



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



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ABSTRACT

A transient one-dimensional model, including the description of the chief chemical and physical mechanisms of the thermo-oxidative decomposition of poly(methyl methacrylate)/carbon nanotube composite and the parent polymer, combined with the critical mass flux criterion, quantitatively predicts the ignition times measured in a cone calorimeter. At low heat fluxes, the ignition times are longer for the composite, owing to the flame retardancy action of the carbon nanotubes resulting in the formation of a surface charred barrier, prior the attainment of sufficiently high rates of volatile release. Instead, at high heat fluxes, surface (versus in depth) absorption of the thermal radiation locally enhances the decomposition rate leading to shorter ignition times for the composite. Of paramount importance for the quantitative prediction of the ignition time is not only the empirical criterion (critical surface temperature or volatile mass flux) but also accurate kinetics taking into account the polymer properties, in particular the polymerization degree, and the presence of oxygen during the initial transient stage.

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1. Introduction

The dispersion of nanoparticles of different nature within a polymeric matrix leads to improved fire retardancy performances of composite materials [1–4]. The analysis of a huge amount of experimental data, also with the aid of mathematical modeling [5–10], demonstrates that the formation of a thermally insulating layer at the heat-exposed surface of the specimen highly protects the virgin material underneath, in this way delaying the devolatilization reactions. It is possible that the formation of a charred superficial layer also affects the mass transfer processes, such as the escape of bubbles in the polymer melt [8].

In accordance with the data produced from cone calorimetry tests [11], flame retardancy of polymer nanocomposites usually causes a drastic reduction in the peak of the heat release rate and the average mass loss rate. However these positive features are associated with a rather low impact on the ignitability [12,13], often with a reduction in the ignition times (see, for instance [14–22]). Different explanations have been given for this undesired result

which include modifications in the medium thermal properties (surface absorption and/or effective thermal conductivity) [17,19,23,24] or thermal degradation of the additive [15,25] and modifications in the thermal degradation pathways [22,26–29]. Although the mechanism responsible for the acceleration in the ignition of nanocomposites can be material specific, it is evident that there is not sufficient experimental data to reach a consensus about this issue. Moreover, from the theoretical point of view, only a qualitative analysis, essentially using the heat conduction equation for thermoplastic polyurethane and polyamide-6 [23], is available. It is speculated that the effective thermal conductivity of the nanocomposite and the parent polymer are functions of the temperature. Though at low temperatures the nanocomposite exhibits higher thermal conductivity subsequently, due to the changes in the rheological behavior, that of the polymer becomes higher. Thus, given the same ignition temperature, the nanocomposite ignites first. However, it is understandable that, given the highly simplified model, this conclusion cannot be considered of general validity and further investigation is also needed from the theoretical side.

Detailed modeling of the solid phase processes of nanocomposites and the parent polymer could indeed represent a

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powerful tool to ascertain the mechanisms responsible for flame retardancy as shown by the comprehensive solid-phase model [9,10] recently developed for the degradation of thermoplastic polymer/carbon nanotube composites and the parent polymers. The model was experimentally validated against temporal profiles of the mass loss rates for a configuration mimicking cone calorimeter heating under an inert environment and exploited to understand the role of the chemical and physical processes. By coupling with an adequate empirical criterion, the transport model can also be extended to simulate nanocomposite ignition whose controlling mechanisms, as already pointed out above, are unknown. This approach is used in this study in combination with experimental investigation, stressing that none of the other comprehensive models available in the literature has ever been adapted/applied to investigate the ignitability properties of thermoplastic polymer nanocomposites.

In this study thermogravimetric curves are measured, at variable heating rates, of a high-molecular weight poly(methyl methacrylate) (PMMA) sample, for both inert and oxidative environment, and applied for the development of multi-step mechanisms including the estimation of the kinetic parameters. Then the comprehensive transport model of the degradation of poly(methyl methacrylate)/carbon nanotube (PMMA/CNTs) composites and PMMA, previously developed [9,10] but extended to include the multistep kinetics, is applied to predict the ignition times for the two materials using the criterion based on the attainment of either a critical surface temperature or a critical mass flux. Both criteria are examined owing to their possible influences on the determination of the controlling mechanism. Experimental validation is made using the measured ignition times in a cone calorimeter for irradiances in the range 15–75 kW/m². A parametric analysis (influences of the critical surface temperature/mass flux values, thermal versus thermo-oxidative decomposition, low- and high-molecular weight polymer) is also carried out. Finally the simulations are analyzed to shed light on the role of carbon nanotubes on PMMA ignition.

2. Experimental details

In order to carry out the experimental validation of the model, experimental activities have been undertaken for PMMA and the PMMA/CNTs nanocomposite. PMMA in powder (code M0088, CAS: 9011-14-7 Lot: QNS4G) was purchased from Tokyo Chemical Industries (TCI) CO. Ltd. Japan. Multi-wall carbon nanotubes (Nanocyl™ NC 7000, Nanocyl) were used as flame retardant fillers. Pure polymer and composite were processed on a twin counter rotating internal mixer connected to a control unit (Rheomix 600 and PolyLab QC, respectively, Haake, Germany). Before mixing, the materials were previously dried in vacuum oven for 24 h at 333 K. The temperature profile used during the extrusion was 493/513/503 K in the respective feeding/mixing/matrix zones with rotation of 45–50 rpm. The selected extrusion conditions were in the range of the optimal ones previously determined [30] by electron microscopy for the dispersion of CNTs into the PMMA matrix, minimizing the aggregate size. Good dispersion was generally achieved for CNTs loadings between 0.1 and 10 wt% with the best dispersions at the lower loading levels, such as that applied in this study. Moreover no nanotube damage (tube breakage or alterations in the surface morphology) was observed. The extruded materials were cooled in water and subsequently reduced to granules with the aid of a pellettizer. Carbon nanotubes were added in the proportion of 1 wt% to PMMA. After extrusion, pure polymer and composite were compression molded at 513 K and 50 bar into 15 mm-thick slabs by a hot press (P300P, Collin, Germany).

Experiments were made, by means of a thermogravimetric

system, for pure PMMA, aimed at the analysis of the thermal and thermo-oxidative kinetics, and a cone calorimeter for both pure PMMA and PMMA/CNTs slabs, focused at the evaluation of the ignition times. Thermogravimetric curves were measured using the commercial system Mettler TGA/1, with a pulverized sample mass of 5 mg heated under a flow of 50 ml/min, using heating rates of 2.5, 5 and 10 K/min up to 800 K, both in air and nitrogen. It was observed that a kinetic regime, required for the determination of intrinsic kinetics, is certainly established for heating rates below 15 K/min and sample mass up to 5 mg. In general, for this regime, it is necessary to measure weight loss curves in the absence of heat and mass transfer limitations, that is, the sample temperature must coincide with the heating temperature and the oxygen concentration (this only for thermo-oxidative kinetics) across the sample should be the same as the that at the sample surface (no spatial gradients and negligible differences between the sample conditions and those of the surrounding environment). From the practical point of view, such conditions are accomplished by lowering the heating rate and the sample mass (thickness) until no change is seen in the measured mass fraction and devolatilization rate curves. The DSC1 STAR system Mettler was used for the evaluation of the global decomposition heat using a sample mass of 5.5 mg heated at 10 K/min up to 800 K. The combustion tests were carried out by the Oxygen Consumption Calorimeter (Cone Calorimeter) following the ISO 5660 procedure (horizontal configuration). Specimens of 100 × 100 mm² and thickness of 15 mm were employed for cone irradiance levels of 15, 20, 25, 35, 50 and 75 kW/m². The ignition time was evaluated as in Hopkins (1995) [31], that is, as “the time at which a continuous flame is supported on the material surface”, independently from the appearance of prior flashing events.

3. Thermal and thermo-oxidative decomposition kinetics

The decomposition kinetics of PMMA depends on the polymerization process and the molecular weight/polymerization degree [32]. The reaction environment, either inert or oxidative, also affects the decomposition of polymeric materials [20]. The thermogravimetric curves measured for the PMMA sample (Fig. 1, heating rate 5 K/min) confirm the important role of oxidative versus thermal degradation with results that are in agreement with those reported in Ref. [33]. Oxygen increases the polymer stability at low temperatures and enhances random scission at high temperatures. In fact, compared with the inert atmosphere, the devolatilization rates are initially (temperatures below 500 K) lower but successively they become higher with the absolute peak rate

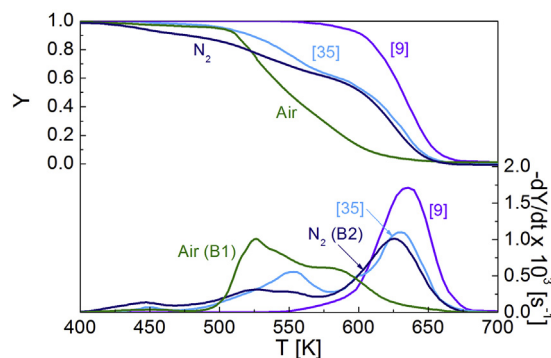


Fig. 1. Thermogravimetric curves for the mass fraction, Y , and mass loss rate, $-dY/dt$, versus temperature for the PMMA sample of this study in air and nitrogen and the PMMA samples discussed in the studies of Ref. [9] and Ref. [35] in nitrogen (heating rate 5 K/min).

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