



Modeling the thermal degradation of poly(methyl methacrylate)/carbon nanotube nanocomposites

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ABSTRACT

The thermal degradation is modeled of a one-dimensional disk of poly(methyl methacrylate) (PMMA) with and without the dispersion of carbon nanotubes exposed to a fire-level heat flux. The description of the chief transport processes (conductive, convective and radiative heat transfer, convective mass transport) is combined with a one-step finite-rate reaction for polymer decomposition resulting in surface ablation (absence of nanotubes) or the formation of network-structured continuous layer of carbon nanotubes. Good agreement is obtained between the predicted and measured mass loss rates for the two cases. The presence of nanotubes reduces the peak in the mass loss rate and increases the conversion time, owing to the insulating effects of the surface layer and the much larger surface re-radiation losses. The effects of flame retardance are enhanced by increasing the growth rate and/or the thickness of the surface layer.

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1. Introduction

A continuous growth in the use of composite materials is observed and they are now challenging the use of traditional materials in many markets [1]. The widespread use of composites in a variety of applications is due to their many outstanding physical, thermal, chemical and mechanical properties, although they are flammable and require the addition of flame retardants. In the last decade nanoscale reinforcing fillers have been extensively used to produce polymeric nanocomposite materials with even improved mechanical, thermal and biodegradability properties. Furthermore, the fire performances are also improved, providing an alternative to conventional flame retardants [2–6]. Polymer nanocomposites generally reduce the heat (and mass) release rate, especially the peak value. However, they tend to have shorter ignition delay times (or no significant increase in ignition delay) and about the same total heat release as that of the pure polymers. In other words, they tend to burn slowly and nearly completely. The specific heat of combustion (the measured heat release rate divided by the measured mass loss rate) also remains unvaried, with respect to pure polymers, implying that the reduction in the heat release rate and mass burning tends to be due to chemical and

physical processes mainly in the condensed phase rather than in the gas phase [3].

There are two different types of carbon nanotubes (CNTs), small-diameter (1–2 nm) single-walled nanotubes (SWNTs) and larger-diameter (10–100 nm) multi-walled nanotubes (MWNTs) [6], which are a good candidate as flame retardant additive because of their elongated shape (high aspect ratio). Indeed, incorporation of low amounts of CNTs (typically below 3%wt), which guarantee a good dispersion, has been found to improve the flame retardancy of some thermoplastic polymers [7–12]. The formation of a continuous (without openings or cracks) network-structured protective layer from the nanotubes is critical for significant reduction in the heat release rate because the layer acts as a thermal shield for the virgin polymer from energy feedback from the external radiation and the flame. On the other hand, its high porosity does not represent a barrier for the outflow of the volatile products of polymer degradation. For a good nanotube dispersion, which can actually give rise to a continuous, network-structured protective layer, apart from the initial transients when small bubbles are formed and their bursting is observed at the surface, a solid-like behavior is established with no overt fluid motion [4,9]. Instead samples with poor nanotube dispersion lead to the formation of many surface islands, with in-between vigorous bubbling, and poor fire performance. The shrinkage characteristics of the network layer, with respect to the initial size of the nanocomposite, seem to be related mainly to the shape of the nanotubes,

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especially the aspect ratio [11], which dominates above the number of nanotubes or their total surface area. The development of a physically integer surface layer and the reduction in the melt viscosity are also key features for other nanometric additives [3,5,13].

Mathematical modeling of the solid phase is an important tool for determining the dominant mechanisms in fire through a quantitative representation of the physical and chemical processes. Numerous predictive models have been proposed for the behavior of polymeric materials under fire conditions in some cases including the effects of flame retardants [14–27]. However, the analysis of the current state of the art reveals that only a semi-empirical model is available for the combustion of nanocomposite materials [28,29]. It combines the information about the mass loss rate measured in a cone calorimeter with a simplified description of the thermal processes of the solid phase introducing, as a characteristic variable, the heat flux ratio (the ratio between the heat flux at the surface of the polymer, for the case there is no surface layer, and the heat flux at the interface between the particle layer and the virgin material), which avoids the description of the nanoparticle layer. The main result of the study is the formulation of an empirical correlation between the heat flux ratio and the depth of the already pyrolyzed region. Although this can be useful to interpret the experimental data, the model cannot predict the detailed evolution of the main process variables or the interaction between chemical and physical processes that gives rise to the conversion of nanocomposite materials.

In this study a comprehensive dynamic model is presented for the thermal decomposition of thermoplastic nanocomposite materials, which couples the energy and mass conservation equations with the decomposition kinetics for a variable-volume system. It takes into account the changes undergone by the material during conversion and the development of a nanoparticle surface layer, permitting the detailed simulation of the evolution of the main process variables. The simulations are made for PMMA and PMMA/SWNT nanocomposites heated in a gasification apparatus under a nitrogen flow as in the experiments carried out by Kashiwagi and coworkers [4,9]. After experimental validation, a parametric analysis is carried out to investigate the effects of some process parameters on the thermal response of the nanocomposite material.

2. Mathematical model

The problem modeled considers the decomposition of PMMA/SWNT nanocomposite heated by the radiant gasification apparatus as used in Refs. [4,9]. This system, similar to a cone calorimeter, was designed and constructed to study the thermal conversion process by measuring the mass loss rate and temperatures of the sample exposed to a fire-like heat flux in a nitrogen atmosphere, thus avoiding the combustion reactions. Apart from the advantages from the experimental point of view, this system is also easier to model as the processes of interest occur only in the condensed phase with reactions that are representative of thermal decomposition. Moreover, the external heat flux to the sample surface is well defined and nearly constant over the duration of the entire experiment (and over the spatial extent of the sample surface) due to the absence of heat feedback from the flame. The mathematical model is unsteady and describes the thermal decomposition of a nanocomposite disc (diameter D and initial thickness L_0) subjected to an external radiative heat flux on the top surface. The system is schematized as one-dimensional in the axial direction (thickness of the disk). For comparison purposes the case of neat PMMA (without any CNT dispersion) is also examined. Several assumptions are made in the formulation of the conservation equations.

When describing the behavior of neat PMMA, melting occurs at a predefined temperature but the effects associate with the melting enthalpy are assumed to be negligible as they are very small. However, the changes in the properties of the polymer (thermal conductivity [30] and specific heat [31]), as melting occurs, are described via a temperature dependence. Moreover, the melt does not drip and the phase change (solid PMMA \rightarrow PMMA melt) is not associated with volume variation.

Thermal degradation of PMMA occurs according to a one-step global reaction, PMMA \rightarrow V (MMA monomers), with Arrhenius kinetics and a first-order dependence on the mass fraction of the molten polymer. The addition of CNTs is shown (for instance, Refs. [9,11]) not to affect the thermal stability of the polymers, indicating that the resulting fire retardant effect is of physical origin. Therefore, the kinetic parameters determined for pure polymers are retained to remain invariant for the corresponding nanocomposites. The kinetic parameters for PMMA thermal degradation are obtained by re-examining the thermogravimetric curves in nitrogen (at 5, 10, 15 and 20 K/min up to a final temperature of 873 K) reported in Ref. [32]. The polymer molecular weight (100,000 g/mol) is the same as that of the samples used for the preparation of nanocomposites [4,9]. The method of parameter estimation employed here has already been presented elsewhere [33]. It makes use of a numerical solution for the mass conservation equations and a direct method for the minimization of the differential and integral form of the objective function taking simultaneously into account the differences between the model predictions and the experimental measurements for all the four heating rates data. The analysis leads to an activation energy of 188 kJ/mol and a pre-exponential factor of $1.32 \times 10^{13} \text{ s}^{-1}$, which are in the range of literature values. A good agreement between measurements and predictions is obtained as indicated by the integral and differential curves shown in Fig. 1A, B (the deviations between predictions and experiments, defined as in Ref. [33], are around 1.2% and 2.3% for the integral and differential data). As the density of the polymer is assumed to be constant, in the transport model where polymer decomposition kinetics is linked to a suitable heat and mass transfer description, the volume occupied by the polymer decreases in proportion to the mass lost by thermal degradation.

The condensed phase and the gas phase are in local thermal equilibrium. The addition of CNTs to polymers modifies their thermal properties, specific heat and thermal conductivity. For the system PMMA/SWNT these increase with the nanoparticle content, exhibiting temperature dependences similar to neat PMMA [34]. This trend is consistent with the dispersed nanoparticles forming an ever denser random network within the host polymer. The geometric mean model of effective thermal conductivity has been shown [34] to produce good agreement with the experimental results at low SWNT contents (up to mass percentages around 3.4%), which are in the range of interest for fire retardancy (around 0.5–1% [4,9]), whereas more sophisticated models are required at higher contents.

The formation of a surface network-structured layer is modeled following the extensive information made available from the experimental analysis [4,8,9,11]. As anticipated, the thermal characteristics of this layer are important in determining the flame retardant effectiveness of nanocomposites. In the case of poor dispersion of CNTs, the surface layer does not cover the entire sample but surface islands are formed. These cannot be described by a one-dimensional model. Instead, as in the case of good dispersion, it is assumed that the network-structured layer covers the entire sample surface and extends to the bottom, in accordance with the solid-like behavior exhibited by the nanocomposite. Therefore, its formation occurs simultaneously with the

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