ORGANIC/INORGANIC HYBRID MATERIALS FROM AN EPOXY RESIN CURED BY AN AMINE SILSESQUIOXANE

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The thermal behaviour of an epoxy resin cured with an amine-POSS was studied using differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The kinetic of polymerization reaction and the thermal degradation have been analyzed based on an iso-conversional model. The obtained results showed that the activation energies of both processes depend on the degree of conversion.

Introduction

Thermosets differ from most other polymers in their processing, that includes polymerization. The cure reaction of epoxy resins involves the formation of a rigid three-dimensional network and it is a complex process. In order to convert epoxy resins to hard, infusible thermoset networks it is necessary to use crosslinking agents [1, 2]. The hardener used in this work was a polyhedral oligomeric silsesquioxane (POSS) with a reactive amine group.

Silsesquioxanes are a class of oligomeric organosiliceous compounds with the following empirical formula, $R(SiO_{1,5})_n$, where R is an organic chain or a hydrogen atom and n is an even number. One of the possible structures that can adopt these materials is an inorganic structure in cage with a sesqui ratio between oxygen and silicon atoms and that it is surrounded by the organic chains, R. As these compounds have a structure with both, organic and inorganic parts, the POSS can be used to create novel hybrid materials, which display enhanced properties intermediate between of an inorganic and an organic polymer [3, 4]. Moreover, due to the reduced size of the inorganic core (~0.53 nm), these kinds of materials have a great interest to modify other systems at nanometric scales [5, 6].

The aim of this work was to use the differential scanning calorimetry (DSC) to study the polymerization of an epoxy resin cured with an amine-POSS through an iso-conversional method [7]. Other studies of this system are going to appear in forthcoming publication. The thermal degradation of the mixture cured was analyzed by thermogravimetric (TG) analysis. The goal of this paper is the novel hardener.

Theoretical analysis

All kinetic studies start with the basic rate equation that relates the rate of conversion at constant temperature, $d\alpha/dt$, to a function of the concentration of reactants, $f(\alpha)$, through a rate constant, $k(T)$,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

where α is the extent of reaction at any time and $f(\alpha)$ is assumed to be independent of temperature, but depends on the reaction mechanism [8]. The temperature dependence is assumed to reside in the rate constant through an Arrhenius relationship, given by,

$$k(T) = A\exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

where E_a is the activation energy, R is the universal gas constant, T the temperature and A the pre-exponential factor or frequency factor. By combination of Eqs (1) and (2), and considering that in dynamic cured processes, the temperature varies with a constant heating rate, $\beta=dT/dt$, it is obtained the following expression:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \qquad (3)$$

where T_0 is the initial temperature and T is the final temperature.

To perform the iso-conversional analysis of both, curing and degradation process, the reaction mechanism is assumed to be constant, and $f(\alpha)$ in Eq. (1) does not change at each degree of conversion, α. Equation (3) can be integrated using the methods of Kissinger or Flynn-Wall-Ozawa [9]. The values of

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the activation energies and the pre-exponential factors can be obtained by fitting of experimental curves to the equations described by these methods.

Experimental

The epoxy resin used was the diglycidyl ether of bisphenol A, DGEBA, GY 260, from Ciba-Geigy, (Summit, NJ) with molecular mass of 376 g mol^{-1}. As curing agent was used the amine propyl iso-butyl-POSS, in the following named API, AM0265, from Hybrid Plastics^{TM}, (Fountain Valley, CA) and molecular mass of 874.58 g mol^{-1}.

Amine-POSS was characterized by DSC and TG measurements. Two melting points were found by DSC for API with values of 61.5 and 266.2°C, as occurs with other POSS [6, 10]. The corresponding crystallization temperatures appear in the cooling scans. It can be due to the presence of two different morphologies in the amine.

By TG analysis, the onset of degradation, T_o, was obtained at 277.6°C in argon atmosphere and at 265.3°C in oxygen atmosphere. There is hardly no difference in the beginning of the degradation in function of the atmosphere used. With respect to the char yields, in argon atmosphere the degradation is practically complete, but, in oxygen atmosphere the char yield obtained is of 43.68%. It can be attributed to the possible formation of siliceous oxides in presence of the atmospheric oxygen.

Dynamic scans for the study of the cured reaction were performed in a differential scanning calorimeter model DSC-7 of Perkin-Elmer, (Nortwalk, CT) equipped with an intracooler and supported by a Perkin-Elmer computer for data adquisition and analysis. All experiments were conducted under a dry nitrogen flow of 20 mL min^{-1} as purge gas. Samples of about 5–10 mg were enclosed in aluminium DSC pans and heated from 30 to 300°C at different heating rates of 2.5, 5, 10 and 20°C min^{-1}. Thermal degradation was followed with a thermogravimetric balance model TGA-7 of Perkin-Elmer, (Nortwalk, CT), connected to a computer PC1022 with a specific software for the thermal analysis. Samples tested were cured for one hour at 170°C and post-cured for one hour at 180°C. Then, they were heated from 150 to 650°C at different heating rates of 5, 10, 25 and 50°C min^{-1} under argon atmosphere [11, 12].

Results and discussion

The peaks of the dynamic DSC curves at different heating rates are shifted to higher temperature values as the heating rate increases. To perform iso-conversional analysis, the DSC curves have to be transformed into the form α_i *vs.* T_i at each value of heating rate as can be seen in Fig. 1a. At a given value of conversion, the temperature is higher when the reaction rate increases. In the other hand, the obtained conversions are smaller at higher reaction rates at the same temperature.

In order to obtain the activation energy of the cure process, the temperature values obtained for a given conversion degree at each heating rate are fitted to the following expression,

$$-\ln\left(\frac{\beta}{T_{\alpha_i}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_{\alpha_i}}\right) \qquad (4)$$

From the slope of the straight lines obtained and showed in Fig. 2a, activation energies, E_a, and pre-exponential factors, A, of the cure process can be calculated in the whole range of conversion, (Table 1). It can be seen that the values of activation energy are
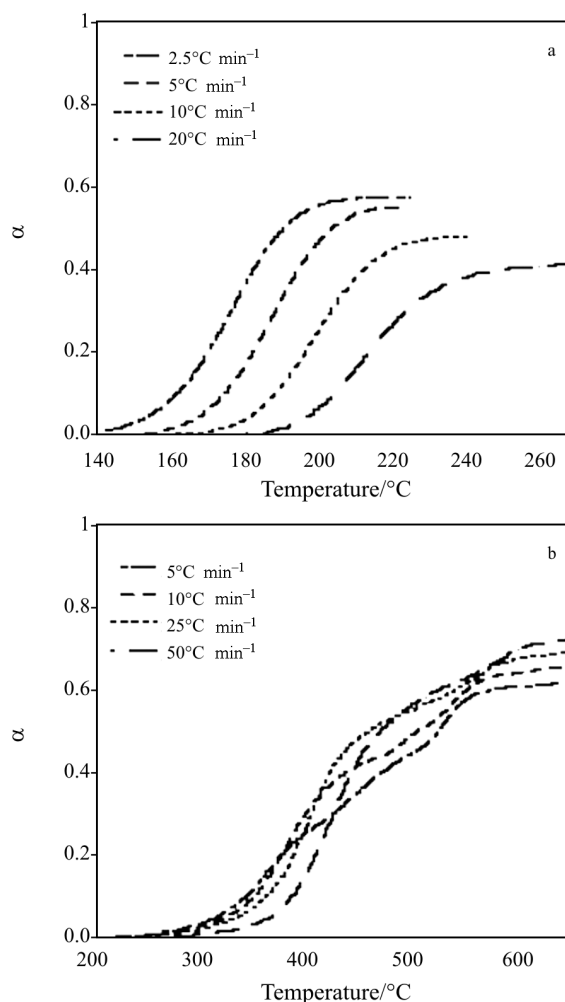

Fig. 1 Degree of conversion in function of the temperature for a – DSC and b – TG scans
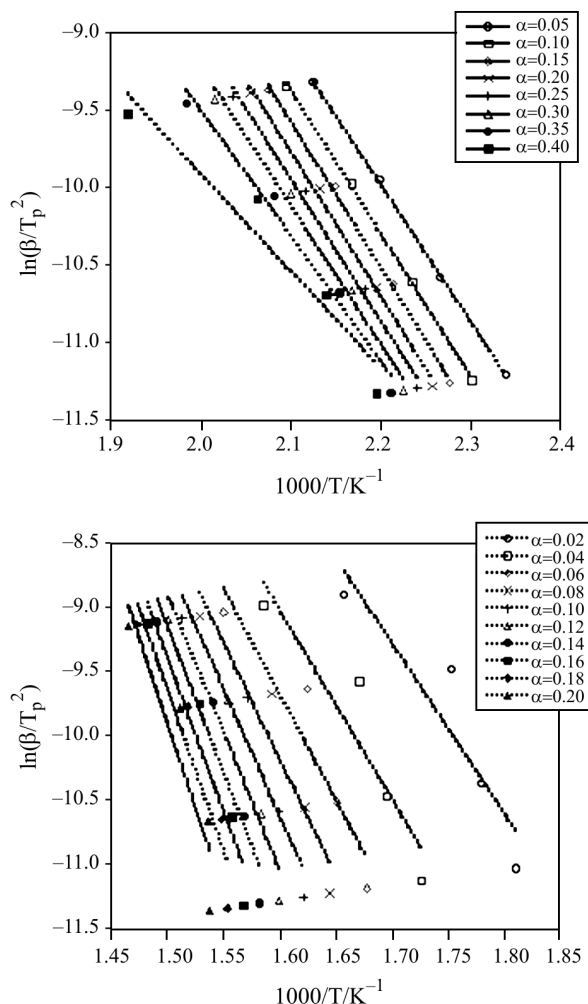
Fig. 2 Iso-conversional plots for epoxy compounds obtained by a – DSC and b – TG analysis

between 70–80 kJ mol^{-1} until reaching the conversion of 0.3, then, the activation energy values decreases considerably. This can be attributed to the presence of hydroxyl groups formed during the cure, which act as catalyst in the epoxy ring opening reaction [7].

The pre-exponential factors were too calculated using the method given in ASTM E698-79 [13], where it is assumed that the conversion degree reached in the exotherm peak, α_p, is constant and does not depend on the heating rate. The pre-exponential factor can be calculated with the following expression,

$$A = \frac{\beta_i E_{a,p}}{RT_{p,i}^2} \exp\left(\frac{E_{a,p}}{RT_{p,i}}\right) \qquad (5)$$

where T_p is the temperature at which maximum conversion rate occurs on DSC curves. In Table 1 can be seen the pre-exponential factors obtained by application of ASTM E698 method at each heating rate.

The characteristic parameters used to define the pyrolysis of the epoxy system were the onset temperature of decomposition, T_o, the temperature of the maximum rate of decomposition, T_m, and the char yield obtained at 650°C.

As occurs in DSC scans, T_o and T_m shift to higher values with the heating rate. In the other hand, the char yield values are higher at smaller heating rates, because the degradation of the samples is minor.

The iso-conversional analysis can be used to analyze the degradation kinetics as was done with cure process. Plotting the degree of degradation, α as function of the temperature, Fig. 1b, and fitting them to the Eq. (4), Fig. 2b, the values of activation energy of the degradation process can be calculated from the slope of the straight lines, (Table 1).

Table 1 Activation energies and pre-exponential factors in function of the degree of conversion and calculated by ASTM E698-79 method at different heating rates

Differential scanning calorimetry (DSC)									
α	0.05	0.10	0.20	0.20	0.25	0.30	0.35	0.40	
E_a/kJ mol^{-1}	73.7	76.6	78.1	77.7	76.2	74.2	67.3	52.2	
A/min^{-1}	$1.2\cdot10^5$	$2.0\cdot10^5$	$2.4\cdot10^5$	$1.8\cdot10^5$	$1.0\cdot10^5$	$5.0\cdot10^4$	$6.5\cdot10^3$	$0.9\cdot10^2$	

Arrhenius parameters obtained by ASTM E698-79 method									
β/°C min^{-1}	T_p/K	α_p	$A\cdot10^{-4}$/ min^{-1}	E_a/ kJ mol^{-1}					
2.5	451.1	0.33	1.55						
5	460.3	0.27	2.97	102.0					
10	471.5	0.23	5.66						
20	485.4	0.19	10.67						

Thermogravimetric analysis (TG)									
α	0.02	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.18	0.20
E_a/kJ mol^{-1}	101.5	121.9	135.1	150.5	164.1	177.6	189.4	198.0	207.9	219.3

The activation energy values for the degradation process increase continuously with the degree of degradation, α, and this fact shows the good thermal stability of these materials.

Conclusions

The amine-POSS presents two melting points by DSC scans, which correlate with two different types of crystallization. By TG analysis, API presents a smaller residue in argon atmosphere than in oxygen atmosphere. This fact is attributed to the formation of siliceous oxides in presence of the atmospheric oxygen.

The cure and thermal degradation behaviour of this system can be analyzed using an iso-conversional model that does not require the previous knowledge of the reaction rate equation $f(\alpha)$. It is clear that the reaction mechanism is very complex and that the activation energy depends on the degree of curing. At the early stage of cure reaction, the activation energy takes a constant value, which decreases when the degree of conversion rises, due to the catalysis of the hydroxyl groups generated during the reaction. On account of the thermal degradation process of cured material, the activation energies obtained increase with the conversion. This fact shows the good thermal stability of this system.

Acknowledgements

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