Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 153–157

STUDY OF AN OCTAEPOXYSILSESQUIOXANE CURED WITH A DIAMINE

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Cubic silsesquioxanes offer access to organic/inorganic hybrids. A system formed by a polyhedral oligomeric silsesquioxane (POSS) with eight epoxy reactive groups per molecule, octaepoxycyclohexyldimethylsilyl-POSS, cured with an aliphatic diamine (bisaniline) was studied in different ratios. The characterization of the POSS was carried out by differential scanning calorimetry (DSC) and thermogravimetry (TG). The distribution of species in the reaction of the mixtures POSS/diamine was followed by gel permeation chromatography (GPC). The degradation was studied by thermogravimetric analysis.

Keywords: *diamine, gel permeation chromatography, octaepoxycyclohexyldimethylsilyl-POSS, silsesquioxane, thermal analysis*

Introduction

The term silsesquioxane refers to all structures with the empirical formulae $(RSiO_{1.5})_n$, where R is hydrogen inert or organic reactive groups. The polyhedral oligomeric silsesquioxanes, designated by the abbreviation POSS, have a cubic silica core, rigid and completely defined (0.53 nm diameter) and eight organic functional groups are appended to the vertexes of the cube via Si–O linkages. These materials allow to obtain nanocomposites due to the architecture of the organic components between the cubes can be modified in a systematic manner. In principle, the reactions, that form organic tethers between cubes, will also be well defined so as to ensure complete control of the length scales of each component in the resulting nanocomposite [1].

The incorporation of POSS derivatives into polymeric materials can lead to improve in polymer properties, which include increases in use temperature, oxidation resistance, improved mechanical properties as well as reductions in flammability and viscosity during processing [2–5].

The aim of this work was to study the behaviour of the hybrid system epoxy-POSS/diamine in different ratios by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetry (TG) [6, 7] and, in consequence, to select the suitable ratio. A study of comparation of this POSS/diamine and the epoxy system based on diglycidyl ether of bisphenol A (DGEBA) and the same diamine, will be done at an early date.

Experimental

Materials

The chemical structure of the selected POSS is shown in Fig. 1. It is octaepoxycyclohexyldimethylsilyl-POSS (OECh-POSS) from Hybrid Plastics (Fountain Valley, CA). The OECh-POSS has an inorganic silico-like core and it is surrounded by eight organic reactive groups, epoxy. Its chemical formula is $C_{80}H_{152}O_{28}Si_{16}$ with a molar mass of 2011.41 g mol^{-1}. Its appearence is a white power, and it is soluble in solvents such as tetrahydrofuran and dichloromethane, but insoluble in hexane.

The diamine used as hardener was 4,4’-(1,3-phenylenediisopropylidene)bisaniline (BSA) from Aldrich (Milwaukee, WI), >98% purity, and molar mass of 344.5 g mol^{-1}. Its chemical structure is also shown in Fig. 1. Its melting temperature was 113.7°C, determined by DSC. The thermal stability was analyzed and the results suggest that at 200°C the BSA can not be used.

In formulating OECh-POSS/BSA composites, a variable N was defined as the molar ratio of epoxy ring (in POSS) to NH_2 (in diamine). Thus, when N=0.5, there are equal numbers of hydrogen and epoxy groups in the sample mixture [8, 9]. The formulations used in this work were 0.25, 0.5 and 1.

Suitable amounts of POSS and BSA were mixed at room temperature for one hour. For thermal analysis, the mixture was cured 3 h at 130°C and postcured 4 h at 150°C.

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1388–6150/$20.00

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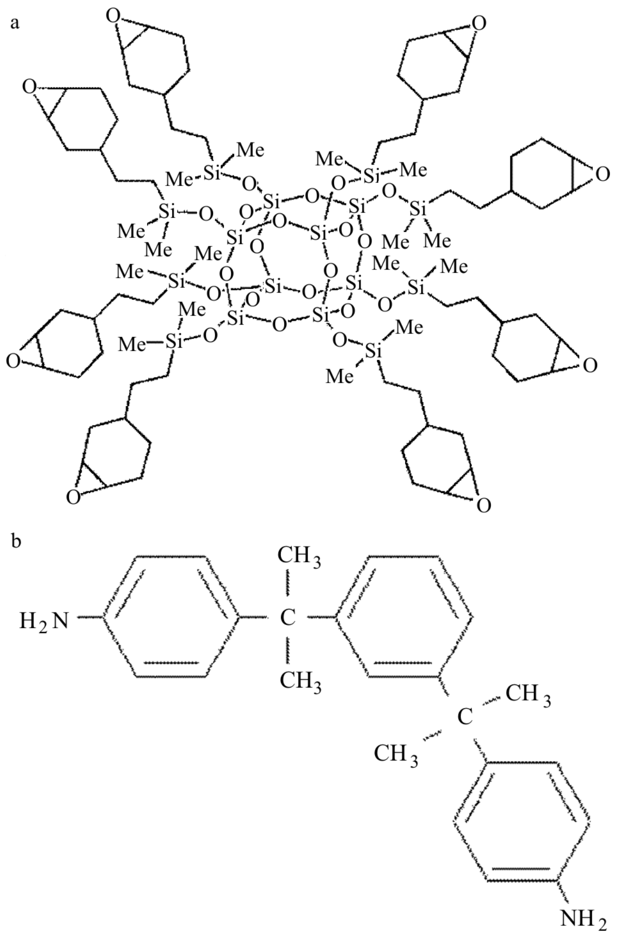

Fig. 1 Chemical structures a – OECh-POSS, b – BSA

Techniques

The reactions between the POSS and the diamine in different ratios were followed by GPC. It was employed a Waters 2695 separations module (Waters Chromatography Division/Millipore, Mildorf, MA) equipped with a quaternary bomb and an automatic injector. Detection was performed with a Waters 996 UV/VIS photodiode array detector and Millenium software (Version 3.20) was used for the acquisition and treatment of data. The column was a Styragel HR 1 THF 7.8×300 mm. The chromatographic conditions used were as follows: elution in the isocratic mode with mobile phase tetrahydrofuran (THF), (Merck, Darmstadt, Germany) 0.3 mL min^{-1} flow rate, and injection volume of 10 μL. Chromatograms were obtained at the 254 nm line. Calibrations were performed by external standard method. The working standards were prepared by dilution of 1000 mg L^{-1} stock solution prepared in THF.

DSC measurements were performed with a Perkin Elmer DSC-7, supported by a Perkin Elmer Computer for date acquisition (Perkin Elmer Cetus Instruments, Norwalk, CT). The DSC was calibrated with high-purity indium. A dry nitrogen flow of 40 mL min^{-1} was used as purge gas.

Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 microbalance coupled with a Perkin Elmer microprocessor under an argon and oxygen atmosphere, flowing at a rate of 100 mL min^{-1} was used. Nickel and perkalloy were used in the calibration.

Results and discussion

The OECh-POSS was characterized by DSC. The scan obtained at 10 K min^{-1} shows well defined peaks both heating and cooling (Fig. 2). The melting temperature is the extrapolated used [10] and the melting peak temperature was 123.4°C (melting heat of 21.1 J g^{-1}) and in the cooling scan the peak was at 93.4°C (crystallization heat of 15.9 J g^{-1}). The second heating scan shows the peak at lower temperature, at 110.1°C, and heat of 16.3 J g^{-1}. Besides, it was tested by TG, in inert and oxygen atmosphere. The dynamic runs were made at 10 K min^{-1} and the isothermal runs at different temperatures in both atmospheres. The results are shown in Table 1, where T_i is the beginning temperature, $T_{5\%}$ is the temperature at 5% mass loss, T_{max} is the temperature at which the maximum degradation rate is exhibited and the last column is the char at 800°C. The temperature region comprising melting and degradation of the OECh-POSS defines its processability window [11, 12].

The reactions of the different systems POSS/diamine were followed by gel permeation chromatography. Several vials were prepared containing known masses for each formulation. The mass of each sample was 20 mg. The glass vials with the samples were heated to different temperatures in an oven and were maintained at that temperature for the time necessary to complete the reaction. At a designated time interval, one

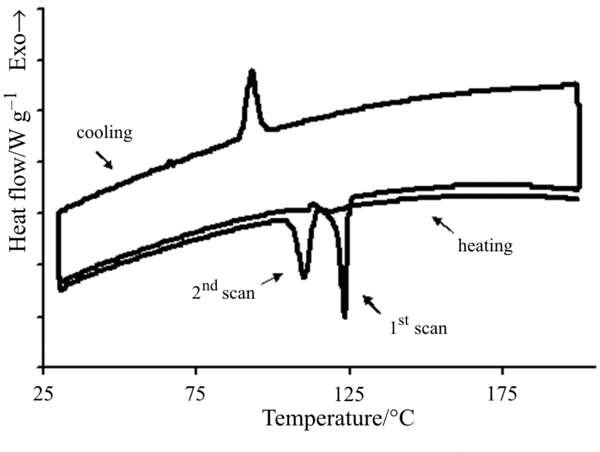

Fig. 2 DSC scans of OECh-POSS at 10 K min^{-1}. Heating and cooling scans

Table 1 Results obtained of OECh-POSS by TG

Dynamic runs				
	T_i/°C	$T_{5\%}$/°C	T_{max}/°C	%Char (at 800°C)
Argon	239.8	335.6	470.0	45.2
Oxygen	250.7	336.9	440.0	45.8
Isothermal runs				
	T/°C	t for 5%/min	%Char (at 120 min)	
Argon	280	0.73	96.1	
	300	0.88	94.8	
	320	0.88	94.2	
	340	0.73	92.0	
Oxygen	260	1.03	92.5	
	280	1.91	85.9	
	300	1.25	79.2	

vial was withdrawn from the oven and the reaction was suddenly stopped in ice water. Subsequently, it was loaded with a premeasured volume of THF solvent.

The reactions were made at 150, 160, 170 and 180°C. At the temperature of 160°C, for the mixture rich in silsesquioxane, the samples were reacted at different times until 480 min. The mixture rich in amine at 240 min begins the gelation and the reaction stops. The chromatograms of the reaction made at this temperature show the evolution of the different species at the end of the reaction (Fig. 3). The OECh-POSS did not have any significant absorption at 254 nm, so the signal of the UV detector was only sensitive to the amount of BSA. Therefore, the relative areas (or heights) of different peaks represent the molar fractions of the different species obtained in the mixture of the reaction. At t=0, there was not conversion and only appear the peak corresponding to the unreacted amine. The peaks of the mono-, di- and trisubstituted amines appear in the three systems at various time periods. The tetrasubstituted amine does not appear if the mixture is poor in amine. As much amine the system has, the reaction evolves for a longer time. At 240 min, the unreacted amine was similar for the three concentrations, however the distribution of species is different and this fact can be due to the compact structure of the silsesquioxane.

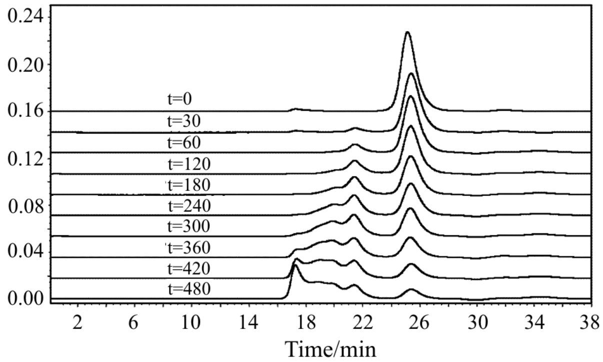

Fig. 3 GPC chromatograms of the system OECh-POSS/BSA rich in POSS obtained at different times reacted at 160°C (t=0 min, t=30 min, and from t=60 min to t=480 min with increments of 60 min)

Figure 4 shows the distribution of species where A_0, A_1, A_2, A_3 and A_4 are the integration of the areas of the peaks corresponding to the unreacted and substituted amines and A_t=ΣA_i with i=0–4. A_0/A_t is the fraction of initial monomer that remains unreacted, A_1/A_t is the fraction that arises from the simultaneous probability that one functionality has reacted and the other three remain unreacted, and the other fractions were obtained using similar arguments.

The curing process, barely, can be gone on by DSC, but this technique is useful to determine the

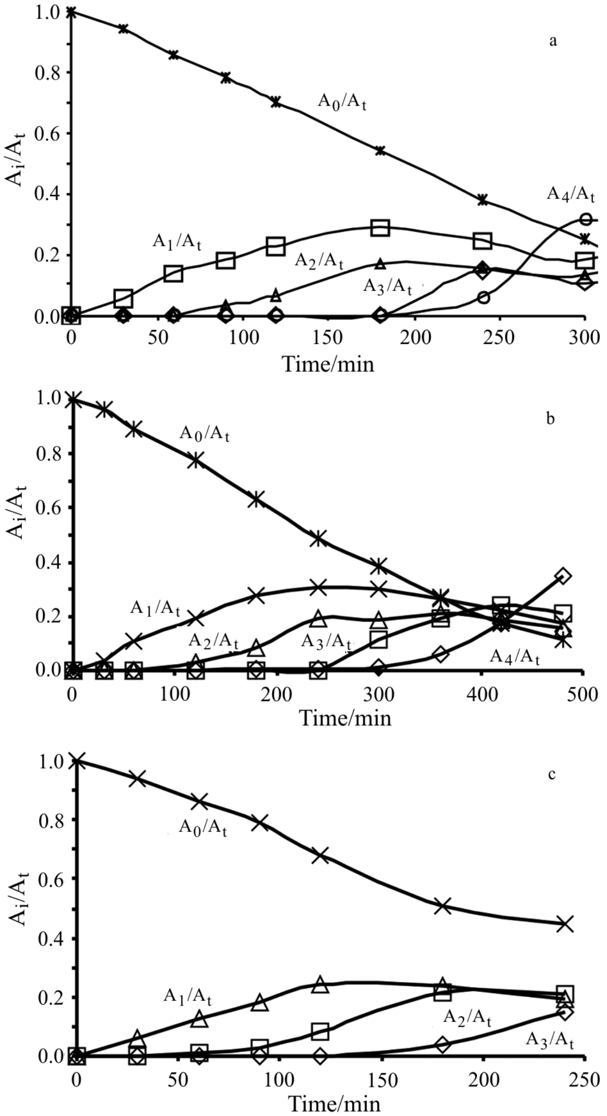

Fig. 4 Distribution of the amine mono-, di-, tri- and tetrasubstituted; a – N=0.5, b – N=1, c – N=0.25

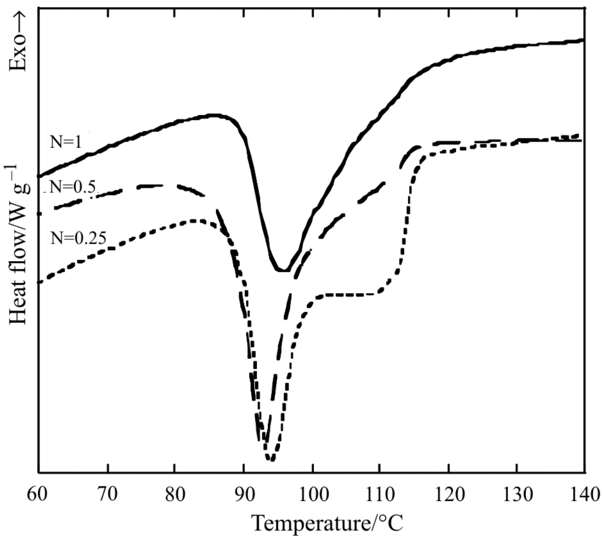

Fig. 5 DSC scans of OECh-POSS/BSA

behavior in the melting process. Figure 5 shows the scans of the three systems POSS/amine. Meanwhile, the POSS and BSA have melting temperatures higher than 100°C (123.3°C for POSS and 113.7°C for BSA), the mixture of both, melts between 92 and 96°C, appearing a clear second peak about 110°C in the mixture rich in amine. The heat reaction can be calculated for the stoichiometric ratio, but this process is not easily detected for the specimens rich in amine and POSS. The determination of glass transition by this technique is not possible and it is to appear in forthcoming publication by dynamo-mechanical analysis.

The thermogravimetric scans of OECh-POSS/BSA nanocomposites with various ratios are shown in Fig. 6, in atmosphere of argon and oxygen. The mass loss process in inert atmosphere takes place in two stages. A minor mass loss that began at 200°C is attributed to the elimination of water formed by the condensation of residual Si–OH groups [13]. The major mass loss occurred beyond 400°C for the mixture rich in POSS and close to 500°C for the other two mixtures, which was connected with the decomposition of the organic polymer. The temperatures for 5% mass loss and at the maximum decomposition rate

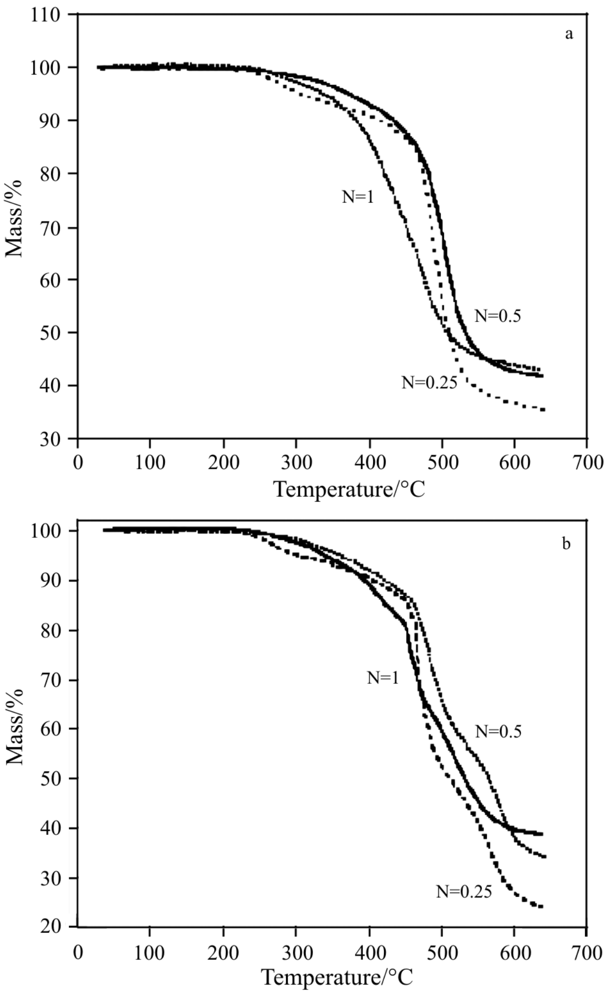

Fig. 6 TG diagrams of OECh-POSS/BSA; a – inert atmosphere, b – oxygen atmosphere

($T_{\max}$) in the TG scans are summarized in Table 2. It is understandable that the introduction of the inorganic phase improved the mass retention at 650°C.

In oxygen atmosphere the behaviour in the decomposition is different. The formation of new molecules by oxidation of silicon involves a degradation in several steps as it can be seen in Fig. 6b. The chars at 650°C (Table 2) are less in oxygen atmosphere than in argon.

Table 2 Results obtained of the three systems OECh-POSS/BSA

Sample	Atmosphere	Inorganic phase content/%	T for 5% mass loss/°C	$T_{\max}$/°C	Mass retention at 650°C/%
N=0.25		17.7	280.4	485.0	35.5
N=0.5	argon	15.4	339.4	506.0	41.8
N=1		12.3	302.9	466.0	42.9
N=0.25		17.7	280.0	469.0	24.3
N=0.5	oxygen	15.4	328.5	485.0	34.5
N=1		12.3	313.1	458.0	38.9

Conclusions

A new material of high molar mass belonging to polyhedral oligomeric silsesquioxanes, the OECh-POSS, was characterized by DSC and TG. The reaction of the OECh-POSS with an aromatic diamine bisaniline at different ratios at the temperatures: 150, 160, 170 and 180°C, was followed by gel permeation chromatography. The temperature of 160°C was considered as the suitable temperature for the different molar ratios. The system OECh-POSS/BSA with *N*=0.5, where there is equal number of epoxy groups and hydrogens, presents the better distribution of species, appearing amine mono-, di-, tri- and tetrasubstituted before the gelation. The tests made by DSC do not show the glass transition. The thermogravimetric analysis shows the degradation of the three systems, which takes place in several steps both argon and oxygen atmosphere. Minor inorganic phase content induces a major char at 650°C.

The system OECh-POSS/BSA (*N*=0.5) cured during 300 min at 160°C will be compared with a system where the POSS will be substituted by diglycidyl ether of bisphenol A.

Acknowledgements

Financial support for this work has been provided by Ministerio de Educación y Ciencia (Spain) and FEDER (MAT2004-01580).

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