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Measurement of kinetics and thermodynamics of the thermal degradation for charring polymers

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ABSTRACT

This work was focused on developing and applying a systematic methodology for the measurement of kinetics and thermodynamics of the thermal degradation of polymeric materials. This methodology employed a simultaneous thermal analysis instrument capable of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A numerical model was utilized to fit thermogravimetric data to obtain thermal degradation kinetics. This model was subsequently employed to analyze DSC heat flow and extract sensible, melting and decomposition reaction heats. The extracted set of kinetic and thermodynamic parameters was shown to simultaneously reproduce TGA and DSC curves. In the current study, this methodology was applied to polymers that produce a significant amount of carbon rich residue (char) upon thermal decomposition. The analyzed materials were a poly(methyl methacrylate)−poly(vinyl chloride) alloy (Kydex), polymerized diglycidylether of bisphenol A, poly(ethylene terephthalate), poly(paraphenylene terephthalamide) (Kevlar), polymerized bisphenol A cyanate ester, poly(phenylene sulfide), polyetherimide and poly(ether ether ketone). The materials that produced less than 40 wt.% of char upon decomposition were found to decompose endothermically. The materials whose char yield exceeded 40 wt.% were found to undergo an exothermic decomposition.

1. Introduction

The pyrolysis of solid polymeric materials is a complex process that involves multiple chemical and physical phenomena such as phase transitions, chemical reactions, heat transfer and mass diffusion [1]. To better understand how these phenomena interact to give rise to gaseous fuel generation, which defines material flammability [2], a number of numerical pyrolysis models have been developed. The solid phase submodel in the NIST Fire Dynamics Simulator [3], ThermaKin [4], Gpyro [5] and Pyropolis [6] are pyrolysis modeling computer codes that were developed during the last few years. For input, these models require property values that describe the aforementioned chemical and physical phenomena. While some progress has been made in the development of experimental procedures for the measurement of these properties [7–15], accuracy, generality and robustness of these procedures clearly require further refinement.

In a recent study [16], we have developed a method for the measurement of the core subset of these properties including mass loss kinetics, heat capacities, heats of melting and heats of decomposition reactions. This method is based on thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) conducted in an anaerobic environment. The main advantage of these techniques is associated with the use of small material samples (3–10 mg) and relatively slow (3–30 K min^{-1}) and steady heating rates. These heating conditions minimize the effects of heat and mass transport inside the sample on mass loss (in the case of TGA) and heat flow (in the case of DSC) and significantly simplify data analysis and interpretation. The data analysis was performed using pyrolysis modeling software, ThermaKin [4], which was ran in an infinitely fast transport mode. The consistency of the derived parameter set was verified by simulating TGA and DSC experiments and comparing the results of these simulations with the corresponding experimental data.

This method was successfully applied to a set of 7 non-charring polymers and corrugated cardboard and was shown to generate property sets that describe material degradation under slow (3–30 K min^{-1}) as well as fire-like (30–200 K min^{-1}) heating conditions [16,17]. In the current work, this method has been extended to synthetic charring polymers. The polymers that produce more than 10 wt.% of solid residue (char) when heated to 1223 K (950 °C) in an anaerobic environment were considered to be charring. On

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Table 1
Source of materials analyzed in this study.

Polymer	Manufacturer	Trade name	Distributor
Poly(methyl methacrylate)–poly(vinyl chloride) alloy (Kydex)	Kydex, LLC	Kydex® T	Professional Plastics
Diglycidylether of bisphenol A	Sigma	Bisphenol A diglycidylether	Sigma–Aldrich
Poly(ethylene terephthalate) (PET)	Ensinger	PET	Curbell Plastics
Poly(paraphenylene terephthalamide) (Kevlar)	DuPont	Kevlar® Plain Weave Fabric	Fiber Glast Developments
Bisphenol A cyanate ester	Lonza	Primaset Cyanate Esters	Lonza
Poly(phenylene sulfide) (PPS)	Ensinger	PPS	Curbell Plastics
Polyetherimide (PEI)	GE Plastics	Ultem 1000	Curbell Plastics
Poly(ether ether ketone) (PEEK)	Victrex plc	PEEK grade 450G	Victrex plc

average, charring polymers tend to have lower flammability than non-charring polymers [18] and, therefore, are of special interest to flame resistant material developers.

A set of materials analyzed in this study included a poly(methyl methacrylate)–poly(vinyl chloride) alloy (Kydex), polymerized diglycidylether of bisphenol A (DGEBA), poly(ethylene terephthalate) (PET), poly(paraphenylene terephthalamide) (Kevlar), polymerized bisphenol A cyanate ester (BACY), poly(phenylene sulfide) (PPS), polyetherimide (PEI) and poly(ether ether ketone) (PEEK). The char yield produced by these polymers varied between 11 and 51 wt.%. A relatively high char yield and decomposition temperature of these materials posed significant challenges to our kinetics and thermodynamics measurement methodology. An augmented methodology that addresses these challenges is the main outcome of this study.

2. Experimental

2.1. Materials and sample preparation

Kydex, PET, PPS, PEI and PEEK were purchased in a form of large, extruded sheets (approximately 1220 × 610 × 6.4 mm in size). Kevlar was purchased in a form of woven fabric samples (150 × 100 × 0.2 mm). DGEBA and BACY were prepared in our laboratory by curing manufacturer supplied resins in a square mold (80 × 80 × 6.35 mm). 1–2 wt.% of 2-ethyl-4-methylimidazole was added to DGEBA resin to promote curing. No curing agent was used for BACY. DGEBA and BACY specimens were cured in a convection oven. In the case of DGEBA, the oven temperature was increased from 293 to 393 K in 50 K increments and was held constant for 4 h after each increase. In the case of BACY, the oven temperature was increased from 293 to 523 K using the same incremental approach. Detailed information on the source of purchased materials is provided in Table 1. Thermal analysis samples were prepared by cutting polymer specimens into thin, flat squares, less than 0.5 mm in thickness and 4–7 mg in mass. These samples were conditioned in a desiccator in the presence of Drierite for a minimum of 48 h prior to testing.

2.2. Thermal analysis experiments

A Netzsch F3 Jupiter STA was employed in this study. This apparatus combines a TGA instrument equipped with 1 μg-resolution microbalance and a heat flux DSC implemented using a Netzsch TGA–DSC sample carrier equipped with P-type thermocouples. Our first attempt to perform DSC-based decomposition heat measurements [7] led to a conclusion that significant heat flow errors may result from a relatively low temperature of the enclosure containing sample and reference containers (due to highly non-linear and poorly controlled heat losses from the containers to the enclosure). In the current apparatus, which was selected to mitigate this problem, the containers were positioned in the middle of a long (26 cm), vertical, uniformly heated furnace, which wall temperature slightly exceeded that of the containers throughout the heating process. These conditions ensured that, even if the heat transfer efficiency between the sample container and surrounding walls were to increase in the course of an experiment (perhaps, due to contributions from radiation), this change would have a minor impact on the container bottom temperature, which the heat flow measurement is based on. More information on the design of the F3 Jupiter STA can be found in a manufacturer's brochure [19].

An anaerobic environment was created inside the furnace by continuously purging it with nitrogen at a rate of 50 cm^3 min^{-1}. TGA and DSC experiments were conducted simultaneously using the following heating program. A sample was first heated to 313 K and maintained at this temperature for 25 min. This period was included to ensure that the system is initially in thermal equilibrium and free of oxygen. Subsequently, the sample was heated to 1223 K at a heating rate of 10 K min^{-1}. The mass and heat flow data were collected only during the second, linear heating phase of the test. The selection of the heating rate was based on a recent theoretical analysis [20] that indicated that using 10 K min^{-1} for <10 mg samples ensures a uniform temperature inside the sample even when the heat associated with decomposition processes is significant. Additional TGA experiments were performed at 30 K min^{-1}. These experiments were used to evaluate how well the mass loss kinetics model developed using 10 K min^{-1} data performs at higher heating rates.

All thermal analysis experiments were performed using Platinum–Rhodium crucibles with lids. The lids had a small (0.25 mm in diameter) orifice for ventilation. This container configuration was used to maximize the thermal contact between a degrading sample and heat flow sensing thermocouple located underneath the crucible. It was shown in a previous study [16] that the lids did not interfere with transfer of gaseous decomposition products out of the crucible.

Each material test was preceded by a baseline test, where empty sample and reference crucibles were subjected to the same heating program. The baseline mass (in the case of TGA) and heat flow history (in the case of DSC) were subtracted from the corresponding data obtained from the material test. All TGA and DSC data presented in the following sections have been baseline corrected.

Seven thermal analysis experiments (simultaneous TGA and DSC) were performed on each polymer at 10 K min^{-1}. Averaged mass and heat flow curves were computed and used in further analysis. Averaging of heat flow curves from multiple experiments was shown to significantly reduce random errors and enable measurement of heat capacity [16]. Multiple experiments also provided the data necessary for the calculation of uncertainties in the extracted properties.

The high (30 K min^{-1}) heating rate TGA experiments were repeated 3 times (and averaged prior to analysis). TGA and DSC experiments on PPS were conducted only at 10 K min^{-1} and only 3