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THERMAL BEHAVIOUR OF A POLYHEDRAL OLIGOMERIC SILSESQUIOXANE WITH EPOXY RESIN CURED BY DIAMINES

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Abstract

A new material belongs to the family of polyhedral oligomeric silsesquioxanes, the 1-(3-glycidyl) propoxy-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.1(3,9).1(5,15).1(7,13)]octasiloxane (glycidylisobutyl-POSS) is characterized by differential scanning calorimetry, thermogravimetric analysis and atomic force microscopy. Epoxy systems based on diglycidyl ether of bisphenol A (DGEBA) cured with the diamines, 4,4'-diamine-diphenylmethane (DDM) and 1,4-phenylenediamine (pPDA), were kinetically studied by differential scanning calorimetry in isothermal and dynamic modes. The thermal behaviour of these systems as the glycidylisobutyl-POSS was added, is discussed later.

Keywords: differential scanning calorimetry, epoxy systems, glycidylisobutyl-POSS, polyhedral oligomeric silsesquioxanes

Introduction

The development of macromolecules containing inorganic or organometallic segments promises to yield plastics with a variety of new and improved properties. The silsesquioxanes (SSQQ) are a class of oligomeric organosiliceous compound of the empirical formulae $RSiO_{3/2}$. The name derives from the non-integer (one and one-half or sesqui) ratio between oxygen and silicon atoms, and the organic substituent. A kind of them, the polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical feedstock technology for the preparation of nanoreinforced plastics. The establishment of broad chemical trees of monomeric POSS reagents and resins, based on well-defined POSS cages, affords new chemical feedstock for the modification of properties in nearly all traditional organic polymeric materials [1, 2].

The POSS molecule contains a polyhedral silicon–oxygen nanostructural skeleton with intermittent siloxane chains $(SiO_{3/2})_n$ which was first reported in 1946 [3]. A variety of substituents can be incorporated on the silicon atom, with recent interest fo-

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cusing on the incorporation of a polymerizable group on one of the silicon atoms, and aliphatic hydrocarbon group on the remaining silicon atoms, to impart desiderable solubility properties. These molecules, POSS monomers, can be polymerized to the corresponding POSS macromers and polymers [4].

The POSS molecules have been successfully incorporated into different polymers by scientists from the Air Force Research Laboratory (AFRL) [5, 6]. Studies have shown that such organic–inorganic hybrid polymers possess improved properties such as higher T_g, increased oxygen permeability, reduced flammability and enhanced mechanical strength [7].

Epoxy resins are by far the most commonly used engineering thermosets [8], in part due to their excellent engineering performance upon curing and ease of processing prior to curing.

In this paper, we report on the thermal behaviour of cured epoxy networks containing POSS–epoxy nanoreinforcements after studying the neat epoxy systems as other similar systems studied by us [9–12].

Experimental

In this study, the POSS molecule $(SiO_{3/2})_n$ has n=8 (cage-like) and is surrounded by eight organic groups, of which seven are inert, isobutyl, and just one is reactive glycidyl. This POSS is the 1-(3-glycidyl) propoxy-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.1(3,9).1(5,15).1(7,13)]octasiloxane, (glycidylisobutyl-POSS), (EP.0418, Hybrid Plastics), which allows its incorporation at the different epoxy nets, which molecular mass is 931.63 g mol^{-1} (Fig. 1a).

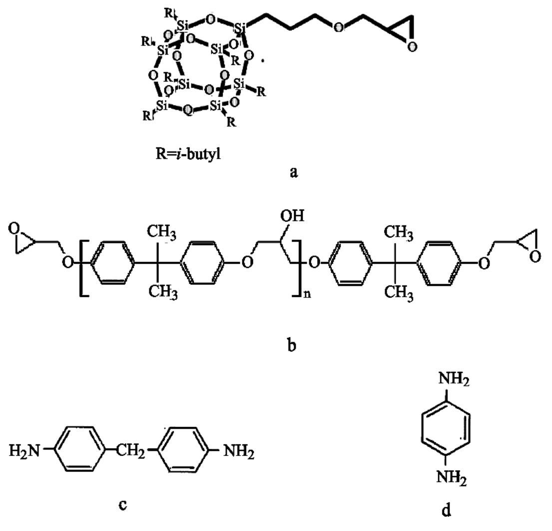

Fig. 1 Structure image of the materials. a – glycidylisobutyl-POSS; b – diglycidyl ether of bisphenol A (DGEBA); c – 4-4'-diamino-diphenylmethane (DDM); d – 1,4-phenylenediamine (pPDA)

The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA), Araldite GY 260 from CIBA, (Fig. 1b), with a mass per epoxy equivalent of 205.1 g eq^{-1} as determined by hydrochlorination [13] in our laboratory.

The diamines used were 4,4'-diamine-diphenylmethane (DDM) from Fluka and 1,4-phenylenediamine (pPDA) from Aldrich and (Figs 1c and 1d) with molecular masses of 198.27 and 108.14 g mol^{-1}, manufacturer purity values of >98 and 97% according to the suppliers, and melting temperatures of 88–92ºC and 143–145ºC, respectively.

All components were used as received without further purification.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-7 equipped with an intracooler. The instrument was calibrated using the melting transition of pure indium. The baseline was checked frequently. The measurements were performed under a continuous flow of dry nitrogen (40 mL min^{-1}).

Results and discussion

Characterization of glycidylisobutyl-POSS

The glycidylisobutyl-POSS was characterized by differential scanning calorimetry (Fig. 2). The curve obtained at 10ºC min^{-1} shows two well defined melting peaks at

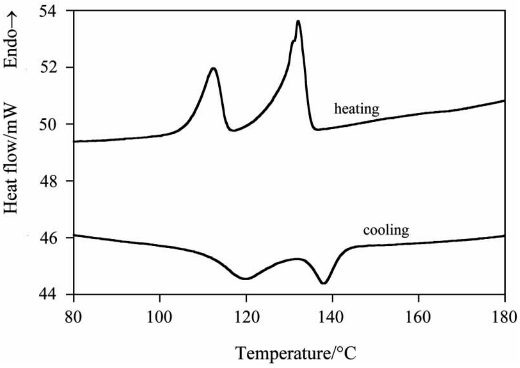

Fig. 2 DSC scans of glycidylisobutyl-POSS at 10°C min^{-1}. Heating and cooling

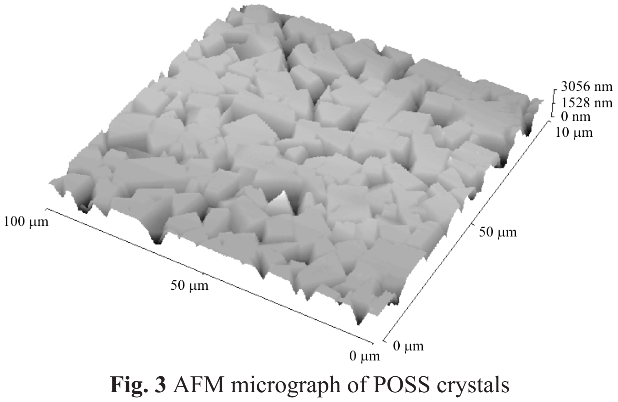

Fig. 3 AFM micrograph of POSS crystals

112.4 and 133.4ºC (total melting heat of 26.1 J g^{-1}) and two crystallization peaks in the cooling scan at 119.1 and 139.2ºC at the rate of 10ºC min^{-1} (total crystallization heat of 15.1 J g^{-1}). This fact proves the POSS is crystalline, as it can see by Atomic Force Microscopy (AFM), μTA 2990 of TA Instruments [14]. The image obtained (Fig. 3) shows the crystal size between 9 and 10 μm.

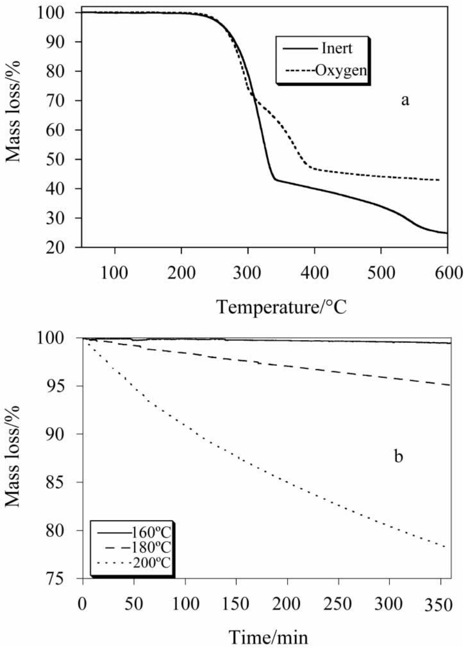

Fig. 4 Degradation of glycidylisobutyl-POSS by TG

To complete the thermal characterization of the glycidylisobutyl-POSS, it was tested by thermogravimetry both argon and oxygen atmosphere in a Perkin Elmer TGA-7 thermogravimetric analyzer. The dynamic runs (Fig. 4a) were made at 10ºC min^{-1}. The mass loss is higher in oxygen than at inert atmosphere, at 600ºC the char is 24.4 and 42.7%, respectively. Isothermal runs (Fig. 4b) were made at 160, 180 and 200ºC. At 360 min the chars were 99.4, 95.1 and 78.1% at inert atmosphere.

Epoxy/amine systems: kinetic analysis procedures

The activation energies for both neat epoxy resin systems were studied. The system DGEBA/DDM was prepared in a ratio 3:4 and the system DGEBA/pPDA in a stoichiometric ratio. Dynamic and isothermal runs were conducted. For dynamic heating, five different heating rates were tested: 5, 7.5, 10, 15 and 20ºC min^{-1} from 30 to 250 and 200ºC, respectively.

Kinetic analysis was performed using Kissinger [15] and Flynn–Wall–Ozawa [16, 17] methods. According to the Kissinger expression

$$\frac{\mathrm{d}[\ln(q/T_\mathrm{p}^2)]}{\mathrm{d}(1/T_\mathrm{p})}=-\frac{E}{R} \tag{1}$$

where T_p is the maximum rate temperature, q is a constant heating rate and R is the universal gas constant. Plotting $\ln(q/T_\mathrm{p}^2)$ *vs*. reciprocal peak temperature, the activation energy, E, is obtained.

The Flynn–Wall–Ozawa method, based on the Doyle's approximation, obtains one equation of the integrated form of the conversion dependence function, $g(\alpha)$

$$\log(q)=\log\left[\frac{AE}{g(\alpha)R}\right]-2.315-\frac{0.457E}{RT} \tag{2}$$

where A is the pre-exponential factor. In this study, this equation is applied to the maximum rate where the peaks appear and with its, the activation energy is calculated. These results are shown in Table 1.

Table 1 Temperature of the peaks of the exotherms from DSC for both systems and activation energies

	q/°C min^{-1}	T_p/°C DGEBA/DDM	T_p/°C DGEBA/pPDA
	5	139.6	113.2
	7.5	150.1	120.6
	10	156.7	125.6
	15	169.1	137.9
	20	177.7	140.8
Activation energies/kJ mol^{-1}	Kissinger	49.1	53.4
	Flynn–Wall–Ozawa	53.6	58.9

Moreover, the autocatalytic method of Sourour and Kamal [18], based in isothermal runs, was studied. The runs were conducted at the temperature of 120, 130, 140 and 150ºC for DGEBA/DDM and 80, 90, 100, 110 and 120ºC for the DGEBA/pPDA, in order to obtain both the cure rate and the extent of reaction as function of time.

The generalized expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2\alpha^{\mathrm{m}})(1-\alpha)^{\mathrm{n}} \tag{3}$$

where α is the conversion, k_1 and k_2 the rate constants and, m and n are the reaction orders, gives activation energies of 42.7 and 41.9 kJ mol^{-1} for DGEBA/DDM and 59.2 and 38.4 kJ mol^{-1} for DGEBA/pPDA.

POSS systems: thermal behaviour

The aim of this work is to obtain a good system epoxy/diamine with POSS to study lately the mechanical behaviour. For that, firstly, the POSS and the diamines, were dissolved in tetrahydrofuran (THF).

The POSS and the DDM were mixed in the ratio 1:4 and tested in DSC at 10ºC min^{-1}. The first scan shows two melting peaks, at about 93ºC from the diamine and about 120ºC from the POSS. The second peak of the POSS does not appear because the reaction already began. A heat reaction of 110 kJ by equivalent is obtained (Fig. 5). In the second scan, a transition temperature appears in 106ºC, and a melting peak at 149ºC.

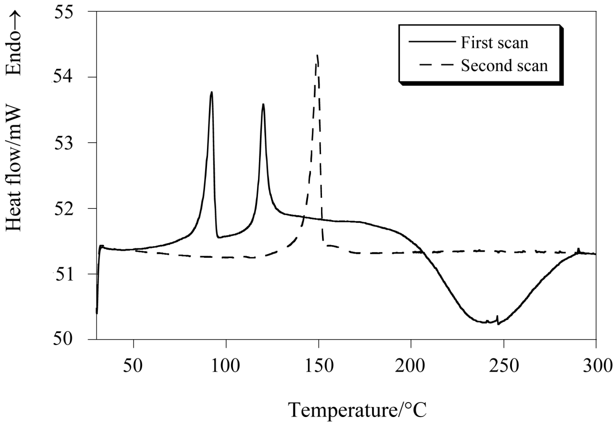

Fig. 5 DSC scans of the system POSS/DDM.

The dynamic run points out, the isothermal temperatures to reaction POSS and DDM. These temperatures have to be less than the degradation temperature of the POSS. The selected temperatures were 160, 180 and 200ºC. POSS/DDM were cured for 10 min and the later dynamic runs show the melting peaks and the reaction between the POSS and the diamine. The dynamic run, subsequent the cure at 200ºC, shows that there is not heat reaction (Fig. 6). The reaction between POSS and DDM has finished.

Finally, the precursor POSS/DDM cured for 2 h at 170ºC was selected, and so, it can not assess the degradation of POSS. The precursor, cured so, was added to DGEBA, until having stoichiometric mixed. The DSC run of POSS/DDM/DGEBA shows two transition temperatures in the second scan (at 103 and 126ºC) and a later small melting peak (Fig. 7).

The other precursor POSS/pPDA was not dissolved in THF, because both reacted. The POSS and the pPDA were mixed in the ratio 0.5:4.

The DGEBA was added at this precursor in a stoichiometric ratio. It was tested in DSC at 10ºC min^{-1}. In the second scan, two T_g's appear at 119.3 and 141.5ºC, this result indicates the two phases of the system (Fig. 8).

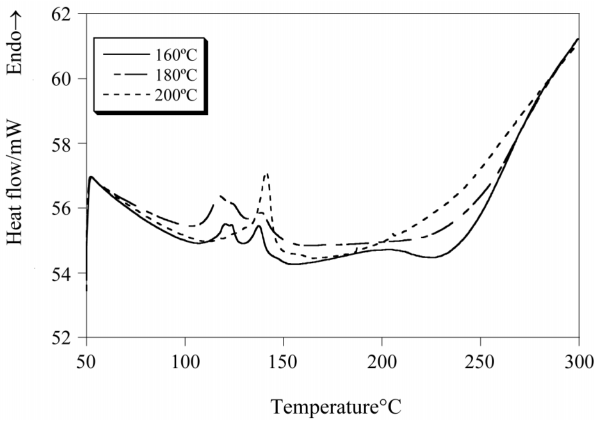

Fig. 6 DSC scans of the system POSS/DDM at 10°C min^{-1} after 10 min at

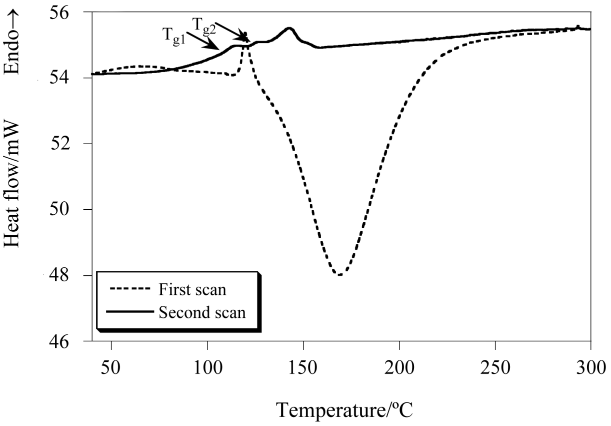

Fig. 7 DSC scans of the system POSS/DDM/DGEBA. First and second scan at 10°C min^{-1}

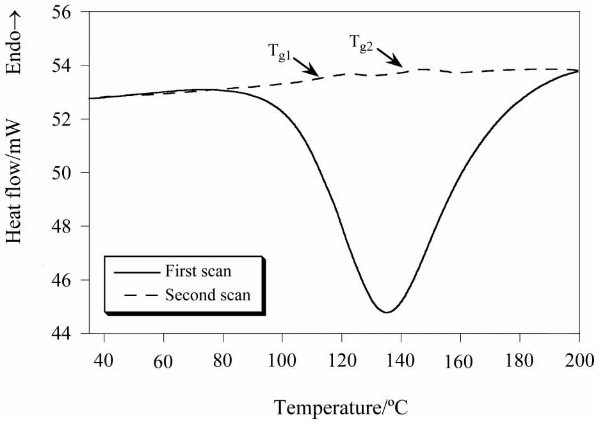

Fig. 8 DSC scans of the system POSS/pPDA/DGEBA. First and second scan at 10°C min^{-1}

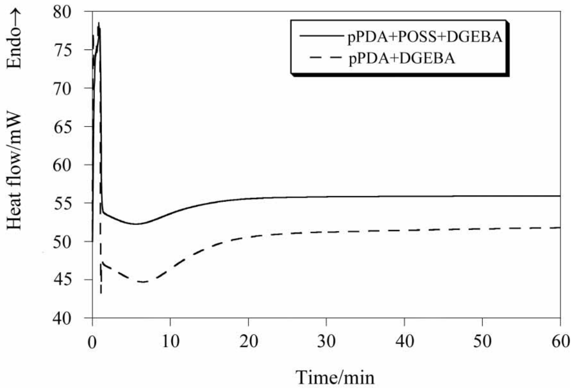

Fig. 9 Isothermal treatment at 100°C

The isothermal behaviour was also studied. Figure 9 displays the isothermals at 100ºC of this system with and without POSS. Lesser heat reaction at all temperatures is registered in the system with the POSS.

Conclusions

A new material belongs to polyhedral oligomeric silsesquioxanes, the glycidylisobutyl-POSS was characterized by differential scanning calorimetry. It was obtained, that it is crystalline, as it was also probed by atomic force microscopy. The used temperature of the POSS is limited by the beginning of degradation at 180ºC, as it can be seen by thermogravimetry. For a short period of time, e.g. 10 min, even the temperature of 200ºC can be used.

The thermal behaviour of the epoxy systems based on DGEBA cured by the diamines DDM and pPDA modified with glycidylisobutyl-POSS are studied. Firstly the precursors, POSS with diamine, were reacted and then the DGEBA was added. The best cured obtained for the system POSS/DDM was 2 h at 170ºC and for the system POSS/pPDA was an hour at 100ºC.

The ternary systems show two transition temperatures in the second scans in the DSC, this fact means the presence of two phases.

After studying both systems, it was determined that, the system cured by DDM offers better possibilities to prepare the specimens to analyze mechanical properties.

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