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Thermodegradation kinetics of a hybrid inorganic–organic epoxy system

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Abstract

Lifetime of the epoxy system formed by diglycidyl ether of bisphenol A, DGEBA/4,4′-diaminediphenylmethane, DDM, modified with the silsesquioxane, glycidylisobutyl-POSS, was calculated from thermogravimetric analysis. The activation energy of the decomposition of this system was evaluated by the integral method developed by Flynn–Wall–Ozawa ($E = 88.9 \pm 2.1$ kJ mol^{-1}) and by Coats and Redfern method ($E = 85.2 \pm 1.5$ kJ mol^{-1}). The kinetic parameters have been used to estimate the lifetime of the system POSS/DGEBA/DDM. The obtained results by two different ways are similar.

Keywords: Inorganic–organic hybrid; Thermogravimetry; Lifetime; Epoxy system

1. Introduction

Macromolecules containing inorganic or organometallic segments have attracted a great deal of attention recently, due to their potential as candidate materials for bridging the gap between organic polymers and inorganic materials. In particular, the use of polyhedral oligomeric silsesquioxanes (POSS) nanoparticles has been demonstrated to be an efficient method in the design of hybrid materials [1–3]. A typical POSS macromonomer has an inorganic Si_8O_{12} core, surrounded by eight organic groups on the corners, where, one at least, is reactive.

In polymer science, thermal analysis methods have found important applications, among them the determination of kinetic parameters. Thermodegradation kinetics can be studied by thermogravimetric analysis, which is an useful tool, because the information can be obtained from a single thermogram. Kinetic parameters such as activation energies and pre-exponential factors are calculated using integral and differential methods reported in the literature [4]. With experimental procedures, information about the kinetics of decomposition and in-use lifetime projections can be obtained. The ability to predict the lifetime is valuable, because the costs of pre-mature failure in actual end use can be high. TG provides a method for accelerating the lifetime testing of polymers so that short-term experiments can be used to predict in-use lifetime [5,6]. The lifetime is considered

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when 5% mass loss is reached from a dynamic thermogravimetric analysis [7,8].

In a previous article, the behaviour degradation by thermogravimetric analysis was studied for epoxy systems [9] and by the other hand, systems based on silsesquioxanes are being studied [10–12].

The main objective of this work was to study the kinetic of thermal degradation of a system based on the epoxy diglycidyl ether of bisphenol A (DGEBA) cured with a diamine, and modified with a polyhedral oligomeric silsesquioxane. Using thermogravimetric data, the lifetime can be calculated and extrapoling the obtained results to high temperatures to usable temperature. It offers a simple and convenient approach to use as an accelerated ageing process for quality control experiments.

2. Experimental

2.1. Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (DGEBA) Araldite GY 260 from Ciba-Geigy (Summit, NJ), with weight per epoxy equivalent of 205.1 g eq^{-1}, as determinated by hydrochlorination in our laboratory. The curing agent was 4,4′-diaminediphenylmethane (DDM) from Fluka (Buchs, Switzerland), with molecular weight of 198.26 g mol^{-1}, manufacturer purity value of 98%, according to the supplier, and melting point of 96.3 °C determined by differential scanning calorimetry.

The polyhedral oligomeric silsesquioxane was 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), EPO418 from Hybrid Plastics (Fountain Valley, CA), which molecular weight is 931.63 g mol^{-1} (Fig. 1a). The glycidylisobutyl-POSS was characterized by different techniques [13]. To complete its thermal characterization, it was tested by thermogravimetry in dynamic (at 10 °C min^{-1}) and isothermal modes (at 160, 180, and 200 ° C) (Fig. 1b and c). At the temperature of 200 °C a significant thermal degradation was observed.

2.2. Sample preparation

The POSS and DDM in a proportion 1:4, were dissolved in tetrahydrofuran (THF), at room temperature with a magnetic stirrer, and the solvent was evaporated at 60 °C in a conventional oven for 24 h. The resulting solid was milled, heated to 160 °C, and kept at this temperature for 120 min, to complete the epoxy amine reaction. The polymer network was synthesized adding stoichiometric amount of DGEBA, mixing at about 115 °C, pouring the solution into a glass and curing at 160 °C for 40 min. The POSS fraction in the resulting polymer network was 64%. The tested samples were about 8 mg.

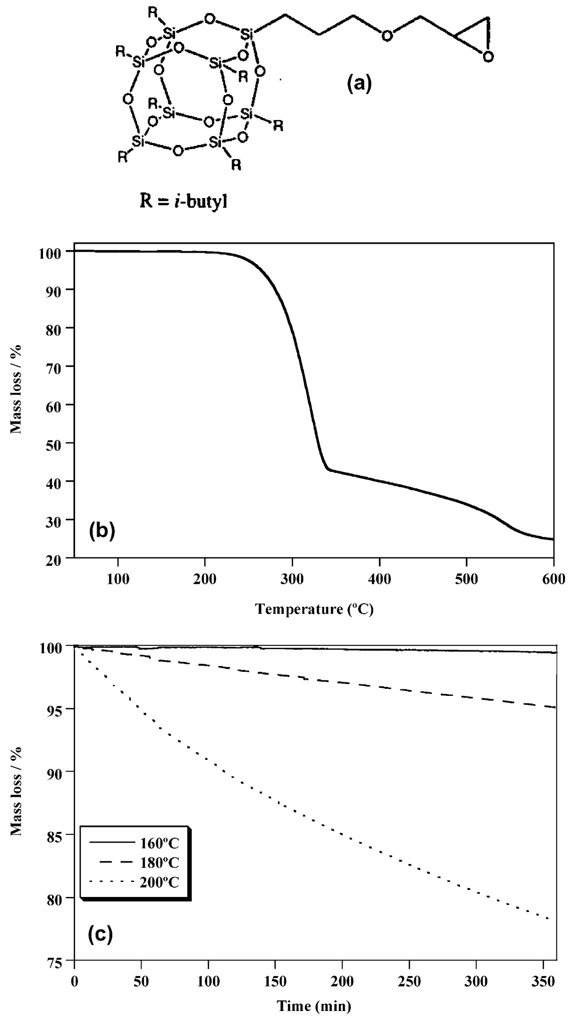

Fig. 1. Characterization of the POSS. (a) Molecular structure; (b) dynamic TG thermogram; (c) isothermal TG thermograms.

2.3. Instrumental method

Thermogravimetric analysis was performed with a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor. The microbalance was calibrated making use of the Curie points of perkalloy and nickel. Dynamic experiments were conducted in an argon atmosphere flowing at a rate of 100 ml min^{-1}. The heating rates were 2.5, 5, 10, 15, and 20 °C min^{-1}. The temperature range of the experiments was from 50 to 600 °C. Fig. 2 shows the TG curves.

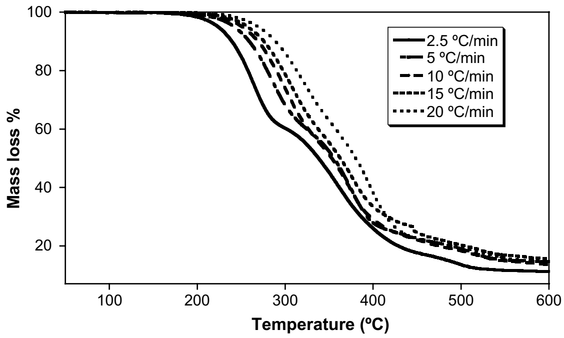

Fig. 2. Experimental TG curves at different heating rates.

3. Results and discussion

The reaction rate of a solid state reaction, dα/dt, can be expressed as a function of conversion and temperature

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

where t is the time, $k(T)$ is the rate constant of thermal decomposition, and $f(\alpha)$ is the conversion dependence function. The reaction rate constant, $k(T)$, has been described by the Arrhenius expression

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

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant. The integrated form of Eq. (1) is generally expressed as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k(T)t \tag{3}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

The method established by Flynn–Wall–Ozawa [14,15] is an integral method for determining the activation energies without any assumption about the reaction order. The integral form of the rate equation is generally expressed as

$$g(\alpha) = \frac{AE}{qR}p(x) \tag{4}$$

where

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2}\,dx \tag{5}$$

and $x = E/RT$, $f(\alpha)$ and $g(\alpha)$ are the conversion dependence functions defined by Eqs. (1) and (3), respectively, and q is the heating rate. Several techniques using different mathematical approaches have been developed for solving the integral $p(x)$ function [16].

Doyle's approximation [17] for the integral $p(x)$, a linear approximation, is used by Flynn–Wall–Ozawa and Eq. (4) has been expressed as

$$\log(q) = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \tag{6}$$

The activation energies, E, can be obtained from a logarithmic plot of heating rates, q, as a function of the reciprocal of temperature, T^{-1}, for a constant $g(\alpha)$, since the slope of such a line is given by $-0.457\ E/R$. This plot is shown in Fig. 3 for $0.05 \leqslant \alpha \leqslant\ 0.20$ in steps of 0.25. As can be seen, the lines are parallel for all conversions, which indicate the same activation energies for the reaction at different heating rate. The average activation energy calculated from the different heating rates is found to be 88.9 ± 2.1 kJ mol^{-1}.

The Coats and Redfern method [18] requires to make an assumption about the functional form of $f(\alpha)$ or $g(\alpha)$, this implies in each case the description of the reaction process to give a value for the reaction order n. Table 1 shows the theoretical kinetic model functions $g(\alpha)$ employed for the kinetic analysis. Coats and Redfern make use of an asymptotic expression to find an approximate solution for Eq. (3) thus obtaining the following expression:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{qE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{7}$$

According to the above equation, a plot of ln[$g(\alpha)/T^2$] against reciprocal of temperature (Fig. 4) should result in a straight line with a slope equal to $-E$/R, for the correctly chosen value of n. Table 2 shows activation energies at constant heating rates of 2.5, 5, 10, 15 and 20 °C min^{-1} for all mechanisms from Table 1. The results of this table, compared with the previously obtained by Flynn–Wall–Ozawa method, seem correspond to a deceleratory mechanism, F_1 [16,19]. The average value for this mechanism is 85.2 ± 1.5 kJ mol^{-1}.

A major application of TG and DTG (differential thermogravimetry) kinetic parameters is to the predict

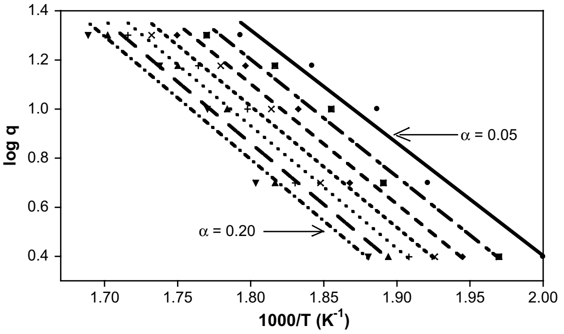

Fig. 3. Typical plots of log q vs T^{-1} at several conversion values in the range from α = 0.05 to α = 0.20, in steps of 0.025.

Table 1
Broad classification of solid-state rate expressions

Mechanism	Equation $g(\alpha)$	Model
Sigmoid α–time curves		
$A_n (n = 2, 3, 4)$	$[-\ln(1-\alpha)]^{l/n}$	Nucleation and growth
Deceleratory α–time curves		
$R_n (n = 2, 3)$	$1-(1-\alpha)^{l/n}$	Based on geometrical models
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion
F_1	$-\ln(1-\alpha)$	First-order
F_2	$1/(1-\alpha)$	Second-order
F_3	$[1/(1-\alpha)]^2$	Third-order

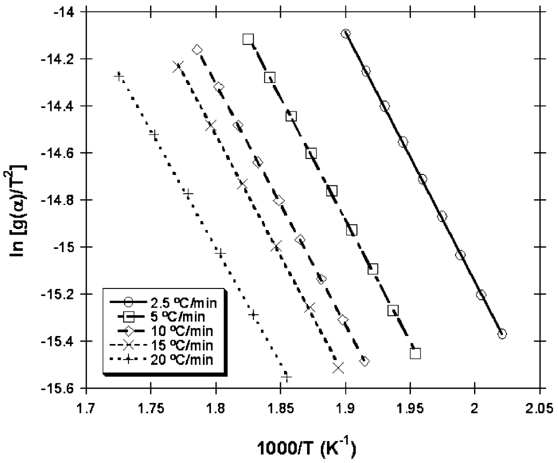

Fig. 4. Plots of Coats and Redfern method for different heating rate corresponding to mechanism F_1.

optimum processing temperature regions, and the estimated lifetime of the polymers [20,21]. The lifetime of polymer to failure is generally defined to be when the degree of decomposition is $\alpha = 0.05$ (or 5% mass loss). The lifetime of the POSS/DGEBA/DDM epoxy system was calculated from TG decomposition kinetic parameters. For this system, it could be estimated using the following expression [6], called scaling factor:

$$\frac{K_2}{K_1} = \exp\left(\frac{-E\Delta T}{RT_1T_2}\right) \tag{8}$$

where K_1 is rate at T_1, K_2 is rate at T_2, and T_1 and T_2 are two arbitrary temperatures.

Taking the energy from Flynn–Wall–Ozawa method, and introducing an error of twice the standard deviation, $\pm 2\sigma$, in the activation energy, the error, which shows a exponential multiplicative propagation, is

$$\text{error} = \exp\left(\frac{\pm 2\sigma\Delta T}{RT_1T_2}\right) \tag{9}$$

and it yields the maximum and minimum values of the lifetime for each temperatures.

Table 3 shows the experimental lifetimes in the range of temperature of 100–600 °C, the scaling factor and corrected lifetime. As shown the lifetime calculated

Table 2
Activation energies for the different mechanisms by Coats and Redfern's method and for different heating rates

Mechanism	E/kJ mol^{-1}				
	$q = 2.5$ °C min^{-1}	$q = 5$ °C min^{-1}	$q = 10$ °C min^{-1}	$q = 15$ °C min^{-1}	$q = 20$ °C min^{-1}
A_2	39.8	38.5	38.2	37.7	36.3
A_3	23.7	22.7	22.5	22.1	21.1
A_4	15.7	14.9	14.6	14.3	13.5
R_2	85.4	83. 2	82.7	81.9	79.4
R_3	86.3	84.0	83.6	82.8	80.2
D_1	174.0	169.9	169.1	167.6	162.9
D_2	177.5	173.3	172.6	171.1	166.3
D_3	181.2	176.9	176.1	174.7	169.8
F_1	88.2	85.8	85.4	84.6	82.0
F_2	2.6	2.0	1.9	1.8	1.2
F_3	13.7	12.8	12.7	12.6	11.7

Table 3
Lifetime for experimental data, scaling factor, corrected lifetime, and lifetime calculated with the mechanism F_1, at different temperatures

T/°C	Experimental, t/min	Scaling factor, k_1/k_2	Corrected, t/min	For mechanism F_1, t/min
100	1.87×10^7	0.0388	1.81×10^7	1.79×10^7
150	7.01×10^5	0.0772	6.88×10^5	6.99×10^5
200	5.31×10^4	0.1260	5.24×10^4	5.40×10^4
250	6.60×10^3	0.1809	6.52×10^3	6.80×10^3
300	1.18×10^3	0.2380	1.16×10^3	1.23×10^3
350	2.77×10^2	0.2946	2.74×10^2	2.92×10^2
400	8.10×10	0.3489	8.02×10	8.62×10
450	2.80×10	0.3998	2.78×10	3.01×10
500	1.11×10	0.4469	1.09×10	1.20×10
550	0.49×10	0.4901	0.45×10	0.54×10
600	0.24×10	0.5294	0.23×10	0.26×10

through the scaling factor does not essentially differ from the experimental values.

On the other hand, as this epoxy system obeys a degradation mechanism, F_1, where $f(\alpha) = (1 - \alpha)^n$, and taking into account the activation energy and pre-exponential value obtained by Flynn–Wall–Ozawa method, the values of lifetime [5,7] were obtained from the expression $t = \frac{0.0513}{k}$. This equation allows the calculation of the lifetime as a function of temperature through the constant rate k, where the results also are in the last column of Table 3. The obtained values this way are the same order that the obtained ones without knowing the degradation mechanism. The extrapolation of these data at room temperature must be considered with caution, so all sorts of other processes can shorten service lifetimes.

4. Conclusions

The kinetic parameters were used to predict the lifetime at different temperatures, based on thermal degradation. The calculations showed that the system POSS/DGEBA/DDM can be used at room temperature for a very long time without failure. It must emphasize that these calculations predict the expected lifetime on the epoxy resin systems based only on thermal degradation data. Other factors, such as photodegradation, diffusion effects, mechanical and chemical degradations, and physical aging will also affect the expected lifetime.

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