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Pyrolysis and flammability properties of novolac/graphite nanocomposites

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ABSTRACT

A large number of studies showed that nanoparticles used even in small quantities improve thermal stability and flammability resistance by reducing significantly the mass loss and heat release rate. Recently, a graphite nano-crystal and nano-clay have been used as an alternative to traditional fire retardants to improve the thermal stability and flammability resistance of polymeric materials.

The objectives of this work are the experimental and theoretical evaluation of the pyrolysis and flammability of the polymer nanocomposites based on novolac type phenolic resin and graphite nano-crystal under the external convection and radiation heat flux. The theoretical results of heat release rate modeling based on conservation equations of mass and energy are then confirmed by the experimental data of thermal analysis.

Nano-graphite shows good potential as flame retardant because upon pyrolysis of polymer, the nano-crystal graphite reinforced phenolic resin can be converted into a uniform carbon layer, which may lead to significantly higher resistance to oxidation compared to neat phenolic resin. Formation of this carbon layer on char formed from the pyrolysis of the nanocomposite at high temperature not only enhances the char mechanical strength, but also acts as secondary protection layer to protect the lower remained nanocomposite.

1. Introduction

Novel polymer composites based on nanotechnology creating nontraditional heat shields and insulators are rapidly changing the technology based for thermal protection systems [1]. The introduction of inorganic nanomaterials as additives into polymer systems has resulted in polymer nanocomposite materials exhibiting multifunctional, high performance polymer characteristics beyond what traditional polymer composites possess [1,2]. Multifunctional features attributable to polymer nanocomposites consist of improved thermal and flame resistance. Through control or alternation of the additives at the nanoscale level, one is able to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current defense, aerospace, and commercial applications [1–3].

Before describing the approach used in this work, it is beneficial to summarize some previous works relating to this subject. One of the first noteworthy studies of composites and fire was performed by Pering et al. [4]. In Pering et al. work, composite samples were subjected to intense heat and the mass loss and strength loss were measured as functions of exposure time. Correlations between strength and mass loss were demonstrated, but no attempt was made to explain or model the relationship.

Blumstein, 1965 reported the improved thermal stability of a polymer clay nanocomposite that combined polymethylmethacrylate and montmorillonite [5]. The first mention of the potential flame retardant properties of these types of materials appears in a Japanese patent application on nylon-6 clay nanocomposites by Fujiwara and Sakamoto in 1976 [5].

Vaia et al. [6] reported the ablative performance of poly (caprolactam) (nylon 6) nanocomposites as a high performance ablative heat shields. In this work, the ablation rate (erosion rate) of the materials was determined from exposure to combustion gases in a laboratory scale solid rocket motor firing rig.

Preparation of polystyrene/clay nanocomposites with different M_w values and clay loading levels was studied by Kashiwagi et al. [7]. Heat release rate (HRR) data for pure polystyrene and polystyrene/clay (10 wt%) nanocomposites were analysis experimentally in this work [7].

Recently, we found that the polymer layered silicate nanocomposites have the unique combination of reduced flammability and improved physical and thermal properties. The results of these works were published in our some papers about thermal stability and pyrolysis [3], burning and flammability properties [2], and ablation mechanism of polymer nanocomposite materials [8,9].

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Nomenclature

A	pre-exponential factor of pyrolysis reaction, [1/s]
c	concentration, [kg/m^3]
c_G	concentration of pyrolysis gases, [kg/m^3]
C_{char}	specific heat of char, [J/kg/K]
C_{polymer}	specific heat of polymer, [J/kg/K]
D_{char}	diffusion coefficient of pyrolysis gases through char, [m^2/s]
D_{polymer}	diffusion coefficient of pyrolysis gases through polymer, [m^2/s]
E	activation energy of pyrolysis reaction, [J/mol]
h	heat transfer coefficient of gas at surface, [J/m^2/K/s]
HRR	heat release rate, [W/m^2]
J	gasification constant,
k	rate constant for pyrolysis reaction, [1/s]
k_c	rate constant of char formation reaction, [1/s]
k_g	rate constant of gas formation reaction, [1/s]
k_p	rate constant of polymer decomposition reaction, [1/s]
$k_{-\mathrm{p}}$	rate constant of polymer formation reaction, [1/s]
K	thermal conductivity, [W/m/K]
K_0	thermal conductivity at initial temperature (T_0), [W/m/K]
K_{char}	thermal conductivity of char, [W/m/K]
m	mass of sample, [kg]
m_c	mass of char, [kg]
m_G	mass of pyrolysis gas, [kg]
$\dot{Q}_{\mathrm{surface}}$	heat flux at surface, [J/m^2/s]
R	gas constant, [J/mol/K]
r	rate of polymer consumption during pyrolysis, [kg/m^3/s]
r_{GP}	rate of gas evolution during pyrolysis, [kg/m^3/s]
T	temperature, [K]
T_{atm}	atmosphere temperature, [K]
T_{cone}	cone temperature, [K]
V	volume, [m^3]
t	time, [s]
T_{atm}	temperature of atmosphere, [K]
T_{Cone}	temperature of cone heater, [K]
x	length in the x-direction, [m]
y_c	char yield,
α	mass fraction of gas that is produced,
β	heating rate,
ΔH	heat of volatilization of polymer, [J/kg]
ΔH_e	heat released or absorbed in other chemical processes in sample, [J/kg]
ΔH_1	heat of combustion, [J/kg]
Γ	char yield,
ε	emissivity,
φ	percent heat transferred by heat of combustion
ρ_{char}	density of char, [kg/m^3]
ρ_{polymer}	density of polymer, [kg/m^3]
σ	Stefan–Boltzmann constant, [J/m^2/K^4/s]
υ	volume fraction,
χ	distance between x_1 and x_2.

In this paper, novolac type phenolic resin and its layered crystalline graphite nanocomposites are analyzed. The main objective of this study is to examine the influence of the radiation external heat flux and nano graphite in estimating the flammability and thermal properties of nanocomposites. In order to achieve this, experimental data of pyrolysis and burning, and mathematical model results are analyzed and compared.

2. Mathematical modeling

2.1. Kinetic models of thermal degradation

The kinetic parameters of the thermal degradation are determined using thermo-gravimetric analysis. The knowledge of these parameters is required to calculate the variation of thermo-physical and other thermal properties and usage of mass and energy equations which will be mentioned in next sections.

2.1.1. Chemical reactions

Thermal degradation simplified in three processes: heating of the polymer, thermal decomposition, and ignition of the gaseous decomposed products in air [11].

A simple solution for the mass loss history of a polymeric material allows estimation of the thermal degradation behavior under isothermal and non-isothermal heating, and can be verified using standard laboratory thermogravimetric techniques. By considering some assumptions, the process of thermal degradation will be reduced and simplified to Eqs. (1)–(3) (derivation of all of thermal degradation equations were reported in Ref. [3]). The following assumptions are considered [11,12];

A The breaking of primary chemical bonds in the polymer is the rate limiting step.
B The reactive intermediate is in dynamic equilibrium with the parent polymer.
C Thermal degradation of primary char to secondary char and gas is slow compared to the formation of the primary char.
D The oxidative environment in the pyrolysis zone of a thermal degradation solid polymer is anaerobic.
E All of the chemical reactions are of first order.

Assumptions *A–E* led to a simplified mass loss model as follows [3,11,12]

$$P \overset{k_p}{\underset{k_{-p}}{\rightleftarrows}} I^* \tag{1}$$

$$I^* \overset{kg}{\rightarrow} \text{Volatiles} \tag{2}$$

$$I^* \overset{k_c}{\rightarrow} \text{Gases} \tag{3}$$

By assuming the first order reaction for all the chemical reactions, the rate equations for the species are

$$\frac{dp}{dt} = -k_p P + k_{-p} I^* \tag{4}$$

$$\frac{dI^*}{dt} = k_p P - (k_{-p} + k_g + k_c) I^* \tag{5}$$

$$\frac{dG}{dt} = k_g I^* \tag{6}$$

$$\frac{dC}{dt} = k_c I^* \tag{7}$$