Chapter

Introductory Chapter: Flame Retardant and Thermally Insulating Polymers

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1. Introduction

Flame retardant and thermally insulative polymers are of technological importance and fundamental interest [1, 2]. Polymers continue to infiltrate modern technologies such as aviation, automotive industry, building construction, electronics, to name a few, thanks to their unique combination of properties not available from any other known materials [3]. Polymers are lightweight, durable, easy to process, electrically insulative and corrosion resistant [4]. Common polymers are also thermally insulative [5]. However, polymers are combustible because of their chemical structures that are made up by carbon and hydrogen atoms [6–8]. To meet flammability standards, flame retardants for fireproof polymers have been developed [9, 10].

To protect human life and property, flame retardant polymers are generally made by adding flame retardants into polymers [11, 12]. There are drawbacks in common halogenated flame retardants, which associate with the release of toxic or corrosive by-products [13–18]. There are environment and health concerns caused by these released toxic gases [19]. Therefore, developing high-performance, non-toxic, low-cost, and environmentally friendly flame retardants are needed [19, 20]. Understanding mechanisms for fire retardancy is essential for developing new effective flame retardants. Improving fire retardant behaviors of polymers play key roles in future industrial applications such as furnishings, transportation products and building construction materials [9, 21–25].

Over the past decades, different flame retardants for polymers have been developed [20]. Mechanisms of polymer flame retardancy have been further investigated [9, 20, 26, 27]. Flame retardants have been generally broken into categories based on chemical compositions, which are grouped based on whether they contain bromine, chlorine, phosphorus, nitrogen, boron, or inorganic fillers (metals, etc.) [28]. It is widely recognized that all categories of flame retardants act either in vapor phase or condensed phase to inhibit or to stop combustion processes through a chemical and/or physical mechanism [29]. Flame retardants can interfere with combustion during a particular stage, e.g., during heating, pyrolysis, ignition, or flame spread [9, 20, 27, 30]. Flame retardants can either act chemically (reaction in the condensed or gas phase) and/or physically (by cooling, formation of a protective layer or fuel dilution) [17]. The polymer flammability properties have been investigated by their ignitability, flame spread and heat release characterizations [20]. Depending on the targeted application of polymers, one or more of specific flammability criteria (e.g. ASTM's fire and flammability standards) need to be satisfied [31].

In addition to flame retardancy, thermal insulation property of polymers can be another significant function that can defend targets against heat damage and save lives [32–35]. Fully understanding the flame retardance and thermal insulation mechanisms in polymers remain challenging. Advanced polymers with combined properties of flame retardancy, mechanical strength and heat insulation are needed. Such polymers will provide broader prospect in civil applications than single-function polymers, for example, building insulation applications [36–38].

This introductory chapter not only aims to present the current landscape flame retardant and thermally insulative polymers, but also highlights next generation of flame retardant and thermally insulative polymers for fire protections applications. This introductory chapter summarize fundamental interests and technological importance of flame retardant and thermally insulative polymers, which include principles of polymer flammability, theory of flame retardance, thermally insulative and fire-retardant polymers, and critical discussion and outlook.

2. History and perspective of flame retardant and thermally insulative polymers

2.1 Principles of polymer flammability

Three ingredients — heat, oxygen, and fuel — are required to initiate and continue a fire [12]. Polymer starts to degrade, when it is heated by external ignition sources and reaches a characteristic temperature [39]. The surrounding oxygen amount plays key roles on polymer surface decompositions (e.g., thermo-oxidative degradation of polymers and/or thermal degradation of polymers). The amount of oxygen for polymer decomposition depends on the specific polymer used. Combustible gases as fuels may be produced at a rate dependent upon polymer decomposition rate and diffuse to the flame front [12]. After ignition and removal of the ignition source, combustion could be self-propagating if there is sufficient heat generated and polymer can absorb enough heat to sustain its decomposition processes. Polymer combustion processes could involve vapor phase and condensed phase reactions [39].

2.2 Theory of flame retardance

2.2.1 Vapor phase flame inhibition

The combustion process of premixed methane-oxygen flame is well investigated [40, 41]. The methane oxygen system can be used as a model for studying more complex polymer flames [41, 42]. Methane combustion is a free-radical chain reaction, which mainly consists of propagation, chain branching, and termination processes [43]. Any flame-retardant material which either decreases the concentration of these chain carrying radicals or increases the rate of termination will inhibit the flame reaction. This is thought to be mechanisms by which vapor phase flame inhibitors [39, 44].

2.2.2 Condensed phase flame inhibition

Cooling and char barrier formation are two main modes in solid phase flame inhibition [39, 44, 45]. We discuss cooling mode first. One important cooling mode used in condensed phase flame inhibition is the use of materials which decompose endothermically in the pyrolysis zone of the burning polymer [39]. For example, due to polyvinyl alcohol's ability to endothermically form water molecules, polyvinyl alcohol is less flammable than the isomeric polyethylene oxide [39, 46]. During polymer burning processes, cooling mode can be also achieved by adding thermally conductive fillers into polymers [39]. Fillers have higher thermal conductivities than that of polymers. Fillers conduct heat better than polymers. Fillers conduct heat away from hot regions more efficiently than unfilled polymers. Fillers enable polymer-filler composites difficult to burn. However, fillers at high volume fraction loadings are needed for good cooling effect, which might lead to limited use [39, 47]. Dripping is another cooling mechanism [39, 48]. Polymers that drip easily during burning processes are more difficult to burn. For example, a regular candle will not burn with no wick, due to its high dripping tendency. This is because heat is dissipated from flaming areas. However, dripping could be a hazard by resulting in the spreading of a fire and thus of limited use [39, 49].

2.3 Thermally insulative polymers with high flame retardancy

Thermally insulative polymer-based materials with high flame retardancy are attracting significant attention [50]. This is because thermally insulative materials can protect overheating damage from burn injuries and save lives [34, 51–58]. There are drawbacks for available fire-resistant polymers. Some flame retardant polymers could be expensive [57]. Some flame retardant polymers have relatively low decomposition temperatures and decompose nearby 400°C [57]. Thus, highly thermally insulative, thermally stable and flame retardant polymer-based materials are desired for advanced thermal management applications [17, 50, 57].

Flame retardant and thermally insulative polymer-based composites have been developed [50, 56, 59–62]. For example, PC–PDMS copolymers have flame-retardant behaviors. Chars can prevent more volatile fuel production and serve as a thermal insulator preventing the temperature from rising [59]. When a specimen of PC–PDMS was in combustion, a lot of fine bubbles and char were formed. These fine bubbles are good for thermal insulation [59]. Moreover, silica particles in situ produced by thermal decomposition of PDMS mostly stay in char layers, which improve the quantity of oxidation-resistant char coatings [59]. The resulting bubble structures and silica materials in the char layer prevented volatile and flammable fuel production, which served as an effective thermal insulator [59]. Although there are progresses on developing flame retardant and thermally insulative polymer-based materials, further understanding flame retardancy and thermal insulation mechanisms will play key roles increating next generation of thermally insulative and flame retardant polymers with outstanding performance. With unique combined properties including simple manufacturing process, low cost, excellent thermal insulation, flame retardancy, superior physical and mechanical properties, thermally insulative and flame retardant polymers will provide new opportunities for existing and unforeseen applications.

2.4 Critical discussion and outlook

To achieve the high-performance fire retardancy of polymers, different strategies have been developed [63]. Followings are selected strategies.

1. By modifying the reaction scheme of pyrolysis of polymers to produce non-combustible, and/or non-volatile products that dilute the supply of oxygen [40, 63].

2. By stopping the combustion through dilution of the combustible gases, or the formation of a char which suppress the oxygen supply [63, 64].

3. By introducing active radical-trapping effects both in the gaseous phase and/or in the condensed phase [63, 65].

4. By reducing the thermal conductivity of the material to limit heat transfer [34, 63].

The different types of flame retardants in polymers based on halogens, heavy phosphorus-organic compounds and/or transition metals have shown good flame retardance performance [26]. However, toxic gases and smoke are formed during burning processes [66]. Environmental safety of flame retardants in polymers is a major issue [22, 63]. Fire-retardant polymer-based materials are desired to have high resistance to ignition, low combustion rate, retention of low flammability, acceptability in properties and appearance, no health safety and environmental issues, and little (or no) economic penalty.

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