CHARACTERIZATION OF NANOCOMPOSITES USING MICROWAVES FOR CURING PROCESS

Francisco Fraga-López *, Hugo Rebolo, Julio A. Seijas, Eugenio Rodríguez-Núñez, José Manuel Martínez-Ageitos, Javier Miragaya, Eva Vázquez-Barreiro

Facultade de Ciencias. Campus de Lugo. Universidad de Santiago de Compostela. 27002. Lugo. Spain.

ABSTRACT

The main objective of this work is the synthesis of epoxy nanocomposites with gold nanoparticles. The curing process was optimized by microwave taking into account variables such as time and temperature.

KEYWORDS: epoxy resin, nanocomposites, gold nanoparticles, microwave

INTRODUCTION

Nanocomposites are multiphase materials of which one phase has one, two or three dimensions less than 100 nm. They constitute a new branch within the broad field of science and technology of polymeric materials with a wide range of applications. The most common are those made of an organic polymer constituting the continuous phase (matrix) and an inorganic solid as the disperse phase. The result of the interaction between inorganic and organic component is a synergistic effect leading to improved material properties, such as: increased stiffness, resistance and new optical properties[1-2].

The curing process of the nanocomposite is provided by the design of experiments obtained in a previous paper[3]. For this curing process is used a Milestone ETHOS D microwave (power 800W). The curing conversion and the different kinetic parameters are performed by differential scanning calorimetry (DSC). The Au nanoparticles are prepared to provide greater nanoparticle stability, as well as increased affinity for the epoxy substrate.

The use of microwave energy for materials processing has been viewed as an alternative for its advantages over conventional processes. The microwave heating is basically in volume, which means that the material is heated by rapid reorientation of dipoles, giving a same temperature distribution across the material. Many studies have been made in the field of microwave processing, such as polymeric compounds processing, drying solid materials, curing adhesives and many other industrial applications. The main advantages of using microwave heating versus conventional: Drastic reduction of reaction times and differences in selectivity[4].

EXPERIMENTAL

Materials

The epoxy resin was a commercial DGEBA (n =0) (Resin 332, Sigma Chemical Co., St. Louis, USA) with an equivalent molecular mass of 173.6 g eq-1. Gold(III) chloride trihydrate with molecular weight 393.83 g eq-1 with 99.9+% purity, 3- mercaptopropionic acid, with molecular weight 106.14 g eq-1 with 99+% purity, methyl alcohol with 99.8% purity and the curing agent meta-xylylenediamine, with an equivalent molecular mass of 151.25 g eq-1 with 97% purity, were purchased from Sigma-Aldrich Chemie, GmbH, Germany. Sodium borohydride for synthesis with molecular weight 37.83 g eq-1 with 96% purity.

Samples preparations

2 g of DGEBA monomer and 0.4 ml of curing agent were mixed homogenously in stoichiometric ratio. Gold nanoparticles have prepared by reduction and stabilization of HAuCl4 with sodium borohydride and mercaptopropionic acid. The process of the reduction was monitored by UV-visible spectroscopy and the reduction was completed after 24 hour. Epoxy nanocomposites containing gold nanoparticles capped by mercaptopropionic acid were prepared by melt intercalation with the epoxy network BADGE n=0/m-XDA[1,14,18]. The nanocomposite is introduced into glass cylinder. For the curing process is used an experimental design (Statgraphics Plus 5.1 for Windows)[3], once that the samples are introduced in a Milestone ETHOS D microwave with following cure cycle: in the first step 30 minutes at 30ºC and the second step 10 minutes at 120ºC.

RESULTS AND DISCUSSION

The glass transition temperatures (T_g) of the nanocomposites were performed using a differential scanning calorimeter and FT-IR spectroscopy. The results for different epoxy/amine ratio obtained with DSC (Q100 V6.19 Build 227 of TA Instruments) are shown in Table 1.

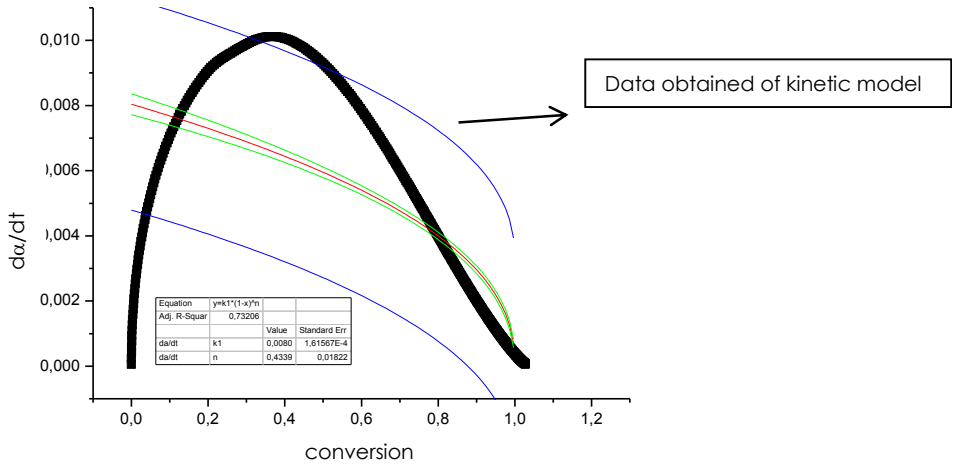
Table 1. T_g obtained with DSC for two epoxy/amine ratio

Epoxy/amine ratio	Prec. Temp. (ºC)	Prec. t. (min)	Cur. Temp. (ºC)	Cur. t. (min)	Tg (ºC)	sample
1:1	40	30	120	10	*121*	
1:2					*118*	

Where the variables selected (from experimental design) were Precured Temperature (Prec. Temp.), Precured time (Prec. t.), Cured Temperature (Cur. Temp.), and Cured time (Cur. t.).

A scan in dynamic mode is used to determine the dynamic heat of reaction (ΔH_D) from 25ºC to 180ºC at a heating rate of 10ºC/min. A second scan has been carried out to determine isothermal heat of reaction (ΔH_I) at 120 ºC (close to T_g). The epoxy amine ratios used in this paper are 1:1. For the experimental data the reaction rate versus time has been calculated. Figure 1 shows the reaction rate versus time at epoxy /amine ratio 1:1. In this figure can be observed a non-linear fitting at n-order equation $\left(\frac{d\alpha}{dt} = k_1 \cdot (1-\alpha)^n\right)$.

Figure 1. Reaction rate versus conversion



The system does not follow the behavior of a kinetic equation of n-order. A new kinetic model (Sourour and Kamal)[5] has been used, with the n-order and autocatalytic contribution. Figure 2 shows a good agreement between an experimental results and kinetic model in all the range of conversion.

Figure 2. Reaction rate versus conversion using Kamal model

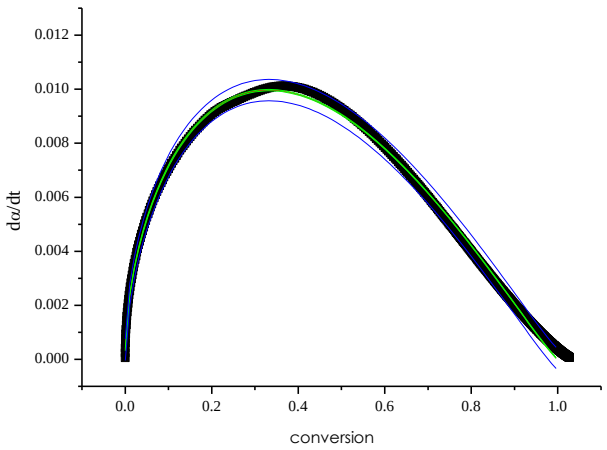


Table 2 shows the constant rates and reaction orders for the n-order and autocatalytic paths at 120°C.

Table 2. Constant rates and reaction orders for n-order and autocatalyzed mechanism

k_1	$3.23 \cdot 10^{-4}$
k_2	0.0279
m	0.492
n	1.137
R^2	0.998
Overall reaction order (m+n)	2

The results suggest that the overall reaction order system is 2, in good agreement with the values obtained by Nuñez et al.[6-7].

The cure reaction is controlled by the chemical kinetics. From a critical conversion (α_c) due to a higher increase in the viscosity the cure reaction becomes diffusion controlled. A semiempirical model based on the free-volume considerations[8] has been used to study the diffusion reaction rate. The diffusion factor of this model ($F(\alpha)$) is defined as follows:

$$F(\alpha) = \frac{1}{1 + e^{[A_1 \cdot (\alpha - \alpha_c)]}}$$

Where A_1 is an adjustable parameter.

The higher value of critical conversion (0.9785) indicate that the diffusion do not affect to the cure kinetic of the system.

CONCLUSIONS

It has been used the experiments design to optimize the curing time of a nanocomposite using microwave. The introduction of the nanoparticles into epoxy resin does not modify the glass transition temperature. The reaction order is the same that those obtained without nanoparticles.

REFERENCES

(1) Garcia Jaca J. et al. La Nanotecnología en los plásticos. Observatorio industrial del sector químico. 2007.

(2) Ramos Carpio M. A., De María Ruíz M. R.,. Ingeniería de los materiales plásticos. Ed. Díaz de Santos. Madrid. 2008.

(3) Fraga F., Rodríguez-Núñez, E., Martínez A.,Miragaya J. Int. J. Nanoparticles. 2014, 7, 100.

(4) Soesatyo B., Blicblau A., Siores E. J. Mater Process Technology. 1999, 89-90, 451-456.

(5) *Sourour S. and Kamal M. R., Thermochim. Acta. 1976,14,41*

(6) *Núñez L. , Fraga F., Núñez M. R. and Villanueva M. J. App. Polym. Sci.1998, 70, 1931.*

(7) *Núñez L. , Fraga F., Núñez M. R. and Villanueva M. J. App. Polym. Sci.1999, 74, 2997.*

(8) Khanna U., Chanda M. J. Appl. Polym. Sci. 1993, 49, 319.