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Material behaviour

Kinetics of thermo-oxidative degradation of PS-POSS hybrid nanocomposite

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ABSTRACT

The thermo-oxidative degradation kinetics of a hybrid nanocomposite comprised of polystyrene and polyhedral oligomeric silsesquioxane (PS-POSS) was studied by dynamic thermogravimetry. The dependence of the activation energy on the conversion ($E_{\alpha(T)}$) was determined by means of a model-free isoconversional method and the kinetic mechanisms involved throughout the degradation process were determined by comparison of convolution functions with master curves of kinetic models. The $E_{\alpha(T)}$ values remained practically constant in the range of 80 to 120 kJ mol^{-1} throughout the process, indicating that the degradation is essentially limited by a single step process. The degradation proceeded via R_n mechanisms (phase boundary-controlled reactions) in the range of $\alpha = 0$ to $\alpha \approx 0.8$, whereas for $\alpha > 0.80$ there was a gradual change to D_n (diffusion-controlled reactions) and F_n (chemically-controlled reactions) mechanisms. This demonstrates that volatilization occurs from the surface toward the center of the sample up to $\alpha \approx 0.8$ and then becomes governed by the concentration, reactivity and diffusion of the gases.

1. Introduction

Hybrid polymeric materials containing nano-scale inorganic fillers have become increasingly important in engineering and high-tech applications such as microelectronics and optics [1]. The performance of these polymeric hybrid nanocomposites is dependent on the polymer structure as well as the chemical structure, shape and size of the nanofillers, the degree of polymer-nanofiller hybridization, and the dispersion, distribution and interfacial adhesion between the nanofiller and the polymer matrix [1,2].

Polyhedral oligomeric silsesquioxanes (POSS) have received considerable attention from the scientific community in recent years as they possess a synergistic combination of properties of organic and inorganic materials [3]. POSS materials have a cage-like structure of 1–3 nm in size containing an inorganic Si-O cage surrounded by organic substituents, with the chemical formula $(RSiO_{1.5})_n$, that is, with a composition between those of silica (SiO_2) and silicones $(R_2SiO)_n$. In POSS, R can be hydrogen or any alkyl, alkylene, aryl, phenyl, or arylene group, or an organo-functional derivative thereof [4–8]. POSS molecules can be incorporated into a polymer matrix by co-polymerization [9–11], solution blending [12,13], mechanical melt blending [14–17] or reactive melt blending [18,19] routes. The use of reactive melt blending for POSS hybridization on polymer backbones has become appealing because the process is environmentally friendly

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(solvent-free), economically viable and simple to scale up to the industrial level [20,21]. Bianchi and coworkers [18,19] have studied the hybridization of a methacryl phenyl POSS on PS chains. PS-POSS materials were prepared by reactive melt blending using dicumyl peroxide (DCP) as a free radical initiator. Alternatively, a styrene monomer has been used as a chain transfer agent to enhance POSS hybridization and avoid PS chain scission owing to the generation of free radicals. PS-POSS nanocomposites containing 5 wt% of POSS with hybridization degrees of up to 40 wt% were obtained [19].

In this study, the kinetics of the thermo-oxidative degradation of a PS-POSS hybrid nanocomposite was studied by dynamic thermogravimetry (TG). Neat PS and POSS were also analyzed for comparison. The kinetic analysis of the TG data was carried out within the framework of a multi-step solid-state process. The dependence of Arrhenius parameters on the reaction conversion was determined by means of a model-free isoconversional method applying the Cai approach [22]. From these data, the kinetic mechanisms throughout the degradation process were determined by means of the Criado approach [23,24], which compares the plots of the convolution functions of kinetic models obtained from experimental data with the master curves of theoretical kinetic models.

1.1. Theoretical background

The basic assumption in studies on the degradation of a solid polymer subjected to thermogravimetry (TG) is that solid and gaseous decomposition products are formed: $A_{solid} \rightarrow B_{solid} + C_{gas}$. The extent of the degradation reaction α (conversion) is given by the relative mass loss Eq. (1) due to the release of gaseous products, where w is the sample mass at any time and subscripts 0 and f refer, respectively, to the masses at the beginning (initial) and end (final) of the degradation event, respectively:

$$\alpha = \frac{w_0 - w}{w_0 - w_f} \tag{1}$$

The differential expression for the reaction rate of a single-step process ($d\alpha/dt$) has the following general form:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{2}$$

In Eq. (2), α is the extent of reaction (conversion), t is the reaction time, k is the rate (kinetic) constant which is dependent on the absolute temperature T, and $f(\alpha)$ is the kinetic (reaction) model, which describes the dependence of the reaction rate on the extent of reaction and is related to the kinetic mechanism of the process.

The combination of Eq. (2) with the Arrhenius equation for the dependence of the rate constant k on the temperature T yields:

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \tag{3}$$

In Eq. (3), A is the pre-exponential (frequency) factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. If the thermogravimetric analysis is carried out under heating at a constant rate ($T = T_0 + \phi \cdot t$), where T_0 is the onset temperature, T is the temperature at which a given conversion α is reached and $\phi = dT/dt$ is the heating rate, and considering that $d\alpha/dt = d\alpha/dT \cdot dT/dt = \phi \cdot d\alpha/dT$, Eq. (3) becomes [25,26]:

Table 1
Weight-average molecular weight (M_w), polydispersity index (M_w/M_n) and POSS hybridization degree (α_{POSS}) of the materials under study.

	M_w (g/mol)	Polydispersity (M_w/M_n)	α_{POSS} (wt%)
PS	212,000	2.0	–
PS-POSS 95/5	201,000	2.2	27.8

$$\frac{d\alpha}{dT} = \frac{A}{\phi} \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \tag{4}$$

Rearrangement of Eq. (4) and integration between the limits $\alpha = 0$ at $T = 0$ and $\alpha = \alpha$ at $T = T$ gives the integral form $g(\alpha)$ of the reaction model $f(\alpha)$ [27]:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_0^{T} e^{-\frac{E}{RT}} dT \tag{5}$$

The integral of the right side of Eq. (5) is called the temperature integral or Arrhenius integral. It has no analytic solution, requiring a numerical approximation. The numerical solution of Eq. (5) can be given by Eq. (6), where $\pi(x)$ is an approximation of the Arrhenius integral obtained through the integration of conversion α over the temperature T and $x = E/RT$:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{AE}{\phi R} e^{-x} \left[\frac{\pi(x)}{x} \right] \tag{6}$$

Several numerical approximations of varying complexity and precision have been proposed as a solution for the Arrhenius integral [28,29]. Cai et al. [22] obtained approximation constants for the Arrhenius integral based on the Pattern Search numerical solution method considering one-degree rational. The Cai approximation shows a low percentage deviation when compared to other methods proposed in the literature.

$$\pi(x) = \frac{x + 0.66691}{x + 2.64943} \tag{7}$$

Substituting Eq. (7) into Eq. (6), and solving the exponential equation by taking the natural logarithm of both sides, we obtain an equation for the evaluation of non-isothermal kinetic parameters [22]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\phi E} \cdot \frac{E + 0.66691 \cdot RT}{E + 2.64943 \cdot RT}\right] - \frac{E}{RT} \tag{8}$$

Equation (8) describes the behavior of a single-step solid-state process where the activation energy E and the pre-exponential factor A (i.e., the Arrhenius parameters) are independent of the conversion α. However, for multi-step solid-state processes such as thermal and thermo-oxidative degradation, the Arrhenius parameters are usually dependent on the conversion α. This means that more than one algebraic expression related to the kinetic model