

Thermal degradation kinetics of epoxy-silica organic-inorganic hybrid materials

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Abstract

Degradation kinetics of organic-inorganic hybrids based on epoxy resin was investigated by thermogravimetric analysis (TGA). The hybrid materials were prepared from diglycidyl ether of bisphenol A (DGEBA) as organic precursor, and 3-glycidyloxypropyltrimethoxysilane (GLYMO) as inorganic precursor, polymerised simultaneously by poly(oxypropylene)diamine (Jeffamine D230). Energy of activation (E_a) of degradation processes for the hybrids with varying inorganic content, as well as for the unmodified epoxy-amine system, was determined by isoconversional methods. The complete process of degradation was described by appropriate kinetic models. It was found that the hybrid materials have significantly higher E_a of degradation than the unmodified epoxy-amine resin, and that the inorganic network influences the mechanism of degradation of organic phase.

Introduction

The organic-inorganic hybrid materials, where inorganic phase is dispersed in polymer matrix at molecular or nano level, are expected to possess superior properties in comparison with classical polymer composites. Inorganic phase, formed *in situ* by hydrolysis and condensation of metal (usually silicon) alkoxydes [1], can enhance thermal properties of polymer materials, both acting as flame retardant and by increasing char formation [2, 3]. In this work, thermal degradation kinetics of epoxy-silica organic-inorganic hybrids, with 3-glycidyloxypropyltrimethoxysilane (GLYMO) as the inorganic precursor, is studied. These hybrid materials were previously characterised and their cure kinetics studied [4, 5].

Experimental

An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol, and 3-glycidyloxypropyltrimethoxysilane (GLYMO, 98%, Aldrich Chemicals) were used to synthesize organic-inorganic hybrid materials, making use of poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) as a curing agent for epoxy and as a basic catalyst for GLYMO hydrolysis. The materials were used as received. Hybrid

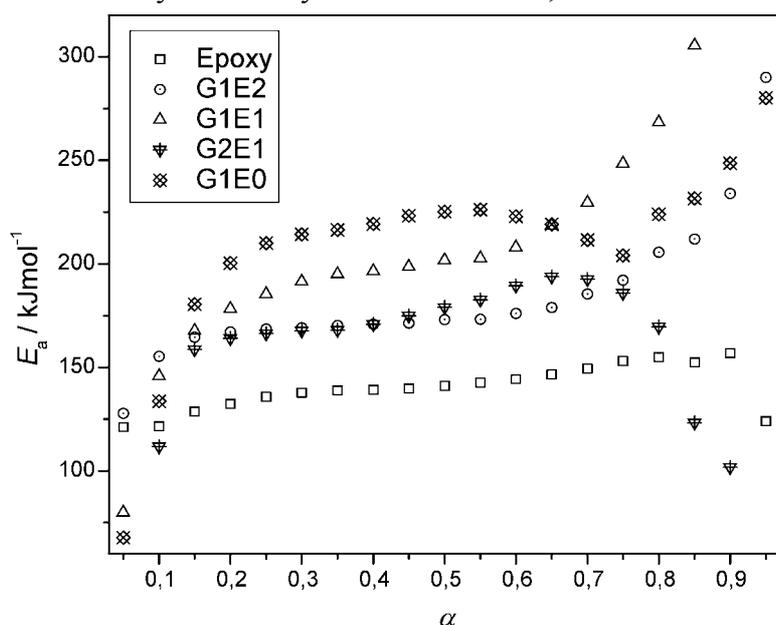
materials and unmodified epoxy-amine resin were prepared as described [4], adding stoichiometric amount of Jeffamine D230. Samples were designated according to the mass ratio of GLYMO to DGEBA: G1E2, G1E1 and G2E1 for ratios 1:2, 1:1 and 2:1 respectively, and G1E0 for hybrid material prepared solely from GLYMO. Curing was effected at room temperature for 30 days, making use of air humidity for GLYMO hydrolysis. The materials were then postcured for 24 h at 120°C in an oven. Loss of weight of such samples was measured by thermogravimetric analysis (TGA), using a Perkin Elmer thermobalance TGS-2. Samples weighted at ~10 mg were heated from room temperature to 1000°C at the heating rates of 5-25 K min⁻¹ in a nitrogen gas flow.

Results and discussion

The degradation of polymer materials often follows a complex mechanism, and elucidating the kinetics for every step is a very demanding procedure. But if the degradation is studied only in order to ascertain the processing parameters and appropriate working conditions for the material, the kinetic analysis using simple empirical models is justified [6]. The conversion, α , was calculated according to the equation (1), where m_0 is the initial, and m_∞ final sample mass, disregarding the initial loss of mass at temperatures under 300°C due to evaporation of adsorbed moisture:

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_\infty} \quad (1)$$

The value of activation energy, E_a , was obtained by Kissinger-Akahira-Sunose (KAS) [7] isoconversional method for values of α 0.05-0.95. The results are displayed in Figure 1. As E_a doesn't vary extremely with conversion, the whole reaction interval can be described by a single



kinetic model. Simple nth order reaction (eq. 2) and autocatalytic model (eq. 3) were chosen for the purpose, and fitted simultaneously to experimental datasets obtained with varying heating

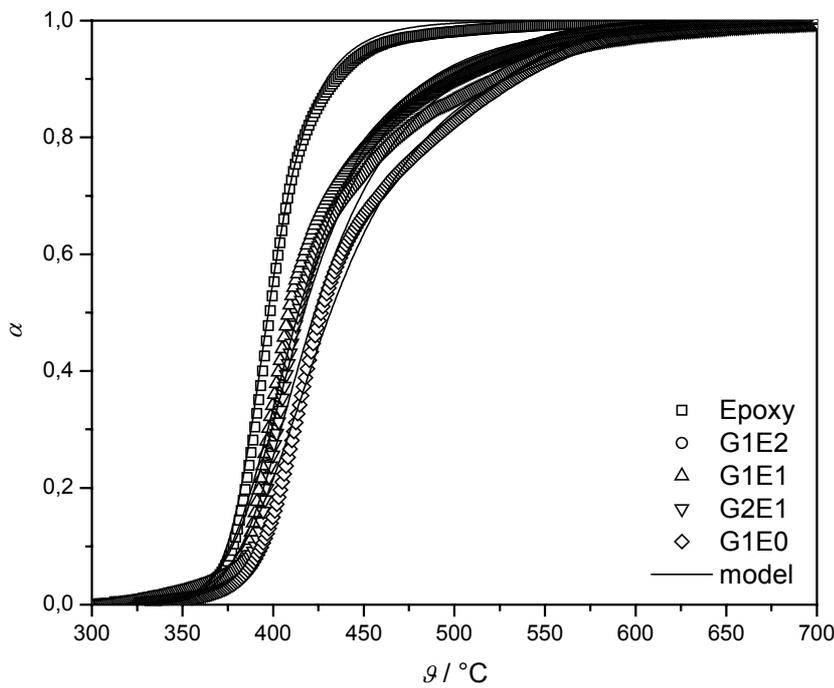
Figure 1 – Dependence of activation energy, E_a , obtained by KAS method, for all investigated systems.

rates (program Wolfram Mathematica 5.0). The average value of $E_{a,KAS}$ obtained from KAS was used as the initial value, and changed if necessary to obtain the most satisfying fit. The results of kinetic modelling are displayed in Table 1 and Figure 2.

$$\frac{d\alpha}{dt} = k_0 \exp(-E_a / RT)(1 - \alpha)^n \quad (2)$$

$$\frac{d\alpha}{dt} = k_0 \exp(-E_a / RT)\alpha^m(1 - \alpha)^n \quad (3)$$

It can be seen that all hybrid systems follow significantly different degradation kinetics from the unmodified epoxy-amine resin. Obviously the presence of nano-sized inorganic network not only shifts the degradation of hybrid materials to higher temperatures and facilitates char formation [4],



but also changes the degradation mechanism. Only unmodified epoxy-amine resin and G1E0 hybrid system show satisfying fit with $E_{a,KAS}$, and those are the systems that displayed the least scatter of E_a

Figure 2. - Comparison of experimental data with kinetic models obtained for all investigated systems, heating rate 20 K/min⁻¹.

with α (Fig. 1). In the remaining hybrid systems fitted value of $E_{a,fit}$ is noticeably higher than $E_{a,KAS}$, and it can be supposed that the true reaction mechanism for these systems is a complex one. As kinetic parameters for these three systems vary very little, we propose that the mechanism of degradation is not significantly different. G1E0, with very low content of flexible polymer chains, has lower E_a than the three other hybrids, so the degradation starts more easily, but the lower values of k_0 and n indicate slower course of reaction, due to significant interference of dense inorganic network. In fact, it would be difficult to compare the thermal stability of investigated hybrids solely from the results of kinetic modelling. Another useful value for this is integral procedural decomposition temperature (IPDT) [2], which takes into account the whole degradation curve. As

IPDT necessarily varies with the heating rate, the average value is displayed in Table 1. The value was found to increase linearly with GLYMO content in hybrid materials, which is in accordance of previously published results [4].

Table 1. Activation energy (E_a) preexponential factor (k_0) and empirical exponents for given systems and models, as well as the average integral procedural decomposition temperature (IPDT)

System	$E_a / \text{kJ mol}^{-1}$		k_0 / s^{-1}	m	n	Model	IPDT / °C
	fitted	KAS					
Epoxy	142.77	142.77	exp(22.349)	0.60	1.84	Eq. 3	503.7
G1E2	276.06	177.08	exp(45.422)	--	3.90	Eq. 2	784.9
G1E1	262.72	209.49	exp(42.827)	--	3.90	Eq. 2	863.4
G2E1	271.43	177.31	exp(44.100)	--	4.20	Eq. 2	1007.4
G1E0	216.64	216.64	exp(33.759)	--	3.84	Eq. 2	1300.8

Conclusions

Degradation kinetics of hybrid materials based on epoxy resin and GLYMO was investigated by TGA. Degradation E_a was determined by isoconversional methods, and kinetics described with empirical models. Hybrid materials have significantly higher E_a of degradation and follow a different mechanism of degradation than epoxy-amine resin, probably due to presence of inorganic network. It was supposed that the true reaction mechanism for these systems is a complex one, with sole exception of G1E0 system. To compare the thermal stability of investigated materials, IPDT was calculated, and the results were found to be in accordance with previous investigations.

References:

1. R. C. Mehrotra, in: R. Reisfeld, C. K. Jørgensen (Eds.), *Chemistry, Spectroscopy and Applications of Sol-Gel Glasses*, Springer-Verlag, Berlin, 1992, pp. 1-36.
2. S.-T. Lin, S. K. Huang, *Eur. Polym. J.* **33** (1997) 365-373.
3. G.-H. Hsiue, H.-F. Wei et al., *Polym. Degr. Stab.* **73** (2001) 309-318.
4. J. Macan, H. Ivanković, M. Ivanković, H. J. Mencer, *J. Appl. Polym. Sci.* **92** (2004) 498-505.
5. J. Macan, H. Ivanković, M. Ivanković, H. J. Mencer, *Thermochim. Acta* **414** (2004) 219-225.
6. L. Torre, J. M. Kenny, A. M. Maffezzoli, *J. Mater. Sci.* **33** (1998) 3137-3143.
7. Z. M. Gao, M. Nakada, I. Amasaki, *Thermochim. Acta* **369** (2001) 137-142.