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Melting behavior of typical thermoplastic materials – An experimental and chemical kinetics study

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HIGHLIGHTS

- A new medium-scale melting and pyrolysis experiment instrument for thermoplastics was designed.
- The thermal hazard induced by melting and dripping of thermoplastics was studied.
- The medium-scale experimental results on the thermoplastics pyrolysis suggest some limit for TGA tests.

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ABSTRACT

A medium-scale melting experiment rig was designed and constructed in this study. A detailed experimental study was conducted on the melting behavior and the chemical kinetic characteristics of three typical thermoplastic materials, including polypropylene (PP), polyethylene (PE) and polystyrene (PS). It is observed that the thermal decomposition of the thermoplastic materials mainly consists of three stages: the initial heating stage, the melting-dominated stage and the gasification-dominated stage. Melting of the materials examined takes place within a certain temperature range. The melting temperature of PS is the lowest, moreover, it takes the shortest time to be completely liquefied. To quantitatively represent the chemical kinetics, an *n*th-order reaction model was employed to interpret the thermal decomposition behavior of the materials. The calculated reaction order is largely in accordance with the small-scale thermal gravimetric analysis (TGA). The small difference between the results and TGA data suggests that there are some limitations in the small-scale experiments in simulating the behavior of thermoplastic materials in a thermal hazard. Therefore, investigating the thermal physical and chemical properties of the thermoplastic materials and their thermal hazard prevention in medium or large-scale experiments is necessary for the fire safety considerations of polymer materials.

1. Introduction

Thermoplastic materials have been widely used in industry and everyday life, e.g., in furniture, interior decoration and building insulation. However, thermoplastic materials can be easily heated to soften and melt with strong fluidity under fire conditions, elevating the scope and severity of the fire [1]. Under the effects of heat, the thermoplastic materials usually melt, drip and then flow on the floor during the fire, depending on decomposition behavior of the materials. When the materials setting is in a vertical orientation, molten materials would drip and gather on the floor to form a pool fire because of the high mobility triggered by increasing temperature. Besides, the intensity of the fire is usually enhanced even further due to the interactions between the vertical polymer fire and the induced flowing pool fire.

The behavior of thermoplastic materials' melting flow in fire spread have attracted a lot of interests recently due to its relevance in the vertically developing polymer fires as well as in the subsequently developed pool fires. The fire hazard is strongly related to the melting process when the materials are heated. The study of thermoplastic material fire with melt flow behavior has been the focus of many recent studies. Zhang et al. [2,3] claimed that the flame spread was eventually controlled by the pool fire formed at the base of a solid polymer. Sherratt and Drysdale [4] confirmed this and reported the importance of flooring material in pool fire development. Wang et al. [5] showed the effect of ignition locations on the fire behavior of typical polymers and confirmed that initial conditions have considerably impacts on nearly all the important fire parameters. Butler et al. [6] proved that viscosity is a key determinant of the melting behavior of polymers. Ignitability of flame retardant polymers was extensively investigated using

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a cone calorimeter [7–11]. In our previous work [12], a T-shape rig was used to investigate the flowing distance of several polymer materials' pool fires, the burning feature of thermoplastics was quantitatively compared and it was illustrated that this new experimental setup was useful for quantitatively studying the special burning feature of thermoplastics. Moreover, several earlier works also explored the influence of thickness on polymer flammability, where the importance of thickness in polymer melting behavior was emphasized [13–16]. These existing studies were mainly focused on observations of the physical phenomena. Although the studies showed that the fire behavior is strongly related to the melting process of thermoplastics [17], there is still a lack of characterization method and an in-depth understanding for the complex physicochemical processes involved.

Generally, the special fire behavior of thermoplastic materials is strongly related with their physical and chemical changes during the melting process. When the polymer is heated, the tendency of melting and flow is associated with two factors [18], one is the physical change (i.e. molecular chain slippage) and the other one is the chemical change (i.e. decomposition of the polymer—molecular chain breaking). Wang et al. [19] studied the dripping behavior of eight polymers under UL94 vertical test conditions. The results showed that dripping behavior is dominated by the decomposition mechanism of random-chain scission, low activation energy of viscous flow, and high ratio of effective heat of combustion to heat of gasification. However, all of these existing researches were conducted as small-scale experiments; large scale experiments relevant to real fire applications are still lacking.

General purpose plastic is widely used mainly because of the high production and low cost, which can be broadly divided into five categories, i.e. polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS) and poly (acrylonitrile–butadiene–styrene) (ABS). All of them are thermoplastics, but they exhibit different combustion behaviors. The combustion of PVC and ABS does not present a dripping behavior [3,19]. Previous researches have revealed that the combustion of PP, PE and PS presents the dripping behavior [1–3,5,15,19,20], therefore, PP, PE and PS have been selected in this work.

An in-depth understanding of the physical and chemical changes during the heating process of thermal plastic is helpful for the interpretation of the special melting and dripping behavior. Up to now, standard thermogravimetric analyzer (TGA) equipment is widely used for the measurements of thermal decomposition of materials, which can be used for the analysis of the kinetic models of thermal decomposition. Several models have been proposed to the description of three materials, such as the first-order model, the nth-order model, and the random chain dissociation kinetic model [21–25]. However, these models were usually developed from small-scale experiments, and there is a concern on the compatibility of these models with real situations where the scales are generally larger. In order to understand the materials' melting behavior at larger scales, a medium-scale melting experiment rig was independently designed and constructed, and the melting behavior of PP, PE and PS along with the related characteristic parameters such as mass and temperature changes during the melting process was investigated in this study.

2. Experimental setup

In order to systematically investigate the melting behavior of thermoplastic materials under heating, a laboratory experimental rig was designed and constructed, as shown in Fig. 1. Fig. 1(a) shows the schematic of the melting experimental rig inside which all tests were conducted. It mainly contains a melting vessel, an electric heater, an inert gas protection system and a measurement system. In the melting vessel, thermoplastic material undergoes the melting and pyrolysis process during heating. Along with the rising temperature, the fluid viscosity decreases because of the melting of polymer. Meanwhile, the length of the polymer chains is reduced by chain scission (i.e. pyrolysis process), which yields a mixture with strong fluidity, inevitably, the melting thermoplastic materials will drip. The pyrolysis process also generates compounds with shorter molecular chain, which will vaporize and form a cloud of gas under continuous heating. The generated gas would be ignited under certain environmental conditions. In order to avoid the ignition at high temperature, N_2 was continuously charged into the melting vessel by the inert gas protection system. Electric heater composed by circular electric stove wire heats the melting vessel by a constant power (6000 W) at the bottom. The measurement system is comprised by an electronic balance (measuring the mass change of the melting vessel), thermocouples and a video camera. Locations of the electronic balance and thermocouples are shown in Fig. 1(b). Fig. 2 shows a picture of the experimental rig.

Three typical thermoplastic materials are selected, i.e., polypropylene (PP), polyethylene (PE) and polystyrene (PS). All the materials are particles and the initial mass of each material is 4000 g. The appearance and dimensions of polymer particles are shown in Fig. 3, while their characteristic parameters are shown in Table 1. At the beginning of the experiment, the particles are

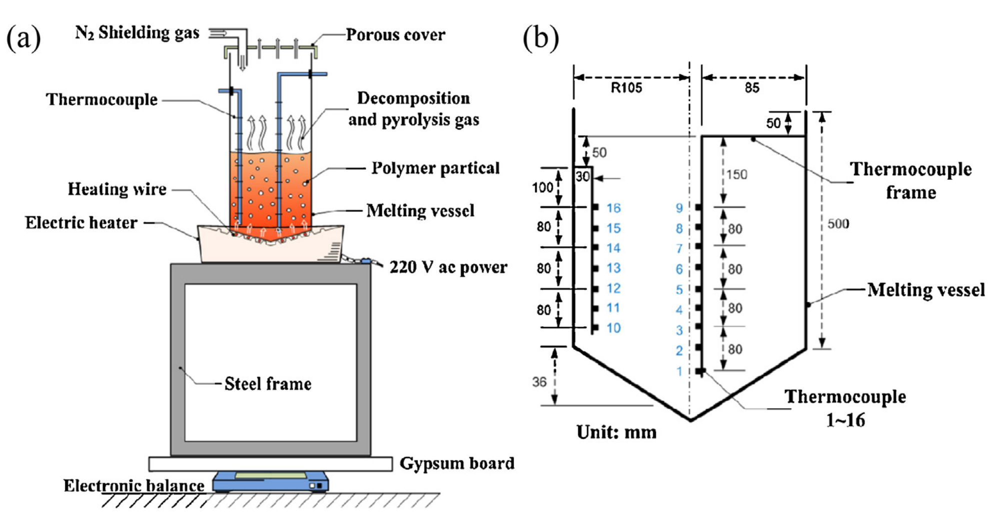

Fig. 1. (a) Schematic diagram of the melting experimental rig and (b) dimensions of the melting vessel and the locations of thermocouples.