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Mechanism of Thermal Degradation of an Inorganic-Organic Hybrid Based on an Epoxy-POSS

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Summary: A novel inorganic-organic hybrid material, belonging to the family of polyhedral oligomeric silsesquioxanes (POSS), was used to reduce the trend of a conventional epoxy-amine system to undergo combustion. The mixtures with different percentages in weight of POSS, and equal number of equivalents between of epoxy and amino groups were tested by thermogravimetic analysis (TGA) in both, argon and oxygen atmospheres. The results indicated that the char/ceramic yield values increase with the content of POSS and therefore, fire resistance is enhanced. Activation energies of degradation processes were obtained by Kissinger-Akahira-Sunose method. An empirical kinetic model satisfactorily explained the degradation mechanism of different blends.

Keywords: degradation; epoxy; silsesquioxanes; thermogravimetric analysis

Introduction

Polymeric materials, when exposed to high temperatures, suffer chemical breakdown or pirolysis and the obtained products can react with atmospheric oxygen providing a combustion process.

The thermal decomposition mechanism of epoxy resins is complex and varied. Crosslinked epoxy resins are combustible and their combustion is self-supporting.[1] In order to reduce their combustion capacity, fire retardant agents are added to the epoxy systems. These retardants can be incorporated by addition or by copolymerization processes.[2] In this work, the fire-retardant used was a polyhedral oligomeric silsesquioxane (POSS). They are inorganic-organic hybrids with the empirical formula $R(SiO_{1,5})_n$ where n is an even number and R is an organic chain.[3,4] The great interest of organic/inorganic nanocomposites lies in the improved properties that they offer, which are enhanced by interfacial interactions between individual components.[5,6]

The aim of this work was to analyze the thermal degradation mechanism of an epoxy system that was modified with fire retardant POSS molecules dispersed in the polymeric matrix.

The ternary mixtures with different percentages in weight of epoxy-POSS were tested by TG analysis in both argon and oxygen atmospheres,[7] and the kinetic of degradation process was analysed by using the integral isoconversional Kissinger-Akahire-Sunose method.

Experimental Part

The system studied is based on a commercial diglycidyl ether of bisphenol A (DGEBA) Araldite GY 260, from Ciba-Geigy (Summit, NJ), with weight per epoxy equivalent of 188 $g \cdot equiv^{-1}$. 4,4′-(1,3-phenylenendiisopropylidene) bisaniline (BSA), from Aldrich Chemical (Milwaukee, WI), was used as hardener agent, with a molecular weight of 344.5 $g \cdot mol^{-1}$ and melting point of 114.5 °C. Octaepoxy- cyclohexyldimethylsilyl-POSS, EP0430, forthwith referred to as OECh, from Hybrid Plastics (Fountain Valley, CA),

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with a molecular weight of 2011.41 $g \cdot mol^{-1}$, was added to modify the epoxy-diamine system. They were commercial products, which were used without previous purification.

Ternary samples with 2.5, 10 and 50 wt % of OECh in the mixture were prepared in the following way. The appropriate amount of DGEBA was heated at 130 °C and then OECh was added through stirring. When the mixture cooled, curing agent was added and hand mixed until a homogeneous sample was obtained. They were cured for 3 hours at 130 °C and postcured for 4 hours at 150 °C. DGEBA/BSA and OECh/BSA mixtures were made in order to compare with the ternary blends.

Weight loss of fully cured samples was measured by thermogravimetric analysis (TGA), using a Perkin Elmer TGA-7 microbalance coupled to a 1022 Perkin Elmer microprocessor. Samples were heated from 50 °C to 700 °C at different heating rates of 5, 10, 15 and 20 $°C \cdot min^{-1}$ under argon atmosphere and at 10 $°C \cdot min^{-1}$ in pure oxygen atmosphere.

SEM images of gold coated fracture surfaces of different blends, before and after thermogravimetric analysis, were carried out in a scanning electron microscopy (SEM) Hitachi S-2700 with a 1.5 kV acceleration voltage.

Results and Discussion

The homogeneity of the cured blends was tested by SEM. The ternary blends seem to be homogeneous and OECh is supposed to be dispersed in the polymeric matrix. The different blends were tested by TGA, in both, argon and oxygen atmospheres, obtaining the results indicated in Table 1 for the heating rate of 10 °C min^{-1}, where T_5 y T_{50} are the degradation temperature at 5 and 50 wt % of weight loss, respectively and T_m is the temperature at the maximum of degradation. In all cases, these temperatures increase with the content of OECh.

In both atmospheres, for all the blends, the temperature of 5 wt % is higher than for the DGEBA/BSA sample and lower for the OECh/BSA sample. The 50 wt % mass loss temperature rises with the content of OECh as well. So, the resistance to degradation of the mixture rises with the inorganic content. This could be due to the combined effects of the formation of aromatic tether structures in presence of OECh cages and the dispersion of cages in epoxy matrix.[8,9]

The ceramic/char yield at 700 °C is higher when the content of OECh increases due to the presence of a higher number of silicon atoms, the inclusion of the inorganic component enhances thermal stability. Fire retardancy of materials can be measured by

Table 1.
Temperatures obtained for ternary systems with different wt % of OECh in both, argon and oxygen atmospheres.

ARGON

% OECh	T_5 (°C)	T_{50} (°C)	T_m (°C)	% Char yield
DGEBA/BSA	385,1	443,0	437,9	14,8
2,5	413,5	473,5	451,1	18,4
10	417,6	489,7	443,0	19,3
50	433,9	549,6	519,2	33,4
OECh/BSA	446,0	584,1	541,5	43,0

OXYGEN

% OECh	T_5 (°C)	T_{50} (°C)	T_m (°C)	% Char yield
DGEBA/BSA	318,1	467,4	407,5	0,0
2,5	361,8	507,0	559,8	0,3
10	290,7	523,2	564,8	1,3
50	383,1	536,4	588,2	21,9
OECh/BSA	380,0	567,9	579,1	31,7

the LOI parameter. The char yields obtained in argon atmosphere under specified conditions can be linearly related to LOI values by the Van Krevelen linear correlation.[10] In all cases the obtained yield is smaller in oxygen than in argon, which indicates that degradation is more intensive in oxygen or the possible presence of carbon atoms in yield of argon atmosphere. It can be expected that studied systems show a better fire retardancy with the higher content of OECh. The OECh acts via a condensed-phase chemical mechanism altering the pyrolitic path of the substrate. It reduces the amount of gaseous combustibles, by favouring the formation of the char. The reduction in flammability is due to the protecting effect of the residue formed during the burning process due to that the char layer acts both as a thermal insulator and as a barrier to oxygen diffusion.[11] The residue obtained by thermogravimetric analysis, under argon atmosphere, for a ternary sample with a content of OECh of 10 wt % can be seen in Figure 1. On the left side of the figure the external face of the residue is shown. The surface is compact, which indicates the formation of the barrier above mentioned. On the right side, the internal face of the residue is shown. This is porous as it was expected.

With respect to the atmosphere, DTG curves show the behaviour of the sample during the degradation. In argon atmosphere, DGEBA/BSA and OECh/BSA samples show degradation in a single step, while in oxygen atmosphere the degradation happens in two steps for all cases.

By the isoconversional Kissinger-Akahira-Sunose (K-A-S), that is a integral method,[12] activation energies of degradation at each value of conversion (E_i) were calculated from

$$\ln\left(\frac{\beta}{T^2}\right) = \left[\ln\left(\frac{A \cdot R}{E}\right) - \ln G(\alpha)\right] - \frac{E}{RT} \qquad (1)$$

Where $G(\alpha)$ is the integrated form of the conversion function, $f(\alpha)$, which depends on the reaction mechanism. In our case, an autocatalytic mechanism will be considered, where $f(\alpha)$ has the following form: $[\alpha^m(1-\alpha)^n]$. $\beta = dT/dt$ is the heating rate, A is the Arrhenius rate constant, E is the activation energy of the degradation process and R is the gas constant.

Results obtained for values of the conversion, α_i, between 0.05 and 0.95 were plotted in Figure 2. If the activation energy does not vary greatly with the conversion, it is possible to describe the whole mechanism by a single empirical kinetic model even if the real mechanism is complex.[13] In this case, E is approximately constant in the conversion range from 0.3 to 0.8.

The autocatalytical model was supposed to explain the degradation kinetic of this system. The general expression of this model is the following

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot \alpha^m \cdot (1-\alpha)^n \qquad (2)$$

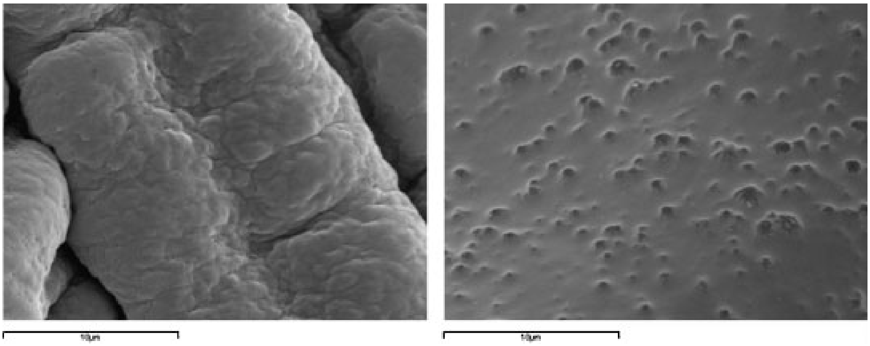

Figure 1.
SEM images of external (left), and internal (right) faces of char residue.

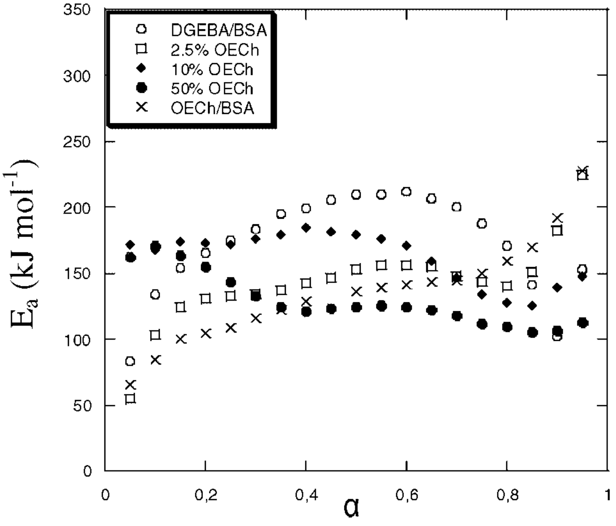

Figure 2.

Activation energy-conversion curves obtained for different contents of OECh.

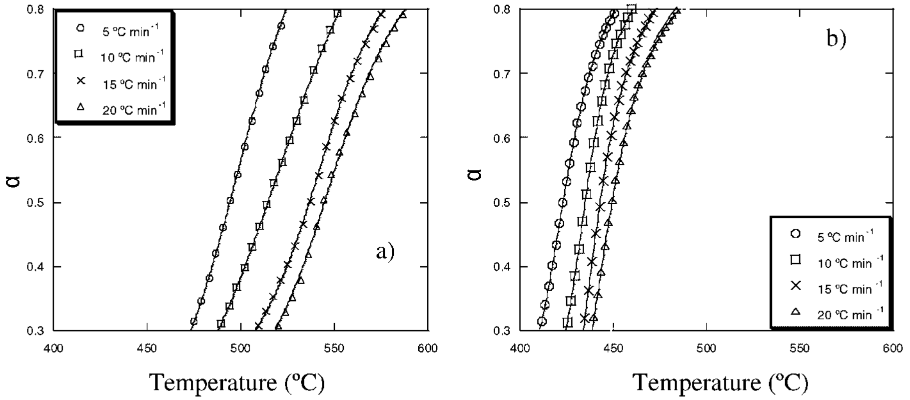

Figure 3.

Comparison of experimental data with kinetic models for studied systems for all heating rates: a) mixture with 50 wt % of OECh, b) unmodified epoxy-amine system

Where *m* and *n* are empirical coefficients. Experimental data were fitted to equation (2) in the range of conversion in which the activation energy is constant. Figure 3 shows experimental curves fit satisfactorily with curves of the autocatalytical model, which indicates that the degradation mechanism of the system does not vary with the presence of OECh.

As can be seen in the figure, it is necessary higher temperatures to reach a determinated degree of conversion when the OECh is added to the epoxy resin. So, it can be concluded that the presence of the inorganic network inhibits the degradation of hybrid materials and it allows the char formation.

Conclusions

The octaepoxy-cyclohexyldimethylsilyl-POSS/DGEBA/BSA composites increase the resistance to degradation of the blend with the percentage in weight of silsesquioxane in inert and oxidant atmosphere. The degradation in oxygen atmosphere is higher than in argon atmosphere, so the char yield values are lower. As the char yield is higher when the content of OECh increases, a better flame retardancy in the samples with the higher percentage of octaepoxy-POSS can be expected. The presence of a protective layer due to the presence of OECh was confirmed by SEM imaging. This fact demostrates the fire retardant effect that OECh produces in the polymeric matrix.

Isoconversional analysis of TGA plots indicates the variation in activation energy of the degradation process with respect to conversion degree. The interval which shows the activation energy approximately constant is used to model the degradation mechanism. It is observed that the presence of OECh does not vary the initial autocatalitical behaviour of the mixture but enhances the thermal stability of them due to its dipersion in the epoxy matrix.

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[1] K. Pielichowski, J. Njuguna, in: "*Thermal degradation of polymeric materials*", Eds., Rapra technology limited, United Kingdom **2005**, p. 206.
[2] E. Manias, G. Polizos, H. Nakajima, M. J. Heidecker, in: "*Flame retardant polymer nanocomposites*", A. B. Morgan, C. A. Wilkie, Eds., Willey & Sons, U.S.A. **2007**, p. 33.
[3] C. U. Pittman, G.-Z. Li, H. Ni, *Macromol. Symp.* **2003**, *196*, 301.
[4] J. J. Schwab, J. D. Lichtenhan, *App. Organometalic. Chem.* **1998**, *12*, 707.
[5] P. Gómez-Romero, C. Sánchez, in: "*Functional hybrid materials*", P. Gómez-Romero, C. Sánchez, Eds., Willey-VCH, Germany **2004**, p. 18.
[6] J. E. Mark, in: "*Hybrid organic-inorganic composites*", J. E. Mark, C. Y.-C. Lee, P. A. Bianconi, Eds., ACS symposium series, Washington DC **1995**, p. 1.
[7] L. Barral, F. J. Díez, S. García-Garabal, J. López, B. Montero, R. Montes, C. Ramírez, M. Rico, *Eur. Polym. J.* **2005**, *41*, 1662.
[8] M. J. Abad, L. Barral, D. F. Fasce, R. J. J. Williams, *Macromolecules* **2003**, *36*, 3128.
[9] J. Choi, S. G. Kim, R. M. Laine, *Macromolecules* **2004**, *37*, 99.
[10] D. W. Van Krevelen, *Polymer* **1975**, *16*, 615.
[11] S. Levchik, C. A. Wilkie, in: "*Fire retardancy of polymeric materials*", A. F. Grand, C. A. Wilkie, Eds., Marcel Dekker, Inc., New York **2000**, p. 173.
[12] P. Simon, *J. Therm. Anal. Cal.* **2004**, *76*, 123.
[13] J. Macan, I. Brnardic, S. Orlic, H. Ivankovic, M. Ivankovic, *Polym. Degrad. Stab.* **2006**, *91*, 122.