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Experimental Study of an Iron-Based Metal-Organic Framework as Flame Retardant for Poly (methyl methacrylate) (PMMA)

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Abstract

Poly (methyl methacrylate) (PMMA) is a kind of widely used thermoplastic in the family of poly (acrylic ester)s due to its good mechanical properties, like good moldability, high resistance to UV light and weathering, high strength, and excellent dimensional stability. However, PMMA is also characterized by limited heat resistance, poor thermal stability, and high flammability. Metal-organic frameworks (MOFs) are a new class of porous materials, which possess unique physicochemical properties and have attracted considerable interests from different fields, such as energy, gas storage and separation, and catalysis. Additionally, because of their inorganic−organic hybrid nature, MOFs are usually compatible with polymers to form composites. PCN-250 is an iron-based MOF with nitrogen-containing structure and it is chemically stable and physically robust. So far, it can be economically synthesized in large scale. In this study, PCN-250 is used as a potential flame retardant for PMMA. To evaluate the performance of PCN-250 with different concentrations, the thermostability and flame retardancy of the PMMA composites are systematically investigated using thermal gravimetric analysis (TGA) and cone calorimetry. This study will give us some insight about the application of MOFs as a new kind of flame retardant to enhance and improve the fire safety of polymer materials.

Keywords: Polymerization, Flammability

Introduction

The polymeric materials provide numerous advantages to society in everyday life, like being versatile, light weight, corrosion-resistant, electrically insulating, and easily processable. They are widely used almost everywhere in buildings, housing, vehicles, aircraft, commercial products etc. However, the high flammability is an obvious disadvantage related to many synthetic polymers, due to their energy-dense hydrocarbon-based nature, which is exposing life safety to more fire hazards [1]. Improving the fire retardancy of polymeric materials is an increasingly important strategy to limit their flammability by adding some flame retardant fillers to the polymers. With a relatively low loading of well dispersed nanoscale flame retardant fillers, the nanocomposites have been found to be able to achieve better thermal stability and performance in a fire, while still maintaining or even improving their mechanical properties [2]. So far, various inorganic nanoscale fillers have been investigated to enhance the flame retardancy of different polymers, like clay [3], graphite [4], metal oxide nanoparticles [5], carbon nanotube [6, 7], and spherical silica [8, 9]. However, for these inorganic nanoscale fillers, they act mostly in the condensed phase by transporting to the surface to forma thermally stable ceramic surface layer and/or promoting the formation of char layer during the flaming combustion of polymers. These protective layers act as a thermal shield to block heat transfer to the polymer and as a barrier to oxygen transfer from flame to the polymer underneath and of degradation products from the polymer to the flame. Through this behavior, the intensity of fire can be reduced noticeably by prolonging the burning process, but for most flame retardant polymer nanocomposites, their total heat release does not change much.

Metal-organic frameworks (MOFs) have received much attention in recent years especially as newly developed porous materials. MOFs are essentially formed by connecting together metal ions with polytopic organic linkers together through coordination bonds and other weak interactions or noncovalent bonds (H-bonds, p-electron stacking, or van der Waals interactions) [10]. Due to the inorganic-organic hybrid nature, MOFs usually have better compatibility with polymers to form polymer composites. Thermal degradation of MOFs is an endothermic process associated with node–linker bond breakage. When being exposed to heat, MOFs not only absorb more heat by their endothermic degradation process, but also decompose the metal-containing units and the organic ligands in this process to release metallic oxides in the condensed phase and gaseous products in the vapor phase. In this condensed phase, these metallic oxides left, especially transitional metals, may be able to quickly from C-C bonds during burning, thus helping convert flammable polymers into thermally stable carbon char [11]. Additionally, if properly designed to contain the elements of oxygen, nitrogen, or phosphorous, the gaseous products can work as smoke suppressants and contribute to reduce the concentration of combustion supporters in the gaseous phase. Through these strong synergistic effect among different flame retardant mechanisms discussed above, NOFs-based polymer composites have the potential to achieve better flame retardancy and thermal stability. However, few research has been conducted in this area.

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Experimental

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