Development of pyrolysis models for charring polymers

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ABSTRACT

Controlled atmosphere, radiation-driven gasification experiments were conducted on a series of synthetic polymers including poly(acrylonitrile butadiene styrene), poly(ethylene terephthalate), poly(methyl methacrylate)-poly(vinyl chloride) alloy (Kydex) and polyetherimide. Mass loss rate and non-radiated surface temperature of coupon-sized material samples were measured simultaneously and recorded as a function of time. These temperature data were combined with the results of broadband radiation absorption measurements and previously conducted thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to characterize the transport of thermal energy inside the gasifying materials through inverse modeling. Subsequently, complete pyrolysis models, based on the kinetics and thermodynamics of the thermal decomposition derived from the TGA and DSC experiments, were formulated and employed to predict the mass loss rate histories obtained at 30—90 kW m^{-2} of external radiant heat flux simulating fire exposure. Satisfactory predictions were obtained for all materials with the exception of polyetherimide, which highly intumescent behavior introduced large uncertainties in the gasification conditions.

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1. Introduction

It is widely recognized that charring polymers, materials that form solid, thermally stable and oxidation resistant residue upon thermal decomposition, tend to have lower flammability than non-charring polymers. One of the main strategies to improve flame resistance of a polymeric solid is to alter its molecular structure or compound it with chemicals that increase its propensity to char [1]. Polymer flammability can be generally characterized by the evolution of the rate of gaseous fuel production (or mass loss rate) in response to application of a radiative or convective heat flux to a defined area of the material sample. Multiplication of this rate by the effective heat of combustion of the gaseous fuel yields heat release rate, which is the single most important parameter describing dynamics of fire growth [2].

A significant benefit can be derived from a capability to simulate pyrolysis of charring polymers in order to predict their mass loss rate. Such simulations, if accurate, enable fast and effortless evaluation of material flammability in a wide range of fire scenarios and may offer critical insights into optimization of the material's

composition and structure to achieve better performance. Atreya [3], Di Blasi [4], Moghtaderi [5], Staggs [6] and Delichatsios [7], among others, developed essential mathematics of continuum pyrolysis models for charring materials and proposed approaches to their parameterization. It should be noted that the majority of their effort has been focused on lignocellulosic materials.

Our group has recently developed a method, based on carefully calibrated milligram-scale thermal analysis experiments, that provides a comprehensive characterization of the kinetics and thermodynamics of the thermal decomposition for non-charring [8] as well as charring polymers [9]. This method yields a set of parameters including semi-global decomposition reaction kinetics, heat capacities, heat of melting and heats of decomposition reactions, which represents the core of the input required for the state-of-the-art pyrolysis models [10—12]. In the current study, these parameters were combined, through modeling, with the results of simple infrared radiation absorption measurements and new gram-scale gasification experiments utilizing simultaneous sample mass and temperature monitoring to produce fully parameterized pyrolysis models. The absorption measurements were used to define radiative heat transport through the unpyrolyzed materials, while the gasification temperature measurements provided the information necessary to compute the

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condensed-phase thermal conductivities as a function of temperature and local composition. The mass loss rate histories obtained from the gasification experiments were employed to validate these pyrolysis models.

This approach to pyrolysis model parameterization has already been demonstrated to provide accurate mass loss rate predictions for non-charring polymers [13]. In the current work, an applicability of this approach to charring polymers including poly(acrylonitrile butadiene styrene) (ABS), poly(ethylene terephthalate) (PET), poly(methyl methacrylate)-poly(vinyl chloride) alloy (Kydex) and polyetherimide (PEI) was examined. These materials are listed in the order of increasing char yield with ABS being essentially non-charring (<3 wt.% char yield) and PEI having the highest char yield ($\approx$50 wt.%). ABS was included into this study because, as the subsequent analysis shows, its char still produces a thermally insulating layer, which impact on the material's mass loss rate cannot be neglected.

2. Materials and methods

2.1. Materials

ABS, PET, Kydex and PEI were purchased in a form of large (approximately 1.2 × 0.6 m), extruded sheets. These sheets were 6.4, 6.7, 6.1 and 6.6 mm thick, respectively. Detailed information on the source of purchased materials is provided in Table 1. The density of these materials was measured at room temperature ($\approx$300 K) and found to be 1050, 1385, 1350 and 1285 kg m^{-3}, respectively. To minimize variation in the moisture content, all material samples were stored in a desiccator in the presence of Drierite for a minimum of 48 h prior to testing.

2.2. Thermal analysis experiments

4–7 mg, thin-film samples were cut from the extruded sheets and subjected to a linear heating at a rate of 10 K min^{-1} in a nitrogen atmosphere using a simultaneous thermal analyzer, Netzsch F3 Jupiter, capable of thermogravimetric analysis and differential scanning calorimetry. Sample mass and heat flow into these samples were recorded as a function of time and temperature and a numerical analysis was conducted to derive both kinetics and thermodynamics of the material's thermal decomposition. A detailed description of these experiments and analysis is provided elsewhere [8,9].

2.3. Gasification experiments

80 × 80 mm square plates were cut from the extruded sheets and gasified using controlled radiant heating. These experiments were performed in a Govmark CC-1 cone calorimeter [14] equipped with the Controlled Atmosphere Pyrolysis Apparatus (CAPA) [15]. The cone calorimeter radiant heater was employed to deliver a steady heat flux to the top surface of a horizontally mounted sample. This surface was initially located 40 mm below the bottom of the heater. The calorimeter's precision balance was used to monitor the sample's mass loss. The calorimeter's exhaust system, which was operated at 1440 L min^{-1}, was used to remove gaseous pyrolysis products.

The CAPA, which was operated at 225 standard L min^{-1} of nitrogen, was used to create a near anaerobic environment, oxygen concentration <3 vol.%, in the vicinity of the sample. The oxygen concentration was measured by sampling from the atmosphere above the initial position of the top sample surface and analyzing this atmosphere with Servomex 4100 gas analyzer. Anaerobic conditions were used in both thermal analysis and gasification experiments to simulate material degradation under a laminar flame sheet. It should be noted that, during the experiments on Kydex and PEI, significant changes in the pyrolyzing sample size and shape made it impossible to control oxygen concentration at the sample surface for the full duration of these experiments. Both materials demonstrated highly intumescent behavior; their samples expanded outside of the CAPA boundaries and into the cone heater (oxygen concentration >10 vol.%) late in the gasification process. These factors were taken into account during subsequent analysis of the experimental data.

The CAPA was modified to add additional diagnostics. A schematic of the modified CAPA is shown in Fig. 1. A portion of the CAPA's external wall was replaced with a quartz plate to enable videotaping of the changes in the sample's geometry during gasification. The CAPA's sample holder was redesigned to provide an optical access to the bottom sample surface. The sample was placed on a 0.8 mm thick aluminum mesh. For materials that demonstrated significant melt flow, ABS and PET, a layer of 0.03 mm thick aluminum foil was placed between the sample bottom and the mesh to prevent dripping through the mesh. The perimeter of each sample was wrapped with a 0.1 mm thick paper tape and thermally insulated with a 5 mm wide strip of Kaowool PM.

A temperature-calibrated infrared camera, FLIR E40, was focused on the bottom sample surface through a gold-coated flat mirror (0.97 reflectivity in 0.8–10 μm range). A coat of high emissivity, 0.95, paint was applied to the sample, aluminum mesh and foil surfaces facing the camera to ensure correct temperature reading and provide well-defined thermal conditions at this boundary. The temperature readings were taken through the spacing in the aluminum mesh, which covered only about 20% of the bottom sample surface. The validity of this approach to sample surface temperature measurement was examined and verified in previous studies [13,16].

The experiments were performed at 30, 50 and 70 kW m^{-2} of set radiant heat flux for all materials with the exception of PEI, which was studied at 50, 70 and 90 kW m^{-2} because of its exceptional thermal stability. The data from the PET experiments conducted at 30 kW m^{-2} were compromised by intense dripping and spattering of the pyrolyzing material and were excluded from further consideration. The heat fluxes were set using a water-cooled Schmidt-Boelter heat flux gauge, which was positioned at a location corresponding to the geometric center of the initial position of the top sample surface. 30 kW m^{-2} heat flux corresponded to the heater temperature of about 915 K. 90 kW m^{-2} heat flux corresponded to the heater temperature of about 1200 K.

Spatial variation in this heat flux was examined in an attempt to account for the changes in the heating conditions experienced by

Table 1
Source of materials studied in this work.

Polymer	Manufacturer	Trade name	Distributor
Poly(acrylonitrile butadiene styrene) (ABS)	Westlake Plastics	Absylux	Modern Plastics
Poly(ethylene terephthalate) (PET)	Ensinger	PET	Curbell Plastics
Poly(methyl methacrylate)-poly(vinyl chloride) alloy (Kydex)	Kydex, LLC	Kydex T	Professional Plastics
Polyetherimide (PEI)	GE Plastics	Ultem 1000	Curbell Plastics