Numerical analysis of composition effects on the ignition delay of polymeric composites

Y. Zhou, A. Stevanovic, S. Mehta, A. C. Fernandez-Pello
Department of Mechanical Engineering
University of California at Berkeley, USA

Abstract

A numerical approach based on the enthalpy method is applied to predict endothermic pyrolysis and piloted ignition delay of thermoplastics and polymeric composites exposed to an external radiant heat flux. The model considers the coupled thermo-chemical processes that take place in the condensed phase, and therefore describes the piloted ignition of solid combustible materials only under conditions of fast chemical kinetics in gas phase. The condensed phase processes considered in the model include oxidative and thermal pyrolysis, phase change, heat and mass transfer in a multi-phase and multi-composition medium, and in-depth radiation absorption. Ignition is considered to occur when a critical pyrolysate mass flow is reached at the composite surface. The implication is that the ignition of the material is subjected to the attainment of a minimum concentration of fuel in the gaseous mixture adjacent to the pilot (lean flammability limit). The ignition delay is predicted over a wide range of external heat fluxes for low-density polyethylene, low-density polyethylene/fiberglass and polypropylene/fiberglass composites with varied composition. The results agree well with the available experimental data, and show that the ignition delay and critical external heat flux for ignition depend on the composition of the material, increasing as the fiber content is increased. From the results it is possible to identify the fiberglass content required to prevent ignition at a given radiant flux, a result that could provide guidelines toward the development of fire safe composites.

1 Introduction

Composite materials are widely used in the electronic and transportation industry. Typically, composite materials consist of two components: the structural constituent (fibers, laminae, flakes and fillers) and the body
structural constituent (fibers, laminae, flakes and fillers) and the body constituent (matrix). The matrix for most structural composites is commonly resin materials or thermoplastics. Compared to the traditional materials, composite materials usually possess unique and superior structural properties. However, they are in general more vulnerable to fire hazards because the matrix is usually made of a combustible polymer. Thus, concerning fire safety, it is important to understand the combustion characteristics of composites, in particular the conditions and factors that can affect ignition.

Combustion of polymers is a complex phenomenon that involves chemical and physical processes in both the gas and condensed phases. Under the condition of fast chemical kinetics, thermo-chemical processes in the condensed phase primarily determine the piloted ignition delay of polymers. Particularly important among these processes are pyrolysis, phase change, charring, and heat and mass transfer in multi-phase medium. Pyrolysis has been studied extensively from the view points of chemical kinetics and of physical mechanisms[1-2]. More related to the present work are the numerical analysis by Nelson et al.[3], Staggs[4], and most recently by Sohn[5]. The effects of the molten layer on pyrolysis has been studied by Kashiwagi et al.[6], and bubble-forming phenomenon during pyrolysis by Wichman[7]. The effect of charring has been studied by Chen et al[8]. A comprehensive review of the role of the condensed phase on the polymer combustion and flammability can be found in the article of Kashiwagi[9].

The objective of this paper is to apply a numerical model developed earlier by the authors[10] to predict the pyrolysis and piloted ignition delay of a pure low-density polyethylene sheet (LDPE), a low-density polyethylene/fiberglass (LDPE/GL) composite and a polypropylene/fiberglass (PP/GL) composite. The two composites are formed from a blend of thermoplastics matrix and loose fiberglass, and the uniform distribution of fiberglass whiskers within the matrix results in globally isotropic properties that simplify the analysis of the problem. The PP/GL composite is a practical material and typically used for casing and paneling in the electronic and transportation industry. In addition, LDPE and PP have several thermo-physical properties that make it particularly interesting to study the interaction of pyrolysis, melting and oxygen diffusion. These include: (1). The melting temperature of LDPE and PP is relatively low, and melting takes place before ignition occurs; (2). No char is formed during its combustion; (3). Oxygen has significant effects on the decomposition mechanism of LDPE and PP, which in turn influences the rate and products of the pyrolysis[11].

The work provides theoretical support to a program funded by NASA to study the flammability characteristics of solid combustible materials in microgravity. In an attempt to search for guidelines for fire safety, this paper investigates effects of composition on pyrolysis and ignition delay.

2 Numerical model

The problem considered in this analysis is illustrated in Fig 1. The front surface of a sample sheet is suddenly exposed to a uniform, and constant, external
External radiant heat flux

\[ U \]

Pyrolysate

Pilot

oxidative pyrolysis layer

thermal pyrolysis layer

Insulated

Matrix (PP)
Fiberglass (GL)

Melting interface

**Fig 1. Configuration of the physical problem**

radiant heat flux, and to a flow of oxidizer parallel to the solid surface. Its back surface is insulated to both heat and mass transfer. At first, the transient heating of the material is an essentially inert process, controlled by the balance of solid phase heat conduction, in-depth absorption of radiation, and convective and radiant heat losses from the exposed surface to the environment. Eventually, an endothermic melting and pyrolysis processes begin within the solid. The pyrolysis is oxidative in a thin layer near the sample surface, and thermal endothermic in the rest of the solid. The evolved pyrolysate gas is diffused away from the surface mixing with the oxidizer flow. If the conditions are such that a flammable mixture is formed near the pilot, ignition occurs.

The problem describes the experimental conditions of the Forced-flow Ignition and flame-Spread Test (FIST) developed at the micro-gravity combustion laboratory at UC Berkeley. FIST measures the piloted ignition delay and the rate of flame spread under various external heat fluxes, flow velocities and oxidizer concentrations. A detailed description of the FIST is given in [12].

The objective of the present analysis is to capture the essential characteristics of the problem, while reducing the complexity of the mathematical problem; thus the following assumptions are made in formulating the model:

1. Since the external heat flux is uniform along the surface, and the sample characteristic length is considered much larger than its thickness, the problem is formulated as one-dimensional.
2. Thermal conductivity of the composite follows the mixture roles and depends locally on the transient density and temperature. GL in this composite is assumed to be uniformly distributed and inert to PP pyrolysis.
3. Motion of the molten layer is neglected, so that the interaction of pyrolysis with melting is restricted to the change of physical properties.
4. A first-order Arrhenius law is incorporated to model the oxidative and thermal pyrolysis of LDPE and PP. The chemical kinetic parameters for both pyrolysis rates are obtained from the experimental data of Stuetz et al.[11],...
Ven[13], Ranzi[14] and Bockhorn[15]. 4. Thermal equilibrium between polymer, fiberglass and trapped pyrolysate are assumed locally at every point of the medium. 5. The pyrolysate flows through the multi-phase medium with no resistance.

With these assumptions, the governing equations are reproduced here for convenience,

\[
\frac{\partial \rho_m}{\partial t} + \frac{\partial \dot{m}_{m,v}}{\partial x} = 0
\]  

(1)

\[
\frac{\partial (\rho_m h_m)}{\partial t} + \frac{\partial (\rho_f h_f)}{\partial x} - \frac{\partial (\dot{m}_{m,v} h_m)}{\partial x} = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + Q_m \frac{\partial \rho_m}{\partial t} + \dot{q}_{\text{rad, ind-depth}}(x)
\]  

(2)

where

\[
\rho_m = \chi_m \rho_{m,\text{pure}}, \quad \rho_f = (1-\chi_{m,o}) \rho_{f,\text{pure}},
\]

\[
h_f = \int_0^T C_f dT, \quad h_{m,v} = \int_0^T C_{m,v} dT,
\]

\[
\dot{q}_{\text{rad, ind-depth}}(x) = \varepsilon \dot{q}_{\text{rad}} \chi_m \gamma_m \alpha_m \exp(-\int_0^x \alpha_m dx) + (1-\chi_{m,o}) \chi_f \alpha_f \exp(-\int_0^x \alpha_f dx)
\]

The negative signs in the RHS of Eq. (1) and (2) are due to the assumed direction of mass flow rate, which is along the negative-x direction. The Arrhenius rate equation and composite thermal conductivity are:

\[
\frac{\partial \rho_m}{\partial t} = -Z \dot{q}_{\text{rad}} \exp \left( -\frac{E_a}{RT} \right)
\]  

(3)

\[
k = \chi_m k_m(T) + (1-\chi_{m,o}) k_f(T) + (\chi_{m,o} - \chi_m) k_{m,v}(T)
\]  

(4)

The thermodynamic relation between enthalpy and temperature for thermoplastics is given as

\[
h_m = \int_0^T C_{m,s} dT, \quad h_m = \chi_{m,s} = \int_0^T C_{m,s} dT
\]

\[
T = \int_0^T \frac{\partial T}{\partial m,M} = \frac{h_m}{k} \leq h_m \leq h_m + L_m
\]  

\[
h_m = h_{m,s} + L_m + \int_0^T C_{m,s} dT, \quad h_m > h_{m,s} + L_m
\]  

(5)

The initial and boundary conditions are taken as:

at \( t = 0 \)

\[
\rho_{m,o} = \chi_{m,o} \rho_{m,pure}, \quad \rho_{m,o} = (1-\chi_{m,o}) \rho_{f,pure} = \rho_f
\]

\[
h_{m,o} = h_m(T_o), \quad h_{f,o} = h_f(T_o)
\]

at \( x = 0 \)

\[
\varepsilon \dot{q}_{\text{rad}} \left[ \chi_{m,o}(1-\gamma_m) + (1-\chi_{m,o})(1-\gamma_f) \right] = -k \frac{\partial T}{\partial x} + h_{\text{conv}}(T_{\text{surf}} - T_{\text{amb}}) + \varepsilon \sigma T_{\text{surf}}^4
\]
For clarification purposes it is worth mentioning the following points inherent in the above equations. First, in the energy equation (Eq.2), enthalpy changes of matrix and GL are considered separately because GL remains in solid state and does not interact with matrix during the pyrolysis process. This approach considerably simplifies the numerical computations. Secondly, melting of the matrix is incorporated in the thermodynamic relation of enthalpy and temperature (Eq.5). This formulation may seem only to describe the phase change phenomenon occurring at a specific constant temperature, such as that in crystalline materials. But in fact it is capable to model the thermodynamics of glass transition, softening or phase change in amorphous materials, which occurs over a range of temperature without a sharp jump in enthalpy. To model this behavior, it is only necessary to set a high artificial dummy melting temperature and to use a polynomial fit for the specific heat over the entire range of interest, so that only the first part of Eq. 5 is actually used in the calculation. Thus, Eq. 5 is in a general form, which allows to model phase change both at a fixed temperature and over a range. Thirdly, two pyrolysis processes, oxidative and thermal pyrolysis, are considered. In accordance with the experimental evidence in [11], oxidative pyrolysis is assumed to occur in a layer 0.4 mm from the surface, and the rest of which is assumed to be thermal pyrolysis. Finally, a distinction is made at surface and in-depth radiation absorption in order to properly model polymers whose radiation absorption depends on the wavelength of the incident radiation.

Uniformly spaced grids are used. The control volume method[16] is used to discretize the governing equations (1)-(5). The ensuing equation, together with the corresponding boundary and initial conditions, results in a set of algebraic equations to be solved numerically by the Newton iteration method[17]. An enthalpy-temperature hybrid method[18] developed by the authors in a separated study is employed to model melting process.

3 Numerical results

The numerical analysis is applied to the description of the heating and pyrolysis of the LDPE, LDPE/GL and PP/GL composites used in the FIST tests. The LDPE is purchased from King Plastic Corporation. It is opalescent and 1/2 inch thick. The PP/GL composite is commercially available from Montell North America Inc., as BJ22GC. It contains 70% PP and 30% GL by mass, is black and 1/8 inch thick. The LDPE/GL is hypothetic, in order to study the composition effect on different polymeric composites. The properties are summarized in Table 1. The numerical calculations are compared to the available experimental data. Calculations are also made for samples with other composition and thickness.
Table 1. Physical properties of PE, PP and GL

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>LDPE</th>
<th>PP</th>
<th>GL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>kg/m$^3$</td>
<td>918$^a$</td>
<td>900$^a$</td>
<td>2500$^b$</td>
</tr>
<tr>
<td>$k$</td>
<td>W/m K</td>
<td>0.5995 - 7.0 x 10^{-4} T (T &gt; 433 K)$^c$</td>
<td>0.186 (T &lt; 366 K)$^e$</td>
<td>0.33$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.715 - 9.8 x 10^{-4} T (T &gt; 433 K)$^c$</td>
<td>0.34511 - 4.7368 x 10^{-4} T (T &gt; 433 K)$^{f}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.66 + 4.67 x 10^{-3} T</td>
<td>-6.43 x 10^{-6} T$^2$ (others)$^e$</td>
</tr>
<tr>
<td>$C$</td>
<td>J/kg K</td>
<td>1918$^a$</td>
<td>10.1T - 1230 (solid)$^c$</td>
<td>825$^b$</td>
</tr>
<tr>
<td>$T_{\text{melt}}$</td>
<td>K</td>
<td>385$^a$</td>
<td>433$^a$</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>J/kg</td>
<td>5.0 x 10^4$^a$</td>
<td>5.02 x 10^4$^a$</td>
<td></td>
</tr>
<tr>
<td>$Z$</td>
<td>1/s</td>
<td>1.094 x 10^6 (thermal)$^d$</td>
<td>4.613 x 10^{10} (thermal)$^e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.569 x 10^8 (oxidative)$^f$</td>
<td>1.569 x 10^8 (oxidative)$^e$</td>
<td></td>
</tr>
<tr>
<td>$E_a$</td>
<td>J/mo l</td>
<td>2.621 x 10^5 (thermal)$^d$</td>
<td>2.43 x 10^5 (thermal)$^e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.225 x 10^5 (oxidative)$^f$</td>
<td>1.225 x 10^5 (oxidative)$^e$</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>J/kg</td>
<td>2.0 x 10^6 (thermal)$^f$</td>
<td>2.0 x 10^6 (thermal)$^g$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 x 10^5 (oxidative)$^f$</td>
<td>1.0 x 10^5 (oxidative)$^g$</td>
<td></td>
</tr>
</tbody>
</table>


Fig 2. Surface temperature histories of LDPE at air flow velocity of 1.0 m/s
Ignition delay is one of the major factors that rank the materials' flammability. It is determined by the sum of the pyrolysis, flammable mixture and induction times[22]. Under the circumstance of FIST experiments, the ignition delay is primarily determined by the pyrolysis time. Experimental observation indicates that ignition occurs when the mass fraction of pyrolysate reaches a critical value near the pilot. The implication is that under given oxidizer flow conditions, heating rate, and pilot location, the ignition of the material is controlled by the attainment of a minimum concentration of fuel in the gaseous mixture adjacent to the pilot. This fuel concentration is logically related to the lean flammability limit. Thus this criterion can be used to approximately predict ignition without actually solving the gas phase problem. The numerical predictions for the ignition delay over a wide range of external heat fluxes by using this criterion are shown in Fig. 3 for 1/8 inch LDPE/GL and PP/GL at various volume fractions of the matrix. The reference values used here, \( \dot{m} = 2.25 \text{ g/m}^2\text{s} \) for LDPE and 3.0 g/m²s are obtained by matching the numerical calculation with the experimentally measured delay time at an external heat flux. These values are close to the critical pyrolysate mass flow rate for ignition reported by Tewarson [23], which are 2.5 and 2.7 g/m²s for granular LDPE and granular PP respectively.

The components in a composite possess different physical properties, thus their volume fractions play an important role in determining the composite thermal behavior. The predicted effect of the composite composition on the surface temperature for 1/2 inch LDPE/GL is shown in Fig. 2 for an external heat flux of 27.5 kW/m² and a forced flow of 1.0 m/s. It is seen that the surface
temperature decreases as the volume fraction of LDPE decreases. This is because the heat capacity of GL is larger than that of LDPE in solid phase, therefore, decreasing the volume fraction of PP increases the fraction of GL in the composite and consequently the effective overall heat capacity of the composite.

The effect of the matrix volume fraction on the ignition delay shown in Fig. 3 indicates that as the volume fraction of matrix is decreased, the critical heat flux for ignition is increased. They also show that at a given external heat flux, there exists a critical volume fraction of matrix beyond which ignition cannot occur. The critical volume fractions of PP and LDPE are plotted in Fig 4 as a function of the external heat flux. It shows that the critical heat flux and the critical volume fraction of matrix are inversely related to each other. This result has significance from the viewpoint of fire safety, and could provide guidelines toward the development of fire safe composites.

![Graph showing predicted critical volume fractions of matrix in LDPE/GL at airflow of 1 m/s and PP/GL at airflow of 1.75 m/s.]

**Fig 4.** Predicted critical volume fractions of matrix in LDPE/GL at airflow of 1 m/s and PP/GL at airflow of 1.75 m/s

### 4 Conclusion

A numerical model for pyrolysis and ignition delay of composite materials exposed to an external radiant heat flux has been developed. The model takes into account both oxidative and thermal pyrolysis, melting, heat and mass transfer in a multiple-phase and multiple-composition medium, and radiation in-depth absorption. The numerical results agree well with the existing experimental data, and are consistent with the physical expectations.

The numerical model has been used to predict the effect of the composite composition on the pyrolysis rate and ignition delay. It has been shown that as the volume fraction of the fiberglass is increased, the rate of temperature increase
and pyrolysate mass flow rate decrease, and that as a consequence the ignition delay increases. For a given external heat flux, there is a critical volume fraction of fiberglass beyond which the composite material does not ignite. This observation has potential fire safety implications for composite materials, and could provide guidelines toward the development of fire safe composites.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>( C )</td>
<td>Specific heat</td>
</tr>
<tr>
<td>( h )</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>( k )</td>
<td>Conductivity</td>
</tr>
<tr>
<td>( L_{pp} )</td>
<td>Latent of matrix in a composite</td>
</tr>
<tr>
<td>( \dot{q}_{\text{rad}} )</td>
<td>External radiant heat flux</td>
</tr>
<tr>
<td>( \dot{q}_{\text{rad, indepth}} )</td>
<td>In-depth radiant absorption</td>
</tr>
<tr>
<td>( Q_{pp} )</td>
<td>Heat of pyrolysis</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
</tr>
<tr>
<td>( x )</td>
<td>Coordinate along the sample thickness</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Emissivity of the sample</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Fraction of in-depth absorption</td>
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Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>Radiant absorption coefficient</td>
</tr>
<tr>
<td>( \chi )</td>
<td>Effective volume fraction of matrix in a composite</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Emissivity of the sample</td>
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Subscripts

<table>
<thead>
<tr>
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<th>Definition</th>
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<tbody>
<tr>
<td>( m )</td>
<td>Polymer matrix in a composite</td>
</tr>
<tr>
<td>( f )</td>
<td>Filling material in a composite</td>
</tr>
<tr>
<td>( o )</td>
<td>Initial</td>
</tr>
<tr>
<td>( s )</td>
<td>Solid</td>
</tr>
<tr>
<td>( M )</td>
<td>Phase change</td>
</tr>
<tr>
<td>( \text{amb} )</td>
<td>Ambient</td>
</tr>
</tbody>
</table>

Acknowledgments

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References