Combustion and Flame 177 (2017) 184–192

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Development of kinetic parameters for polyurethane thermal degradation modeling featuring a bioinspired catecholic flame retardant

B.C. Roberts[a,*], A.R. Jones[b], O.A. Ezekoye[a], C.J. Ellison[b], M.E. Webber[a]

[a] The University of Texas at Austin, Department of Mechanical Engineering, Cockrell School of Engineering, 204 E. Dean Keeton St. C2200, Austin, TX 78712, United States

[b] The University of Texas at Austin, Department of Chemical Engineering, Cockrell School of Engineering, 1 University Station C0400, Austin, TX 78712, United States

ARTICLE INFO

Article history:
Received 10 August 2016
Revised 3 October 2016
Accepted 8 December 2016
Available online 6 February 2017

Keywords:
Flame retardant
Polydopamine
Flexible polyurethane foam
Thermal degradation
Kinetic parameters
Thermogravimetric analysis

ABSTRACT

A recently developed flame retardant (FR) nanocoating of polydopamine (PDA) was applied to flexible polyurethane foam (PU) and thermogravimetrically analyzed (TGA). Thermal degradation kinetics were described by a simplified multi-component, Arrhenius expression coupled with a first-order reaction model. Kinetic parameters were then extracted via an optimization solver. By limiting the number of optimized parameters, a mesh adaptive direct search algorithm was employed to extract meaningful kinetic parameters that better simulate the TGA data compared to graphical methods. Through TGA, it was shown that the effect of the PDA nanocoating on PU degradation differs between oxidative (78 vol% nitrogen (N_2) and 21 vol% oxygen) and inert (100% N_2) environments. In nitrogen, the mass loss is delayed and diminished in the first PU reaction, which is the opposite effect of a traditional halophosphate FR. In an oxidative environment, the first reaction of PU is greatly delayed by the PDA coating, but once the reaction begins, it becomes accelerated.

1. Introduction

Used in a variety of cushioning applications, including mattresses, upholstered furniture, and carpeting, flexible polyurethane foam (PU) has been in high demand since becoming commercially available in the early 1950s. PU is the product of a reaction between a reactive hydrogen containing compound and a polyisocyanate. Typical formulations involve a polyol reacted with toluene diisocyanate (TDI) [1]. According to the Polyurethane Foam Association (PFA), over 1.2 billion pounds (544,311 metric tons) of PU are produced in the U.S. annually [2]. Although PU has many benefits, it is a highly flammable material that, depending on the application, can require additional protection to meet U.S. fire codes and standards. Therefore, flame retardants (FRs) are typically incorporated to meet flammability standards. According to a 2015 report by the U.S. Environmental Protection Agency (EPA), there are very few FR options for PU that do not pose a high health concern for humans, aquatic life, and the environment [3]. Although halogenated FRs have been criticized for their toxicity, the EPA indicates that many non-halogenated phosphate alternatives still pose very high aquatic toxicity hazards along with moderate to high human health concerns [3]. Due to the limited availability of non-toxic, environmentally friendly FR options, research and development of new FRs is still needed.

The FR investigated in this study is polydopamine (PDA), which is a synthetic analog of naturally occurring melanins. Melanins are polyphenolic compounds derived from the oxidation of tyrosine or dihydroxyphenylalanine (DOPA), and are produced by living organisms [4]. In 2007, it was discovered that PDA forms as a protective nanocoating on a number of different materials if dopamine hydrochloride is placed in a slightly basic (pH = 8.5) aqueous solution [4]. Since the discovery, PDA has been studied as a beneficial coating in a variety of applications, such as protective light absorption and drug delivery [4]. Recently, a U.S. patent presented the composition of PDA and either tris(hydroxymethyl)aminomethane or gaseous ammonia as a flame retardant coating [5]. Subsequently, PDA was successfully employed as a surface coating to PU for the purpose of decreasing PU flammability [6]. In the study by Cho et al. [6], microscale combustion calorimetry (MCC) and thermogravimetric analysis (TGA) of neat PDA in nitrogen demonstrated that it is relatively inflammable and forms thermally protective

---

[*] Corresponding author.

E-mail addresses: broberts@utexas.edu (B.C. Roberts), ajones@che.utexas.edu (A.R. Jones), dezekoye@mail.utexas.edu (O.A. Ezekoye), ellison@che.utexas.edu (C.J. Ellison), webber@mail.utexas.edu (M.E. Webber).

http://dx.doi.org/10.1016/j.combustflame.2016.12.014
0010-2180/

carbonaceous, porous char. Additionally, PDA was deposited on PU after various coating times and the resultant coating was characterized. A significant reduction (67%) in peak heat release rate was demonstrated using cone calorimetry for foam specimens with 15.9 wt% PDA deposited, which was achieved after three days of coating. This success was attributed to synergistic combinations of physical and chemical actions, which we explore further in the present work through TGA and thermal degradation modeling in both oxidative and inert environments.

A primary step in understanding and quantifying the effects of FRs is the investigation of the impact on thermal degradation. Thermogravimetric analysis is a convenient method of observing changes in physical and chemical properties of materials as a function of a constant heating rate. Only a small sample is required, enabling economical early stage validation of FR viability in new chemical combinations. Sample mass and temperature are monitored throughout heating, which makes observations of condensed-phase changes possible. Solid-state reaction rate models can then be applied to the empirical data to extract kinetic parameters. In theory, these parameters have physical meaning that can describe the mass loss due to chemical reactions. However, an appropriate kinetic model must be applied [7]. One benefit of extracting kinetic parameters is that they aid complex modeling of ignition and combustion of materials [8–13].

Previous studies have investigated pyrolysis and/or oxidation of PU with and without FR via TGA and applied their results to an *n*-order reaction model, similar to the one suggested herein. Consensus among researchers has indicated that an *n*-order model is most appropriate for PU decomposition reactions, although Rogers and Ohlemiller [14] assessed that applying a two-dimensional diffusion model to the first reaction and a nucleation model to the second reaction was best. Chao and Wang [15] proposed thermal degradation mechanisms in both air and nitrogen environments of neat and brominated phosphorus FR PU. Kinetic parameters were graphically determined using the Friedman [16] method. Bilbao et al. [17] used both isothermal and dynamic TGA data to derive kinetic parameters in both inert and oxidative environments for neat PU. A variation of the Arrhenius Plot graphical method was used to extract kinetic parameters. Pau et al. [18] analyzed both neat and chlorinated phosphorous melamine FR PU in a nitrogen environment at multiple heating rates. Three different graphical techniques (Kinetic Analysis, Arrhenius Plot, and Inflection Point) were tested to determine their compatibility with built-in pyrolysis models in Fire Dynamics Simulator (FDS) and Gpyro [18–20]. Prasad et al. [11] simulated TGA, cone calorimeter, and flame spread experiments using FDS after optimizing for kinetic parameters via the built-in genetic algorithm (GA) of Gpyro. Rein et al. [12,13] implemented numerical models for TGA and one-dimensional smoldering combustion under normal and microgravity conditions. Kinetic parameters were estimated using a GA toolbox, GAOT. Garrido and Font [21] extensively studied chlorinated phosphorus FR PU at three different heating rates and environments, with both dynamic and isothermal runs. A proposed degradation model was optimized with the Excel Solver suite. Furthermore, evolution of gaseous compounds was observed with mass spectrometry and Fourier transformed infrared spectroscopy in both inert and oxidative environments [21]. Details on the methods and models used can be found in the Supplementary Material along with a complete list of reported kinetic parameters.

In this study, a theoretical model describing the decomposition kinetics is used to simulate the results of the TGA. Ultimately, the simulation is compared to the empirical data and optimized to find suitable kinetic parameters. These optimized kinetic parameters are compared with literature to confirm the veracity of the model. It is demonstrated that, without the benefit of optimization, graphical methods are not able to effectively describe the mass loss curve. Additionally, discussed in some detail is the indication that PDA plays an active role in preventing PU degradation. Analysis is performed by subtracting a hypothetical composite of PDA and PU from actual TGA data. To the author's knowledge, this method of comparison has not been applied to TGA data before. Furthermore, no published studies have examined the kinetics of PDA flame retardancy, nor critically analyzed TGA results in both oxidative and inert environments. Finally, this study indicates that PDA has a different mode of action than traditional halophosphate FRs.

2. Experimental procedure

2.1. Materials

Polyether-based flexible polyurethane foam (type 1850, Future Foams, High Point, NC) without flame retardant additives (density of 28 kg/m^3) was generously provided and used as received. Dopamine hydrochloride was purchased from Sigma-Aldrich. Tris (tris(hydroxymethyl)aminomethane) base was obtained from Fisher Scientific. Ultrapure water (18.2 MΩ cm) was obtained from a Thermo Scientific Barnstead E-pure water purification system.

2.2. Sample preparation

Allowing three days for PDA deposition, the polydopamine coated flexible polyurethane foam (PDA3D) was prepared as described previously by Cho et al. [6]. In brief, the PU was submerged in a solution of dopamine hydrochloride and 10 mM Tris-HCl buffer solution (2 mg/ml dopamine: buffer, pH 8.5) under continuous agitation for three days. With time, the dopamine polymerized and deposited throughout the foam. Specimens were then rinsed with deionized water, dried in air for two days, dried under vacuum for one day, and then finally dried under vacuum at 70 °C to remove residual water and unbound PDA. The percentage of PDA deposited was 15.9 wt%, as calculated from the initial and final weight of the specimen after coating. It should be noted that the weight of a control foam decreased when immersed in the buffer solution because of leached unattached molecules. The weight of the control foam in the buffer reached steady state after one day, with a total weight loss of about 4.8 wt%. This weight loss was taken into account in the calculation of the mass of PDA deposited.

2.3. Thermogravimetric analysis

A small (∼ 5 mg) amount of open-cell, flexible polyurethane foam, with and without PDA coating, denoted as PDA3D and PU, respectively, was heated from 30 °C to 800 °C using a thermogravimetric analyzer (DSC/TGA 1, Mettler Toledo). Both an oxidative (ultra-pure air, 78 vol% nitrogen (N_2) and 21 vol% oxygen (O_2)) and inert (100% N_2) environment were tested at heating rates of 10 and 20 °C/min for PU and PDA3D. The air and nitrogen flows through the TGA were maintained at 50 mL/min throughout testing.

3. Model description

A number of reasonable assumptions were made to simplify modeling of the thermal decomposition of polyurethane. For a sufficiently small sample size, the time scale for kinetics is assumed to be long compared to the time scales for heat and mass transfer. The material's mass loss rate (MLR) is not spatially dependent; uniform temperature is assumed throughout the specimen due to the small sample size and relatively low heating rate (i.e. lumped capacitance model). It is further assumed that the chemical reactions are not diffusion controlled; there are no porosity effects and gas species are instantaneously released from the solid. Finally, local