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Numerical simulation of decomposition of polymer nano-composites: investigation of the influence of the char structure

Xiaonan REN[1], Ruowen Zong[1*], Yuan Hu[1], Siuming Lo[2], Anna A. Stec[3], T. Richard Hull[3]

1. State Key Laboratory of Fire Science, University of Science and Technology of China, Jinzhai Road 96, Hefei, Anhui 230026, PR China.2. Department of Civil and Architectural Engineering, City University of Hong Kong and USTC-CityU Joint Advanced Research Centre, Suzhou, PR China. 3. Centre for Fire and Hazards Science, University of Central Lancashire, Preston PR1 2HE, UK

Abstract

In recent years, nano-particles such as nano-clays, carbon nanotubes and graphenes have been extensively used in flame-retardant polymeric materials. The surface char layer formed in combustion acts as protective barriers that limit the heat transfer into the unpyrolysed polymer and volatilization of combustible degradation products and diffusion of oxygen into the material. A numerical simulation tool Thermakin is used to simulate the thermal decomposition of the neat polymers (polypropylene (PP), Acrylonitrile Butadiene Styrene (ABS)) and corresponding nano-composites (PP/multi-walled carbon nanotube (PP/MWCNT) and ABS/ graphene nano-sheets /NiFe-layered double hydroxide hybrid (ABS/GNS-LDH) in cone calorimetry experiments. PP/MWCNT forms a porous network while ABS/GNS-LDH forms a compact, dense char layer during combustion. With appropriate input parameters, the heat release rates (or mass loss rates) are predicted very well. Finally, the effect of input parameters on model outputs are discussed.

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Keywords: Polymer nanocomposites, Thermal decomposition, ThermaKin, Flame retardance

1. Introduction:

In recent years, nano-composites such as nano-clays, carbon nanotubes and graphenes have been increasingly used. A number of studies show that the nanoparticles used in small quantities can reduce the heat release rate significantly. The main fire retardant mechanisms are considered to be the formation of char barriers against the heat and volatiles. It is found that a porous network-structured floccule layer is

* Corresponding author. Tel.: 0551-63606439
E-mail address: zongrw@ustc.edu.cn

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formed in PP/MWCNT composites [1]. Different from the MWCNT, graphene nano-sheets (GNS) can promote the formation of more compact char layers [2]. The flame retardant mechanism of layered double hydroxides (LDH) is attributed to the endothermic decomposition of LDH and the barrier effect brought by carbonaceous char catalyzed by clay particles [3].

Mathematical modelling is an important tool to determine the dominant mechanisms in fire retardancy. Some preliminary attempts to model the nano-composites are available. Zhang and Delichatsios[4] make an effort to quantitatively evaluate the surface layer formed after pyrolysis of PA6- or EVA- or PBT-based clay nano-composites in a cone calorimeter. They assume that the heat flux ratio is proportional to the depth of the pyrolysed material. C. Di Blasi [5] builds a comprehensive transport model to simulate the decomposition of thermoplastic polymer/carbon nanotubes. However, Zhang's model is a semi-empirical model and Blasi's model doesn't consider the gas flow resistance.

In this paper, a recently developed numerical model ThermaKin [6] is used to predict the pyrolysis of neat polymer and corresponding nano-composites in cone calorimetry experiments. After validated with experimental data, parametric analysis is carried out to investigate the impact of some parameters on the HRR (or MLR) of the nano-composite material.

2. Experimental and Modelling methods

Experiment cases: The cone calorimeter experiments of PP and PP/MWCNT nanocomposites were carried out by Kashiwagi and coworkers [1]. The mass fraction of MWCNT was 1%. The samples were with a thickness of 4 mm and a diameter of 75 mm. An external radiant heat flux of 50 KW/m^2 was used. The cone calorimeter experiments of ABS and ABS/GNS-LDH were reported by Ningning Hong [7]. The mass fraction of GNS-LDH was 2%. The dimensions of the samples were 100mm*100mm*1.5mm. Tests were performed under heat flux of 35 KW/m^2.

Numerical simulation tool: The numerical model used in this study is ThermaKin, which is developed by Stoliarov and Lyon at the Federal Aviation Administration (FAA), USA. It describes transient energy transport, chemical reactions and mass transport taking place in a one-dimensional object.

Input parameters: **Table 1.** Physical properties of material components

Component	Density ρ (kgm^{-3})	Heat capacity c ($J\ kg^{-1}K^{-1}$)	Thermal conductivity k ($WK^{-1}m^{-1}$)	Gas transfer Coefficient λ (ms^{-1})	Absorption coefficient α (m^2kg^{-1})	Emissivity ε
PP	860	2760	0.24	$1*10^{-5}$	1.2	0.95
PP/MWCNT	860	2760	0.25	$1*10^{-5}$	5	0.9
PP/MWCNT char	20	1000	0.2	$1*10^{-5}$	100	0.9
ABS	1200	2350	0.3	$1*10^{-5}$	2.5	0.9
ABS/GNS-LDH	1200	2350	0.31	$1*10^{-8}$	5	0.9
ABS/GNS-LDH char	300	1000	0.2	$2*10^{-9}$	100	0.9
Insulation	120	840	0.04	10^{-35}	100	0.12

Table 2. Kinetic parameters describing decomposition reactions

Component	A(s^{-1})	E_a($kJmol^{-1}$)	Char yield	Heat of decomposition(Jg^{-1})
PP	$9.6*10^{22}$	350	0	430
PP/MWCNT	$9.6*10^{22}$	350	0.02	430
ABS	$8*10^{13}$	213.3	0.0163	460
ABS/GNS-LDH	$1.0*10^{12}$	189.053	0.061	460

Physical properties of material components are obtained from analysis of literature data and estimation by fitting the experiment curves. The property values used in our calculations are shown in table 1.The density of the material is directly calculated with the mass and the dimensions of the samples. Thermal conductivities of the PP and the PP/MWCNT are reported by Kashiwagi[1]. Conductivities of ABS,

ABS/GNS-LDH are determined in range of values in literatures. Assuming that the value of heat capacity obtained from the middle of the range between the room temperature and temperature of decomposition can provide a reasonable approximation of the real heat capacity. Heat capacities are determined according to the literature [8]. Gas transfer coefficients are set sufficiently high for PP, PP/MWCNT, PP/MWCNT char, ABS to ensure that fluxes of gaseous components out of a material object are always equal to the rates of its production inside the object. While gas transfer coefficients are set relatively small for ABS/GNS-LDH and its char to describe the gas barrier property of graphene nano-sheets and the compact char layer. The absorptivity and reflectivity of composites are estimated according to previous measurements [9]. The char is assumed to be essentially non-transparent to infrared radiation.

The decomposition progress is described with a single step, first order reaction. The decomposition properties are listed in table2.The properties of pure polymer are reported in [10]. Addition of MWCNT doesn't show significant effect on thermal stability of the polymer, so the decomposition parameters are assumed the same with PP. Kinetic parameters of ABS/GNS-LDH are obtained by fitting the results of thermo-gravimetric analysis. The value of the flame flux is determined by fitting experimental HRR (MLR) histories. For all composites the value of flame heat flux is found to be 10 KW/m^2.

3. Results

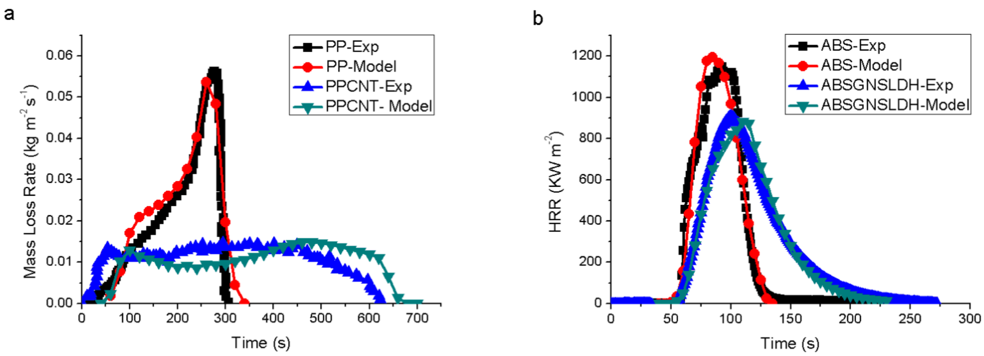

Figure 1. Comparison of the measured and predicted mass loss rates and heat release rate

The comparisons of simulated and experimental MLR (HRR) are shown in Fig. 1. Although there are some minor discrepancies between the calculated and experimental results, the overall agreement is reasonably good. The flame retardant mechanisms of two composites are different. For PP/MWCNT, the char layer is like an insulation barrier to prevent the heat transfer into the underlying polymer. For ABS/GNS-LDH, the compact char reduces the escape rate of generated gas.

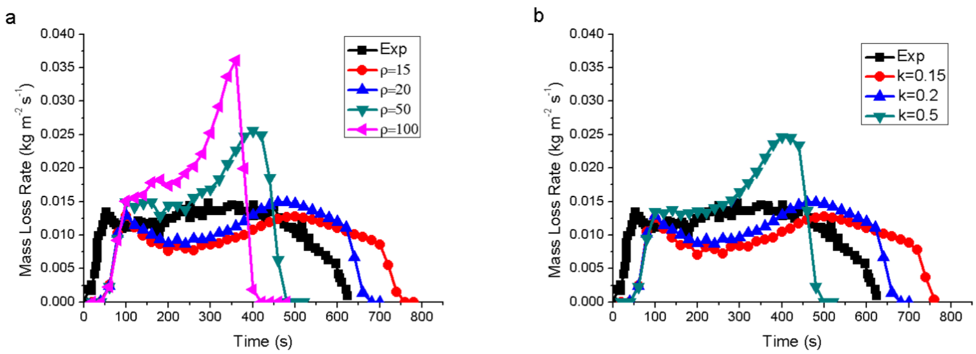

Figure 2. Effect of variations in char density and char conductivity on predicted MLRs

As indicated in Fig. 2, in PP/MWCNT, the char density and char conductivity have huge impact on the mass loss rate. The influence from expansion of char is the same with reduction of its conductivity.

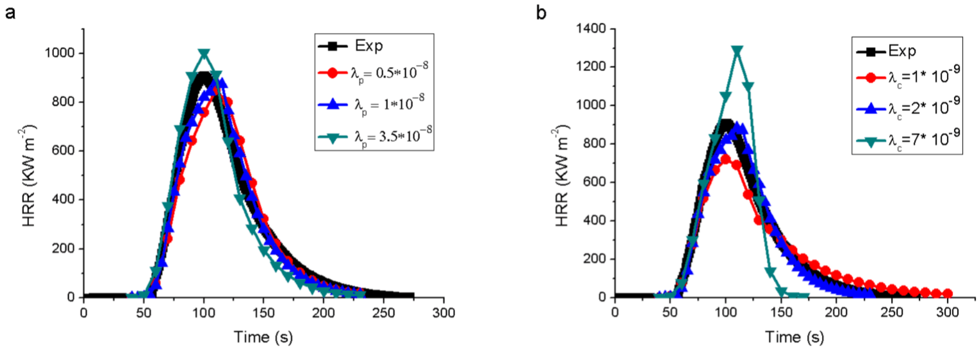

Figure 3. Effect of variations in gas transfer coefficient of nano-composite (left) and char (right) on HRRs

The impacts of mass transfer coefficients on HRRs are presented in Fig. 3. Peaks of HRR decrease when mass transfer coefficients of nano-composites or char residue decrease. The mass transfer coefficient of nano-composites has a large effect on the early stage of the pyrolysis process while the mass transfer coefficient of char has greater influence on the latter part of heat release process.

4. Conclusion

In this work, mass loss rates of PP and PP/MWCNT and heat release rates of ABS/ABS-LDH are predicted with numerical model Thermakin. With reasonable input parameters, predicted and experimental results agree well. In PP/MWCNT, the expansion of char residue plays an important role in the MLR reduction while in ABS/ABS-LDH, the mass resistance of compact char layer is the dominate factor. Finally, parametric analysis is carried out. The influence of char property on the pyrolysis process is significant.

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