

# MODELING THE THERMAL DECOMPOSITION OF POLYMER/CARBON NANOTUBE NANOCOMPOSITES

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## Abstract

A comprehensive transport model (conductive, convective and radiative heat transfer, convective mass transport) is applied to simulate the thermal decomposition of thermoplastic polymer/carbon nanotube nanocomposites and corresponding neat polymers (poly(methylmethacrylate) (PMMA), polypropylene (PP), polystyrene (PS)). The flame retardant effectiveness of nanocomposites is confirmed and good quantitative agreement with measurements is shown.

## Introduction

Nanometric reinforcing fillers, such as carbon nanotubes (CNT) are known to contribute in the enhancement of polymer properties such as thermal, mechanical and fire resistance [1]. Uniform dispersion of CNTs, which is achieved for a narrow range of small concentrations usually below 3%, causes an increase in the melt viscosity with the suppression of bubbling originated by the nucleation of products of thermal decomposition. In this way, via the formation of a jammed structure in the polymeric matrix, the material as a whole behaves rheologically like a gel. This behavior has been proved capable of forming a continuous network-structured protective layer that mainly consists of CNTs without the formation of any opening/crack that compromises the flame retardant effectiveness.

Detailed condensed-phase models for the fire behavior of composite materials, which include the description of heat and mass transfer and thermal decomposition, have been proposed in several cases [2-5]. However nanocomposites have not been given consideration. 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.

### **Mathematical Model**

The problem modeled considers the decomposition of thermoplastic polymer/carbon nanotube nanocomposites (a disc of diameter  $D$  and initial thickness  $L_0$ ) subjected to an external radiative heat flux on the top surface as in the radiant gasification apparatus developed by Kashiwagi and coworkers [6-9]. The system is schematized as one-dimensional in the axial direction (thickness of the disk). For comparison purposes neat polymers (without any CNT dispersion) are also examined. The one-dimensional unsteady model is already described elsewhere [10,11], so only the main features are briefly illustrated here. Polymer decomposition occurs according to a one-step endothermic reaction with Arrhenius kinetics and a first-order dependence on the mass fraction that are not modified by the presence of CNTs. The melting enthalpy is assumed to be negligible while the variations in the polymer properties are taken into account via a temperature dependence of the thermal conductivity and specific heat. The polymer density is assumed to be constant while the volume occupied by the polymer decreases in proportion to the mass lost by thermal decomposition.

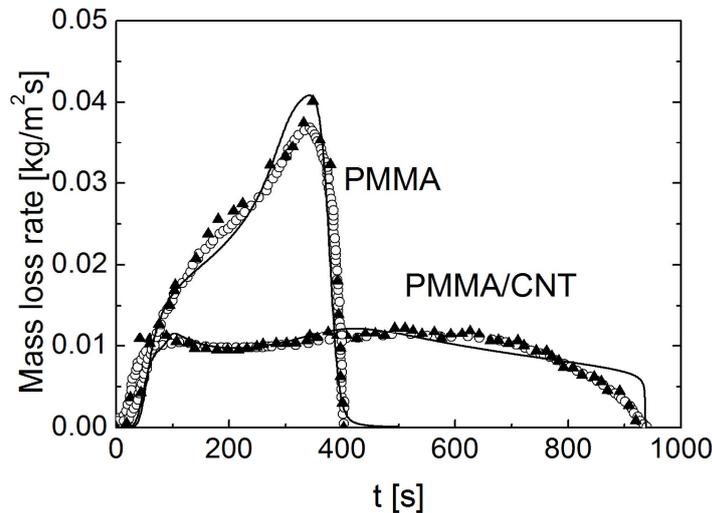
The condensed phase and the gas phase are in local thermal equilibrium. The addition of CNTs to polymers modifies their thermal properties, specific heat and thermal conductivity. The geometric mean model of effective thermal conductivity is applied in all cases whereas the specific heat is described by the usual mixture rule. The formation of a surface network-structured layer occurs simultaneously with the decomposition of the polymeric matrix, covering the entire sample surface and extending to the bottom. The final residue consists of tangled and stacked CNTs with approximately the same initial mass and a thickness (volume) that should be assigned. The thermal conductivity is modeled according to the Effective Medium Theory (EMT) equation, extended to include a radiative contribution. Then the global thermal conductivity of the degrading composite is modeled assuming a parallel configuration for the nanocomposite and the surface layer with contributions weighed by the polymer conversion. The convective transport of volatile products, which obey to the ideal gas law, is taken into account across the reacting medium and the porous surface layer towards the heated surface, assuming that the flow resistance is negligible and the pressure remains constant. The external radiation is absorbed by the neat polymers over some depth, following the Beer law, whereas the polymer/CNT nanocomposites absorb the radiative heat flux at the exposed surface. For both cases surface radiative heat losses are also taken into account.

### **Results**

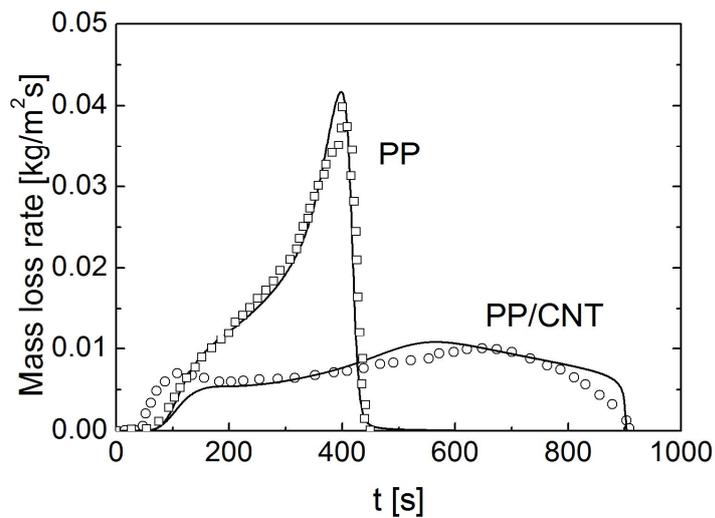
The mathematical model has been applied to simulate the effects of polymer and nanoparticle properties [10,11]. The extensive parametric and sensitivity analyses indicate that activation energy, density, reaction heat and thermal conductivity of

the polymers exert the most significant role. A crucial aspect in relation to the differences in the initial degradation behavior of neat polymers versus nanocomposites is played by the in-depth radiation absorption coefficient. Moreover the effects of flame retardance are enhanced by increasing the growth rate and/or the thickness of the surface layer, the intensity of the radiative heat flux and/or the sample thickness.

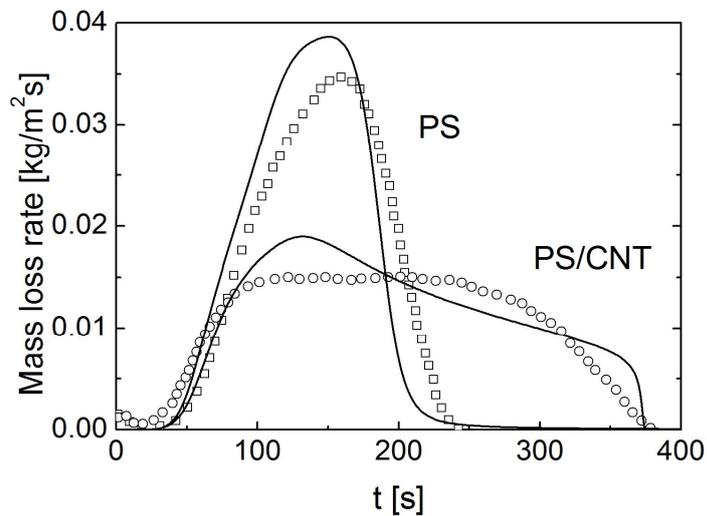
Simulations have been made of the thermal degradation of PMMA/CNT, PP/CNT and PS/CNT nanocomposites and the corresponding polymers as in the experiments reported in [6-9] (external heat flux of  $50\text{ kW/m}^2$  and adiabatic bottom surface), using input parameters derived from literature. An acceptable agreement between predictions and experiments in terms of mass loss rate is shown by Figs. 1-3. In all cases the nanocomposites exhibit a flame retardance action that appears as an increased duration of the conversion time and a reduction in the peak of the mass loss rate indicating both qualitative and quantitative agreement with measurements. The differences between the three systems can be attributed in the first place to the different sample sizes ( $L_0$ ) and final thickness of the surface layer ( $L_f$ ), the different percentages of CNTs and, to a lesser extent, to intrinsic differences in the chemico-physical properties of the polymeric matrix.



**Figure 1.** Predicted and measured [7-8] (symbols) mass loss rate versus time for the samples of PMMA and PMMA/CNT nanocomposite (solid lines).



**Figure 2.** Predicted and measured [6] (symbols) mass loss rate versus time for the samples of PP and PP/CNT (solid lines).



**Figure 3.** Predicted and measured [9] (symbols) mass loss rate versus time for the samples of PS and PS/CNT (solid lines).

### Conclusions

Further work is still needed for a comprehensive experimental validation of the models proposed here. For some input parameters, the range reported in the literature is rather wide. In reality to get quantitative predictions, precise thermal

properties and kinetic parameters should be determined for the same material that is used in the fire tests. Indeed the decomposition kinetics are influenced by the structural differences of the polymer produced by the polymerization scheme adopted, in particular the polymerization degree. Large differences are also evidenced by the reported value of the reaction heat which plays an important role in the process prediction. Moreover, there is large uncertainty about the value and dependence on the operating conditions of the in-depth radiation absorption coefficient. Different sources are also available for the thermal properties of the neat polymers (specific heat and thermal conductivity) but the differences between them seem to exert small influences on the predictions.

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