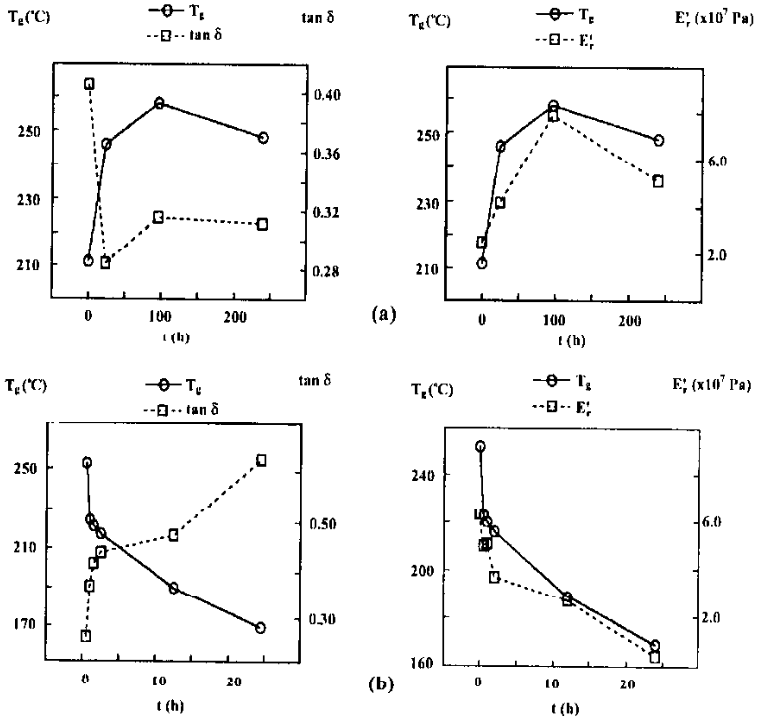
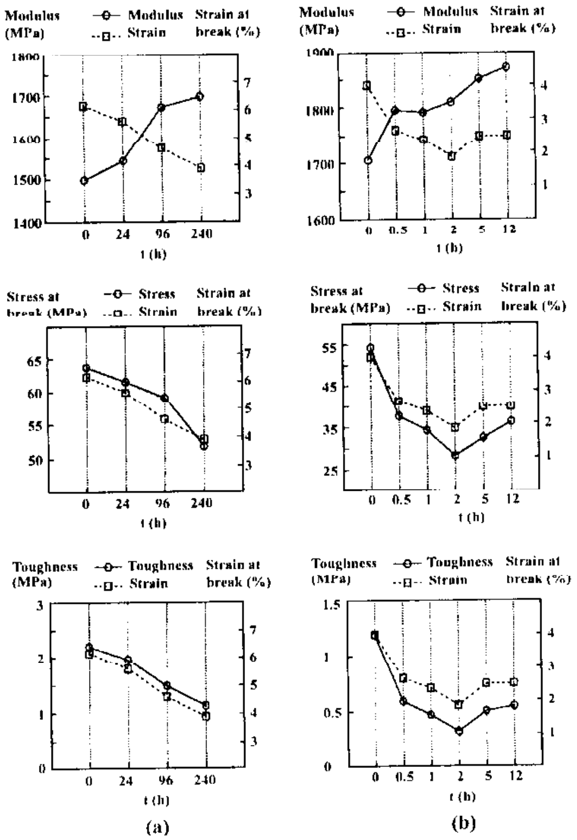


Fig. 5 Dynamic mechanical properties *vs.* aging time; row (a): 200°C; row (b): 280°C



(a) (b)

Fig. 6 Variation of the tensile properties *vs.* aging time; column (a): 200°C; column (b): 280°C

the effective crosslinks density and reduced T_g and E_r' values. The material exposed to 280°C revealed important structural losses. It was observed a decreasing in the crosslinks density and an increasing in the mobility of the chains in the glass transition region.

Tensile tests

The specimens were subjected to a similar thermal conditioning of 200 and 280°C for each cure with different aging times.

Tensile properties such as tensile stress at break (σ_B), percent elongation at break (ε_B), tensile modulus (E) and tensile toughness, calculated as the area under the stress strain curve and representing the tensile energy absorption were determined. No yield points were observed, so the maximum tensile stress is the same as σ_B.

Figure 6 displays the trends of the average values of the tensile properties with the increase of aging time at 200°C in column (a) and the results for the temperature of 280°C in column (b).

These results revealed an increase in the stiffness of the material with the time of degradation. A slight increase in the values of E was observed and σ_B, ε_B and tensile toughness were reduced with increasing time. The loss of properties was progressive for the degradation at 200°C, and faster and more intense for the degradation at 280°C, in a similar mode as dynamic mechanical properties had changed.

It can be noted the marked parallelism in the trends of σ_B, the toughness, and ε_B showing the more brittle nature of this system with the thermal degradation.

The material obtained with the cure path 1 presents better values of the properties at break. The increase in the fragility of the material with a higher conversion, cure 2, may be due to the etherification reactions arising from the cure at elevated temperatures. The rise of T_g because of chemical side reactions as etherification is not desirable with respect to some properties of the material. Usually, epoxy polymers become more brittle and with higher Young moduli due to etherification reactions [11]. This behaviour can be seen in the data obtained.

Conclusions

Thermal degradation changed the dynamic mechanical and the mechanical properties of the TGDDM/EPN/DDS epoxy system. DMA tests showed a decrease in T_g and of the crosslinking density observed in the values of E'_r. A reactivation of the curing reactions was appreciated in the material with less conversion. Mechanical tests revealed an increase in the stiffness with the time of degradation, with appreciable losses in the tensile properties at break. All the changes were faster and more intense with the higher aging temperature.

The material cured 2 h at 180°C presents better tensile properties at break at any aging time. Curing at a more elevated temperature, as in path 2, has increased T_g and the crosslinking density of the material, but has also arisen etherification reactions which have reduced some mechanical properties of the system.

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This work was financially supported by Xunta de Galicia, through grant XUGA-17201A95.

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References

1 N. Grassie and G. Scott, Polymer Degradation and Stabilisation, Cambridge University Press, Cambridge 1985, p. 9.

2 R. L. Clough, N. C. Billingham and K. T. Gillen, Ed., Preface in Polymer Durability. Advances in Chemistry Series 249, American Chemical Society, Washington DC 1996.

3 L. Barral, J. Cano, J. López, P. Nogueira, M. J. Abad and C. Ramírez, J. Thermal Anal., 50 (1997) 409.

4 L. Barral, J. Cano, J. López, P. Nogueira, C. Ramírez and M. J. Abad, Polym. Int., 42 (1997) 301.

5 L. Barral, J. Cano, J. López, I. López-Bueno, P. Nogueira, C. Ramírez and M. J. Abad, J. Therm. Anal. Cal., 51 (1998) 489.

6 H. Jahn and P. Goetzky, Epoxy Resins, Chemistry and Technology,. C. A. May, Ed., Marcel Dekker, New York 1988, chap. 13.
7 P. Nogueira, Ph. D. Thesis, Universidad de Santiago, 1998.
8 L. Nielsen, J. Macromol. Sci. Rev. Macromol. Chem., C3, (1969) 69.
9 ASTM D638M Tensile Properties of Plastics, Annual Book of ASTM Standards, 1989.
10 ISO 527 Plastics-Determination of Tensile Properties, 1993.
11 E. F. Oleinik, Epoxy Resins and Composites IV, K. Dušek, Ed., Springer-Verlag, Berlin 1986, p. 75.