CONE CALORIMETER ANALYSIS OF FLAME

RETARDANT POLY (METHYL METHACRYLATE)-SILICA

NANOCOMPOSITES

By

RUIQING SHEN

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Thesis Approved:

Dr. Qingsheng Wang

Thesis Adviser

Dr. Jindal Shah

Committee Member

Dr. Sundarajan V. Madihally

Committee Member

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Abstract: Flame retardant additives, such as phosphorus-based fillers, metal hydroxides, metal carbonates, and nanocomposites, have been considered as the most common methods to reduce fire hazards of polymers. Specifically, polymer nanocomposites have an advantage in reducing fire hazards efficiently even when the additives are at such a low concentration as 5 wt% or less, like nanoclay and carbon nanotubes. Nanoscale silica particles are a relatively new type of nanofiller. Moreover, in theory, crosslinking between the polymer chains by forming additional covalent bonds, can enhance char formation of polymeric materials to further promote their flammability, because crosslinking creates a carbon-dense structure that is not easy to be volatilized. In this study, crosslinked and non-crosslinked polymer nanocomposites composed of low concentration of silica-containing flame retardants have been prepared via the *in-situ* method of embedding nanoscale silica particles into the poly (methyl methacrylate) matrix (PMMA). The nanocomposite samples were tested by using the cone calorimeter at the heat flux of 50 kW/m², and their corresponding fire behaviors under forced-flaming conditions were evaluated. Although silica-containing flame retardants tend to negatively affect the ignitability and soot production especially at a high concentration, through the condensed phase mechanism, the samples of high loading rate of nanoscale silica particles show better fire retardancy performance in the aspect of flammability, like decreased heat release rate, mass loss rate, total heat release, flame development and spread. Additionally, at the low concentration of nanoscale silica particles, crosslinking was observed to contribute to the better flame retardancy of crosslinked PMMA samples in a certain aspect, like the lowered intensity of combustion. The combination of nanoscale silica particles with the modification of the internal structure of the polymer nanocomposites might be a strategy to improve fire retardancy.

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CHAPTER I

INTRODUCTION

Polymers have widespread applications in different industries due to their low cost, light weight, ease of processing and applicability, and stable structure [1, 2]. While the advantages of using polymers are numerous, consumers must remain vigilant about the potential fire hazards associated with these hydrocarbon-based materials. One potential solution to this problem is to use inherently thermally-stable polymers. However, the use of those inherently thermally-stable polymers is often restricted by their high cost [3]. Another potential solution to reducing risks generated from the fire hazard of polymers is to use flame retardants. There are a variety of flame retardant additives, such as halogen-containing flame retardants, phosphorus-based fillers, metal hydroxides, metal carbonates, and intumescent additives. Nevertheless, most of those traditional flame retardants, like halogen-containing flame retardants, have been restricted in their utility due to potential damage to human health and environment, and other flame retardants like aluminum hydrates are too costly to be widely used in the industry and commerce [4, 5]. Recently, more attention has been on research of flame retardant polymer nanocomposites, which are environmentally friendly and highly efficient, compared to conventional flame retardants [6, 7]. Additionally, polymer nanocomposites have also shown significant improvement in terms of thermal stability, mechanical properties, optical and electric properties when compared to the micro and macro varieties [8].

One of the effective halogen-free flame retardants is silicon-containing compounds, like silica, silicate, polydimethylsiloxanes, which are highly resistant to heat, and more importantly will not produce toxic and corrosive gases during combustion [9]. For silica particles, they mainly have three forms: silica gel, fused silica, and fumed silica. Compared with fused silica, fumed silica and silica gel have relatively larger surface area and lower density, which can accumulate near the polymer burning surface and tend to produce a silica-rich layer without sinking through the melt polymer [10]. The silica layer can act as a heat insulation shield, which can protect the polymer from further thermal decomposition [11, 12]. Additionally, the silica layer can also act as a physical barrier to the transport of thermal decomposition products through the polymer surface to the flame zone [10]. However, fused silica is hard to accumulate on the surface of burning polymer and subsequently form a silica-rich protective layer, so that fused silica is not as effective as fumed silica and silica gel [10]. Recently, in terms of flame retardancy, polymer nanocomposites comprised of organically modified clay dispersed in selected polymer matrixes have attracted considerable attention from researchers with the advantage that flame retardant additives are highly effective at a low concentration of 5 wt% or less, and also with increased thermal stability and mechanical properties, like Young's modulus and storage modulus [13, 14]. The physical principle behind this phenomenon is the tremendously larger interfacial area between polymer and flame retardants than conventional flame retardant systems. Nanoscale silica particle is also a kind of promising flame retardant because of the large interfacial area as long as the particles are finely dispersed within the polymer matrix. However, previous research by Kashiwagi, indicates that nanoscale silica particles by themselves cannot form a tight and continuous silica network, but form loose and granular particles, in which the most majority of the polymer is still directly exposed to the external heat flux without enough protection [15]. But Kashiwagi also suggests one possible approach to forming *in-situ* silica network by enhancing the formation of crosslinks among the nanoscale silica particles through appropriate surface treatment of them [15]. Moreover, there exists a strong correlation between char yield and fire resistance of

polymers in fire conditions [16]. Crosslinking between the polymer chains by forming additional covalent bonds, if possible, can enhance char formation of polymeric materials, because crosslinking creates a carbon-dense structure that is not easy to be volatilized, especially for some non-char-forming thermoplastics, like polypropylene and poly (methyl methacrylate) (PMMA) [10, 17].

In this research, a small amount of nanoscale silica particles (less than 5 wt%) was embedded into the poly (methyl methacrylate) matrix via *in-situ* methods to form polymer nanocomposites. Additionally, crosslinking was introduced in the polymer nanocomposites to study whether this structure modification of polymer chains could further protect the polymer matrix and hence improve fire retardancy during combustion. The reaction of any material to fire is typically represented by: the ability to ignite, heat release rate, flame spread, emission of flammable, toxic, and corrosive gas etc. [18]. This investigation will mainly focus on the ignitability and flammability properties of the low concentration of silica-containing flame retardant polymer nanocomposites and their flame retardancy performance based on cone calorimeter analysis.

CHAPTER II

REVIEW ON THE LITERATURE

In a recent article, Morgan (2013) discussed the application, technology, and future directions of flame retardancy of polymeric materials [4]. Apparently, in the case of fire, the most majority of energy-dense hydrocarbon-based polymers are easily ignitable and can provide a source of fuel, which is a great risk not only to property, but also life safety. The use of flame retardants is often preferred to improve the flammability of polymers that are characterized of inherently high flammability but low cost. This approach usually means reaching an acceptable compromise between cost and the properties of the polymer, but it is also a proven approach and relatively easy to implement [19] . So far, a lot of researchers have conducted studies in this field and have laid the solid foundation of knowledge to further explore various kinds of flame retardant additives.

Recently, generally six classes of flame retardant chemistries are available: halogen-based flame retardants, phosphorus-based flame retardants, mineral filler flame retardants, intumescent flame retardants, inorganic flame retardants, and polymer nanocomposites. Depending on their chemical nature, different flame retardants function chemically, physically, or both in totally different mechanisms to interfere with the combustion process in the gas phase, the condensed phase, or both phases. None of these flame retardants can apply universally to any type of polymer. In fact, each type of flame retardant is specifically molecularly designed and optimized to a particular type of polymer in a specific fire risk scenario, based upon the thermal decomposition

mechanism of the polymer, particular property requirements, manufacturing process, environmental stability, and sustainability issues.

Halogen-based flame retardants are molecules that contain such elements as F, Cl, Br, and I from group VII of the periodic table. They can have totally different chemical structures, including inorganic form, pre-halogenated aliphatic and aromatic carbon subtracts. Among them, organohalogen compounds still appear to be the most effective flame retardant additives for polymer [20]. To function effectively, halogenated flame retardants are supposed to be able to release halogen radical or halogen halide at the same temperature range or even below the temperature of thermal decomposition of the polymer [21, 22]. The main mechanism of halogenated flame retardants is in the gas phase. Initially, halogen radicals are abstracted from the flame retardant when exposed to heat. The halogen radicals immediately react with either the polymer or the flame retardant additives to form hydrogen halides. Subsequently, the hydrogen halides interfere with the radical chain mechanism, in which highly reactive free radicals, like hydrogen or hydroxyl radicals, are consumed by reaction with hydrogen halides and finally replaced with less reactive halogen radicals. Ultimately, the hydrogen halides are regenerated through the reaction of halogen radicals with hydrocarbon. In fact, hydrogen halides are actually the main functional specie in the aspect of flame retardancy. Additionally, the large heat capacity of hydrogen halides and their dilution of fuel gases can lower the mass concentration of combustible gases and the temperature of the flame [23]. However, the emission of toxic and corrosive hydrogen halides is always a big concern to human and environment.

Phosphorus-based flame retardants are an important class of halogen-free flame retardants. They have totally different structures varying from inorganic to organic forms, and between different oxidation states (0, +3, +5), like elemental red phosphorus, inorganic phosphates, organic phosphorus-based products, and chlororganophosphates [24]. These compounds mostly function in the condensed phase by increasing the formation of carbonaceous residue or char through two

mechanisms: (i) redirection of the chemical reactions involved in thermal decomposition in favor of reactions yielding carbon rather than CO or CO_2, and (ii) formation of a surface layer of protective char [11]. However, it is also necessary to note that phosphorus compounds may function in gas phase as well, depending on their specific chemical structure and how they interact with the polymer when exposed to a fire. More uniquely, it is not so uncommon for a particular type of phosphorus compound to be predominately in the gas phase for a particular polymer but in the condensed phase for another particular polymer [25, 26, 27, 28]. In the gas phase, volatile phosphorus compounds can act as potent scavengers of H· and OH· radicals, which is an effective inhibitors of combustion [29]. However, more smoke and CO will be produced simultaneously, because phosphorus-based flame retardants mainly help to inhibit polymer combustion.

To improve flame retardany, the most commonly used mineral fillers as additives are metal hydroxides and metal carbonates [4]. Generally, mineral fillers function based on three flame retardant effects: (i) endothermic decomposition to absorb heat and cool the polymer; (ii) release of such inert gas as H_2O and CO_2 to dilute the combustible fuel gases; and (iii) accumulation of mineral filler residues on the decomposing polymer surface to dilute the polymer fuel available (in the condensed phase) and act as a barrier of heat and mass transport through the polymer surface [30]. Consequently, to be effective, the decomposition temperature of the mineral filler should be above the polymer manufacturing temperature, but below the decomposition temperature of the polymer. As a result, only limited types of metal hydrates and metal carbonates are widely used to meet this requirement, including $Al(OH)_3$, $Mg(OH)_2$, and $MgCO_2$. Mineral fillers are environmentally friendly, and in case of fire, smoke and toxic gas emission are reduced due to the replacement of polymer fuel with non-flammable inorganic mass. However, a high loading rate of mineral fillers is required to achieve an acceptable level of flame retardancy, which usually compromise the mechanical properties of the polymer [30].

Intumescent flame retardants are those materials that will swell in response to a fire or heat source to form a carbon foam in the condensed phase, which can act as a physical barrier to heat, air and pyrolysis products [31, 32, 33, 34]. Typically, an intumescent material formulation is composed of three components to work together to function as flame retardants: a char forming agent, an acid catalyst to char formation, and a spumific or foaming agent [11]. A classical intumescent system mentioned by Morgan is ammonium polyphosphate (acid source), pentaerythritol (char forming agent), and melamine (foaming agent) [4]. In principle, to achieve desired flame retardancy, intumescent system need to be activated well before the thermal decomposition of the polymer has a chance to start. Usually, the temperature range is from 180 to 200 °C, and a few can go up to 240 °C, at which temperature the intumescent system need be activated or lower [4]. Consequently, while the intumescent systems do provide fire protection, their use is restricted to lower-temperature polymer and fire protection barrier.

Except for inorganic flame retardants included in previous classes, inorganic flame retardants still seem to cover a wide range of other chemicals that can retard flame, but actually they are very niche flame retardants. So far the only commercially available inorganic flame retardants include borates, stannates, and silicates [4]. These chemicals are mainly used to corporate with other flame retardants to make them perform better, or address a particular aspect of flame retardancy, for example, smoke emission. Recently, they are still used sparingly. However, due to the increasingly strict scrutiny associated with halogen and phosphorus based flame retardants, the inorganic flame retardants are getting more attention, especially silicon-based flame retardants.

Polymer nanocomposite is the newest technology in the field of flame retardancy. Generally, polymer nanocomposites function in the condensed phase to retard flame, in which a nanoparticle-rich protective layer is formed to slow, but never stop, the mass loss rate of polymer and heat release rate correspondingly [35, 36, 37]. Recently, nanodispersed montmorillonite (MMT) clay, organically treated layered clays, nanoparticles of TiO_2, nanoparticles of silica,

layered double hydroxides (LDH), carbon nanotubes/nanofillers (CNT), and polyhedral silsesquioxanes (POSS) are all reported to exhibit low base flammability and other enhanced properties, like mechanical properties [19]. Among them, organically treated layered clays and carbon nanotubes/nanofillers are the most commonly used nanoparticles for commercial polymer nanocomposites so far [4]. It is important to note that despite the fact that the polymer nanocomposite indeed tends to retard flame growth, the nanocomposite by itself is still not enough to pass regulatory tests, for example, the relatively poor performance in the UL-94 tests and Limiting Oxygen Index (LOI) tests. However, polymer nanocomposite is still a promising approach to improving flame retardancy, because polymer nanocomposite seems to be able to produce synergistic effects with traditional flame retardant additives.

CHAPTER III

POLYMER COMBUSTION AND TESTING

3.1 Polymer Combustion

Polymer combustion is a highly complex process involving both condensed phase and gas phase. In the condensed phase, fuel is generated at the surface via endothermic degradation and subsequent thermal decomposition of the solid polymer. In the gas phase, the fuel is consumed above the solid material when reacting with oxygen in the air, in which a flame is produced and heat is released. Part of the released heat can transfer back to the polymer surface by convection and radiation, which in turn can continue the thermal decomposition of polymer to produce gaseous fuel vapor or volatiles [38]. Namely, polymer combustion is simply regarded as a self-sustaining process, and the thermal decomposition, or more specifically pyrolysis of the solid polymer into smaller fragments, is the driven force of polymer combustion. A general schematic of polymer decomposition and combustion behavior is shown in Fig. 1. However, there exist some differences between thermoplastic polymers and thermoset polymers. When exposed to heat and in fire conditions, thermoplastic polymers tend to drip and flow, which can contribute to flame spread. However, thermoset polymers do not have the tendency to drip or flow, and pyrolysis gases are produced from the surface of thermoset polymers and then directly released into the gas phase.
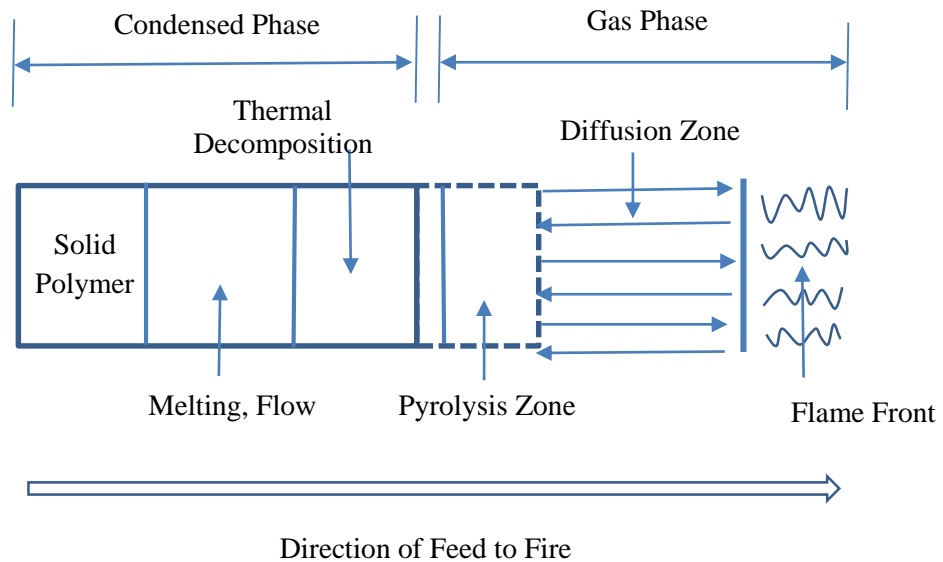
Fig. 1 General Schematic of Polymer Decomposition and Combustion Behavior [4].

Four general chemical mechanisms are important for thermally induced decomposition of polymers [39]:

1. Chain scission;

2. Crosslinking;

3. Side chain elimination;

4. Side chain cyclization.

In the term of structure, polymers are composed of chains of atoms (mainly C, H) bonded to each other. Based upon the position of atoms involved during the thermal decomposition, these four chemical mechanisms can be divided into two groups: main chain reactions and side chain or substitute reactions. More specifically, main chain reactions are those thermal decomposition reactions involving atoms in the main polymer backbone, including chain scission and crosslinking. Side chain or substituent reactions are those thermal decomposition reactions

involving atoms in the principally side chains or groups, including side chain elimination and side chain cyclization. The categories of polymer thermal decompositions are shown in Fig. 2 , and it is of great use in understanding a particular decomposition mechanism.
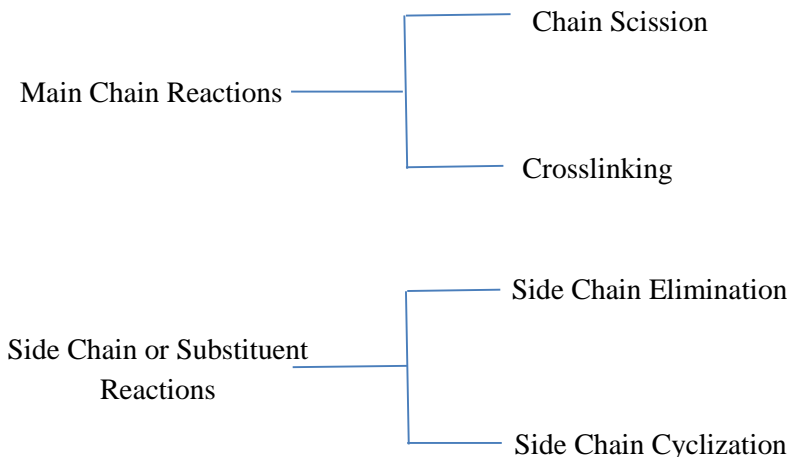
Fig. 2 General Thermal Decomposition Mechanisms [39].

Technically, the chain scission includes random chain scission and chain-end scission. For random chain scission, the polymer decomposes at the random locations in the backbone into smaller fragments, which will generate both monomers and oligomers (polymer units with 10 or fewer monomer units) [39]. For chain-end scission, the polymer depolymerizes at the chain end to produce monomers, which is also known as unzipping [39].

Crosslinking is another thermal decomposition mainly involving main chain. Generally, it occurs after some stripping of substituents and involves the creation of bonds between two adjacent polymer chains. Crosslinking is very important in the formation of chars because it creates a more compact structure, which cannot be easily volatilized into gaseous fuel vapor [40].

As their name indicates, side chain elimination reaction and side chain cyclization reaction are reactions mainly involving side chains or groups of the polymer. In elimination reactions, pendant

side chains break with the backbone of the polymer, but without breaking the backbone. Simultaneously, the eliminated side groups often react with other eliminated side groups to produce small enough products to be volatile. In side chain cyclization reactions, without breaking from the backbone, two adjacent side chains react to form a bond between them. This chemical process will produce a cyclic structure, more specifically, double bonds or triple bonds, which usually is a carbon-richer structure than the original polymer, and thus is important in char formation [39].

It should be noted that only a few number of polymers decompose predominately only through one mechanism; in most common cases, the thermal decomposition of polymers need to be explained in a combination of two or more of the mechanisms above. For example, polyethylene and polypropylene decompose predominately via random chain scission, but in the case of polyethylene some crosslinking also happens.

3.2 Polymer Testing

Fire hazard is always a big concern of polymeric materials. For safe application, it is very necessary to test those polymeric materials under conditions close to the end-use application in reality, or even in real assembly in combination with other materials. Recently, numerous flammability tests have been developed to quantitatively or qualitatively evaluate the performance of a polymer under a specific fire scenario, entirely covering small scale, intermediate scale, and full scale. There are more than 100 kinds of tests in the U.S.A alone and other countries also have their own tests. In those flammability tests, usually, the performance of polymeric materials can be evaluated in several aspects [40]:

- Ease of ignition-how readily a material ignites;
- Flame spread-how rapidly flame spreads across the surface;
- Fire endurance-how rapidly fire penetrates a wall or barrier;

- Heat release rate/total heat evolved-how much heat energy in total is released and how fast it is released;

- Ease of extinction-how rapidly or easily the flame leads to extinction;

- Smoke evolution-amount, emission rate, and composition of smoke released during different stages of fire;

- Toxic gas evolution-amount, emission rate, and composition of gases released during different stages of fire.

In the research field, several tests are widely used in the laboratory, like Underwriters' Laboratories UL-94 test, the limiting oxygen index (LOI) test, and the cone calorimeter test. These tests are relatively simple and economic, but they are capable to screen the materials during product development and quality control in the industrial laboratories, and investigate the polymer flammability in the academic community as well. In the subsequent section, these three commonly used laboratory tests will be introduced.

3.2.1 UL-94 Testing

UL-94 tests are conducted on the basis of UL-94, Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. As the standard name indicates, under UL-94 tests, polymeric materials used for parts in devices and appliance will be exposed to a small flame and the ignitability and flame spread will be accessed particularly, which are expected to serve as a preliminary indication of their acceptability with respect to flammability for a particular application [41]. Based upon their performance in various orientations and thicknesses under UL-94 tests, polymeric materials can be rated into different classifications, like HB, V-2, V-1, V-0, 5VB, and 5VA. However, in the field of flame retardancy, V-0, V-1, and V-2 are the classifications cited most frequently by researchers, which all belong to vertical burning tests. Overall, in UL-94 V-ratings, the polymeric specimen is vertically configured, a small calibrated

flame was applied twice on the bottom of the specimen for 10 seconds, and then the time of extinguishment is measured and recoded after each flame application as shown in Fig. 3. More specifically, the shape of the polymeric specimen is like a bar of 130 mm$\times$13 mm, and during the test the specimen is held from the top vertically. The thickness of the specimen can vary depending on the intended use of the polymeric materials: 3.2 mm, 1.6 mm, and 0.8 mm respectively. According to the knowledge pertaining to fire dynamics, the thinner specimen is much more ignitable than the thicker specimen, because surface ignition temperature can be reached more easily for the thin specimen, if all other factors are kept the same [42]. Thermoplastic materials have the tendency to drip in a fire, which exhibits more fire risks than thermoset materials. Accordingly, some surgical cotton is placed 300 mm under the polymeric specimen to detect the combustible drips, because the combustible drips can ignite the surgical cotton easily. A calibrated Bunsen burner flame (ca. 19 mm) of 50 W is applied under the specimen twice for 10 seconds. After the first application of flame, the time of self-sustained combustion is recoded. Immediately after the self-extinguishment of the specimen in the first application of flame, a second application of flame starts, after which the time of self-sustained combustion is recorded as well. A total number of five specimens is required. Based upon their performance in these two flame applications, the polymeric materials can be rated accordingly. The materials can be rated as V-0, if the specimen is self-extinguished in less than 10 seconds after any flame application, additionally the mean combustion time of the five specimens tested in totally ten flame applications does not exceed 5 seconds, and no combustible drips is observed. The materials can be rated as V-1, if the maximum combustion time is less than 50 seconds, and the mean combustion time of those five specimen is less than 25 seconds, and similarly no combustible trips is observed. The polymeric materials rated as V-2 are those which have the same combustion criteria as V-1, but combustible drips are observed to ignite the surgical cotton.
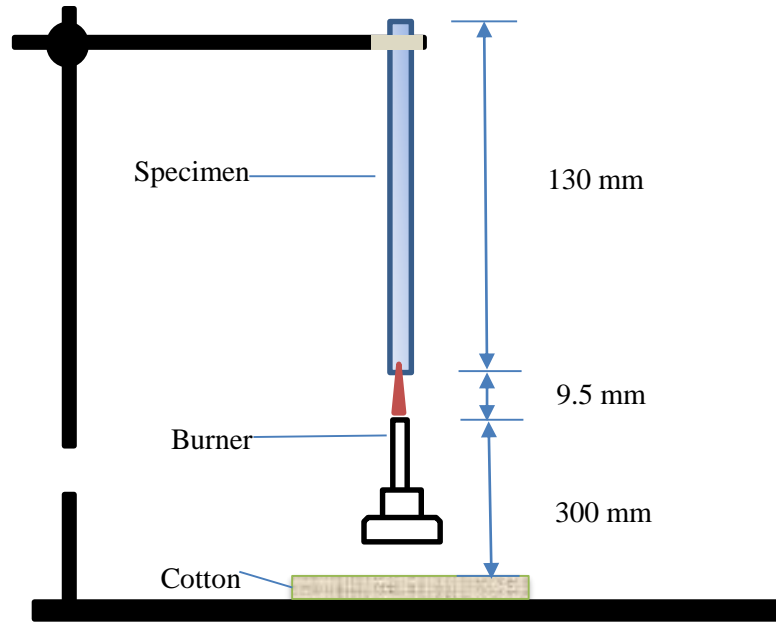
Fig. 3 Experimental Set-up for the UL-94 V Flammability Test (not Scaled) [16].

3.2.2 Limiting Oxygen Index (LOI) Testing

The limiting oxygen index (LOI) test is another method commonly used in laboratory and is recognized as one of the most useful tools for fire retardancy studies of polymeric materials. ASTM D2963, Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics, describes the procedure for measuring the minimum concentration of oxygen in an oxygen/nitrogen mixture that will just support flaming combustion of a polymeric specimen. Six types of specimens of different dimensions are listed in ASTM D2963, specifically depending on the form of material being tested, for example, molding materials, cellular materials, and sheet materials. Among these six types of specimens, the commonly used dimension of the polymeric specimen is 100 mm × 6.5 mm × 3 mm, which falls into the range of alternative size for self-supporting molding or sheet materials, when testing rigid polymeric materials. During the test, the specimen is held at its base and positioned vertically in the center of a glass chimney as shown in Fig. 4. The gas supply of evenly mixed oxygen and

nitrogen should continuously purge into the glass chimney at the base. Gas measurement and control devices should be equipped properly for measuring the concentration of oxygen in the gas mixture entering the glass chimney, by using a paramagnetic oxygen analyzer to continuously sample the mixed gas. The flame igniter, like a Bunsen burner, is inserted into the chimney, and the test flame is applied at the top of the upper end of the specimen until the entire surface is ignited. If the specimen cannot be ignited after 30 seconds of the flame application, the concentration of oxygen in the supply gas should be increased correspondingly until the specimen can be ignited and burn gently. In most cases, the specimen will exhibit stable candlelike combustion. If the specimen could remain burning more than 180 seconds after ignition or the burning can extend 50 mm or more below the top of the specimen, the test specimen should be replaced by a new specimen and the concentration of oxygen in the supply gas should be decreased correspondingly to continue testing. By testing a series of specimens in different oxygen concentrations, the LOI value, is obtained from the limiting concentration at which the specimens tested self-extinguish in less than 180 seconds, and the burning extends less than 50 mm below its top. Namely, the result of LOI tests is on a numerical scale, which makes it possible to compare the polymers based on flammability. For example, a material rated of high LOI indicates that the polymeric material is less easy to be ignited and less flammable under the conditions of this test method. Considering the oxygen concentration in ambient condition is 21%, if a material has an LOI below 21, it is classified as combustible, whereas it is classified as self-extinguishing if the material has an LOI above 21 [16].

Moreover, LOI tests are repeatable, because the typical wide variability of combustion is restricted by carrying LOI tests in carefully controlled conditions [43]. However, it should be noted that the LOI test results relate only to the performance of the specimens under the LOI test, and cannot describe the fire hazards of the polymeric materials in other forms or under other conditions, indicating that the LOI test does not represent a real fire scenario.
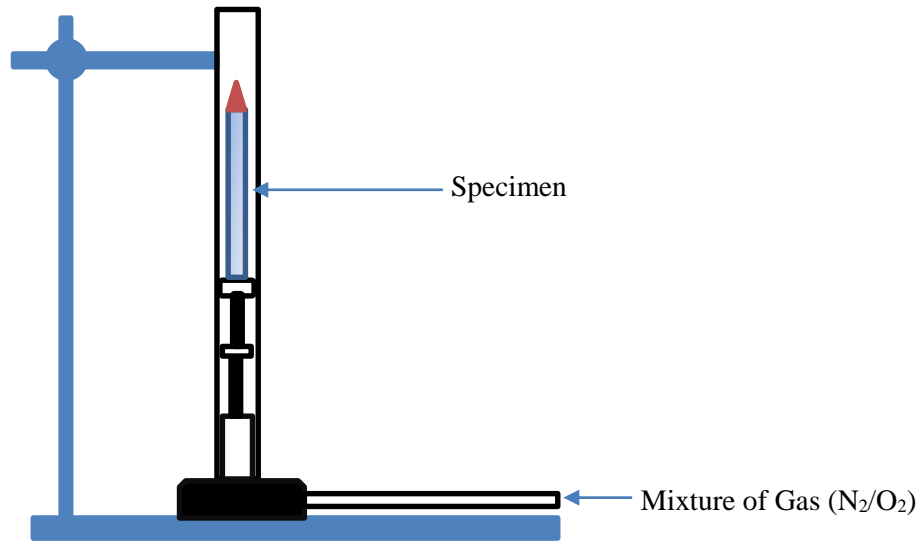
Fig. 4 Experimental Set-up for LOI Measurement (not Scaled) [16].

3.2.3 Cone Calorimeter Testing

Cone calorimeter is a well-known bench-scaled (medium-sized) instrument for testing of fire properties and has been accepted as a standard by International Standards Organization (ISO-5660) and American Society for Testing and Materials (ASTM E-1354). Cone calorimeter functions upon the principle that oxygen consumption is in proportional relationship with heat release rate (HRR) which is one of the most important parameters in controlling fire hazards, and also a very complex parameter, governed by chemical (reaction kinetics), thermal (heat transfer properties), and mechanical (cracking, delamination, etc.) properties [44, 45]. The specimen is sized of 100 mm$\times$100 mm in area and up to 50 mm thick. It can be tested either horizontally (standard testing) or vertically, but vertical orientation of the specimen is only reserved for exploratory studies, because the specimen can drip, collapse, and melt in unpredictable manners, especially for thermoplastic materials. In the experiments, after the calibration of the whole equipment, the specimen located in the load cell, is exposed to a constant heat flux generated by a

conical–shaped irradiation heat source ranging from 0 to 110 kW/m^2. The radiant heat flux can represent different fire scenarios. The higher radiant heat flux levels can give better reproducibility, and more clearly defined ignition phenomena, but they correspond to more fully developed fires rather than developing fires exactly. And the lower heat flux levels are more consistent with fire protection goals, particularly for fire retardant polymers. Usually, 35 and 50 kW/m^2 are the most widely used heat flux levels in the academic community, which correspond to the heat fluxes found in developing fires [46] . Thus this kind of experiments can give a reasonable insight into the fire behaviors of a material in developing fires, but with less developing time and cost, because a relatively small-sized specimen is prepared and tested [46]. When enough combustible fuel volatile fragments are thermally decomposed from the heated specimen, the combustion is initiated by a small electrical sparking igniter. Then the ignitability parameter is recorded as the time to ignition, which strongly depends on critical heat flux, critical mass loss rate for ignition, or critical surface temperature for ignition [46]. Actually, once the specimen is ignited, the cone calorimeter test represents a well-defined flaming condition, typically for developing fire scenarios, forced by external radiation. During the combustion process, the fire is in a well-ventilated condition with a CO_2/CO ratio corresponding to equivalent ratio, represented as ϕ , between 0.7 and 1 [47]. More specifically, the equivalent ratio is defined as

$$\phi = \frac{actual\ fuel/air\ ratio}{stoichiometric\ fuel/air\ ratio}$$

Therefore, if ϕ <1, the flame is a fuel-lean reaction; if ϕ =1, it is a stoichiometric reaction; and if ϕ >1, it is a fuel-rich reaction. Besides the time to ignition, the cone calorimeter apparatus can also record or compute other fire response parameters for fire performance analysis, like mass loss of the specimen, effective heat of combustion of the specimen, smoke and soot production pertaining to smoke obscuration, and optionally toxic or corrosion gases, like HCl and HBr.

However, fire response properties more typically pertaining to fully developed or post fire scenario are not replicated in the cone calorimeter. These data collected are mainly used for four distinct purposes [45]:

1. Comparison between different materials to evaluate their properties and their performance;

2. Obtaining certain thermophysical constants of materials, pertaining to fire properties, like the value of thermal inertia of the material, which is an important fire property influencing both ignition and flame spread;

3. Determining input data to fire models, predication of full-scale fire behaviors, or other engineering calculations;

4. For regulatory compliance, for example, in the Building Code of Australia, it is acceptable to assess the fire retardant treated wood for use in bushfire-prone area, based upon cone calorimeter testing results.

Generally, different purposes of the application of the cone calorimeter testing results require different methods of data evaluation. For example, in the academic field, the end-use condition and comprehensive evaluation of cone calorimeter data in all possible aspects are mainly used to access the response of a specific material to a fire, compare the properties of different materials and then evaluate them accordingly, especially in the fire retardancy field. However, for regulatory compliance, the end-use condition, reproducibility, and the exact evaluation of one or two well-identified characteristic parameters should be treated more seriously.

It also should be noted that little consensus has been reached within the community of fire researchers and fire scientists on the interpretation of cone calorimeter data. But the demand of investigating the properties of new flame retardant materials is true and significant, with cone calorimeter data being comprehensively analyzed and evaluated.

Generally, a lack of strong correlation is observed between UL-94 V-rating, LOI, and cone calorimeter, because they simulate totally different fire scenarios and focus on different fire risks or hazards within a specific fire scenario, although to some extent they all measure the flammability of polymeric materials [48, 49]. Namely, it is very difficult to compare the fire performance of a specific kind of material in different fire scenarios simulated by different test methods. It has to be admitted that all fires are different. Any one of these test methods described earlier can only cover a specific range of fire types and corresponding fire response behaviors, but if they cooperate together, they can help the fire researchers gain a better understanding of the properties of the materials particularly pertaining to fire. In this research, cone calorimeter is the tool used to study the flame retardant properties of PMMA-silica nanocomposites.

Fig. 5 Experimental Set-up for Cone Calorimeter.

CHAPTER IV

FLAME RETARDANCY

Flammability is an inherent risk or hazard of polymeric materials, due to their energy-dense
hydrocarbon-based structure. Recently, primarily three approaches have been emerged to improve
flame retardancy of a specific kind of material, or provide some alternative protection of the
material from a fire [4]:

- Engineering approaches;

- Use of inherently low flammable or flame retardant polymeric materials;

- Flame retardant additives.

Engineering approach is to find a possible solution to get the polymer out of the scenarios of high
risk, for example, installing a fire protection shield, or changing the way how the polymeric
product is used in the end-use application, in which the polymeric product is completely got rid of
the fire risk scenario. This approach is easy to implement and usually is an economic option. But
one drawback of this engineering approach that cannot be neglected in real applications, is that
one minor defect has the potential to cause the total failure of the engineering protection of
polymeric materials. For instance, given a fire proof fabric which intends to protect flammable
foam embedded in furniture or mattress, the foam can involve in fire easily once there is a rip or
small hole appearing on the fire proof fabric.

The second approach is to use inherently low flammable or inherently flame retardant polymers,
which is usually characterized as high resistance to ignition and low heat release rate. Basically,

solely from the consideration of safety, this approach is the most optimum one to reduce or eliminate the fire risks or hazards concerning with polymeric materials, because the combustion process is hard to start initially no matter what kind of fire risk scenario the polymer is exposed to specifically. Moreover, inherently flame retardant polymeric materials are so easy to implement even with little fabrication or modification, that they have the potential to be widely applied in the industry. However, Lyon's studies at the Federal Aviation Administration indicate that the cost of polymers tends to be inversely proportional to their inherent flammability [50]. Namely, the highly aromatic engineering polymers, like PAI (polyamide-imides), which prove to be weakly flammable and highly thermally-stable, are much more expensive than aliphatic polymers, like PVC (polyvinyl chloride), which exhibits high flammability and low thermal stability [4, 50]. Consequently, their wide-range application is restricted by economic reasons, especially when large quantity is needed in the industry. Moreover, another limitation concerning inherently flame retardant polymeric materials is recycling and sustainability, because some of low flammable polymeric materials are hard to recycle due to their interior structure, especially fiber reinforced polymer composites, which can be found in aircraft and mass transportation vehicles [4]. Unless the low flammability and high thermal stability is the highest priority, inherently flame retardant polymers can hardly compete with other polymers in the market.

The third approach is to use flame retardant additives particularly to modify and improve those polymers of relatively high flammability and low thermal stability, which is also the most extensively used approach so far [3]. Generally, commercially available flame retardant additives include, but absolutely not limited to, halogenated flame retardants, phosphorus-based flame retardants, mineral filler flame retardants, borate flame retardants, and silicon-based flame retardants. A lot of fire researchers and fire scientists have done numerous work in this field, and hence a large volume of knowledge on this subject has been established and further developed, so that the navigation of how to implement these flame retardant additives in polymers can be

supported, at least to some degree, by previous research or scientific theory. When tested in a single fire scenario, it is possible to incorporate a particular kind of flame retardant additive to improve a particular aspect of how a particular kind of polymer responses, and finally make the polymer pass the test. But in the end-use application, the polymeric product is still potentially of high fire risk, once it is exposed to a different fire scenario, rather than the one simulated by the fire test. Moreover, the use of flame retardant additives may also be attacked by other problems. The flame retardant additives embedded in the polymers may leach into the environment if they finally function in a fire. More importantly, with the addition of flame retardant additives, usually a compromise must be reached within polymer between flame retardancy and other properties. For instance, for fiber-reinforced composites, the addition of flame retardant additives may adversely affect the degree of crosslinking between the monomer and curing agent, which finally compromise the mechanical properties of them, although flame retardancy performance can be improved in a certain aspect [51]. In spite of these drawbacks mentioned above, flame retardant additives are still the most common method of improving fire retardancy of the polymers in the market, because flame retardant additives can indeed improve the flame retardancy of polymers, and this approach is cost effective and easy to operate.

4.1 Mechanisms of Flame Retardant Additives

Flame retardant additives, as their name suggests, mean to add some chemicals to the polymers to improve flame retardancy performance in a specific fire test. Based upon how the additives bond to the polymer, regardless of their chemical structure, flame retardant additives can be simply classified into two groups: normal additives and reactive additives. Normal additives are those which form physical interaction with the polymer. Usually, normal additives are incorporated within the polymer either during polymerization or during melt compounding process of the thermoplastic materials, in which normal additives are part of polymer formulation. Normal additives usually include mineral fillers, hybrids or organic compounds that can include

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macromolecules, and they react with the polymer only at higher temperatures at the start of a fire [3]. Their application ranges from polymers with pure carbon chain structure such as polyolefin, to polymers with a heterogeneous chain such as polyesters and polyamides [17]. Adversely, reactive additives are those which are chemically bonded to the polymer backbone and become a permanent part of the polymer during polymerization or in a post-processing step. During polymerization, reactive additives are introduced into the polymer as a new polymer monomer or precursor. In the post-polymerization process, their incorporation into polymers is through chemical grafting. Compared with normal flame retardants, reactive flame retardants are tailor-made products, which are preferred for polymers with a heterogeneous chain such as epoxy resins or polyurethanes [17]. Actually, almost all kinds of flame retardant additives have both normal additives and reactive additives. However, typically, normal additives are more versatile than reactive additives in the real field, because of the advantage of low cost and ease of use, although reactive additives can form much more durable flame retardant effect and they do not have the potential of blooming out, plating out, or evaporating from the polymer over time.

The polymer combustion process is comprised of multiple interacted steps involving both condensed phase and gas phase. A detailed schematic description of the self-sustaining polymer combustion process is shown in Fig. 6 [52]. The theory behind flame retardant additives is that these additives may act to prevent, minimize, or even stop any step in the self-sustaining polymer combustion process and consequently control the burning rate or even extinguish the flame. The possible ways that function in such manners include [3]:

1. The modification of the thermal decomposition process to lower the quantity of evolved combustible volatiles, with normally an increase in the char formation, which can serve as a barrier between the polymer and flame;

2. The isolation of the flame from the oxygen/air supply;

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3. The introduction into the polymer formulation of those compounds that will release efficient flame inhibitors;

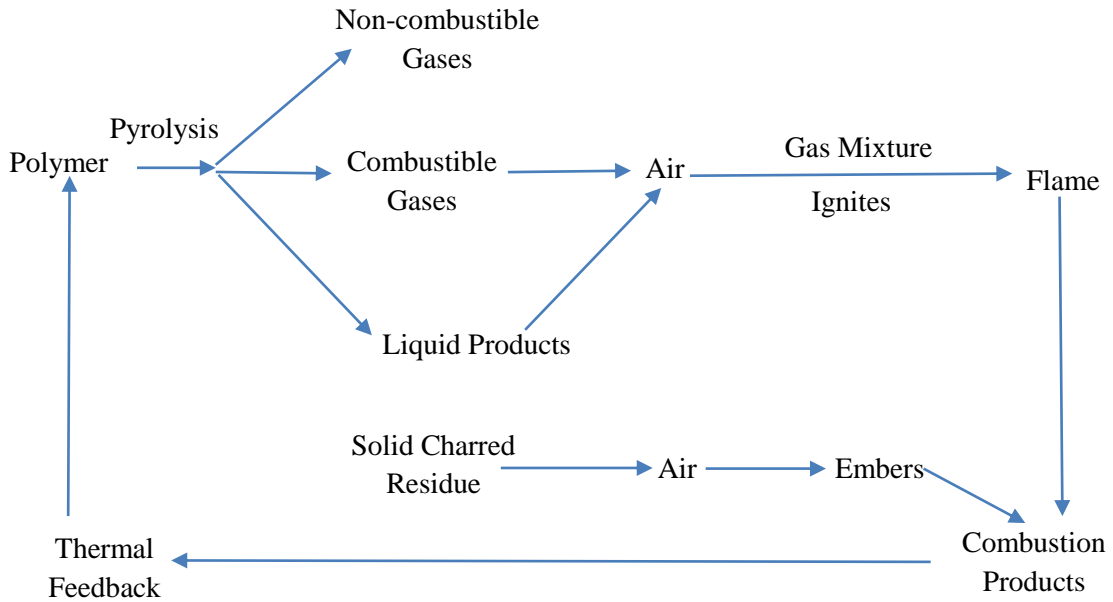4. The lowering of thermal feedback to the polymer to prevent further pyrolysis.

Fig. 6 General Schematic of Polymer Combustion Process [52].

Namely, flame retardant additives may act either physically or chemically in the condensed phase or gas phase. It should be noted that such actions of flame retardant system will cause chain reactions within the self–sustaining polymer combustion cycle in which various individual steps occur simultaneously, but with one dominating. The dominating step is the basic mechanism of that flame retardant system. Although various flame retardant additives have totally different chemical structures, almost all types of flame retardant systems dominate the polymer combustion process based upon one or more of three common mechanisms of flame retardant actions. These three most common mechanisms are gas phase flame retardants, endothermic flame retardants, and char-forming flame retardants [4, 17].

1. Gas phase flame retardants: this is the chemical mechanism in the gas phase. When exposed to fire, flame retardant additives can release specific radicals, like Cl· and Br·, which can react with highly reactive free radicals such as H· and OH· to form less reactive or relatively inert molecules. Thus the free radical mechanism of the combustion can be minimized or even stopped, and finally heat released into the gas phase from polymer combustion is reduced. Usually, halogenated flame retardants function primarily based on this mechanism.

2. Endothermic flame retardants: this is the physical mechanism in both the gas phase and the condensed phase. During the thermal decomposition of the flame retardants, a large amount of noncombustible gases can be released into the gas phase, such as CO_2, H_2O, and NH_3, which can dilute the mixture of combustible gases and lower their concentration. Consequently, the occurrence of combustible gases to ignite is limited. More importantly, the thermal decomposition of flame retardants is an endothermic process. With a lot of heat energy consumed to decompose flame retardants, and heat those non-combustible gas, the temperature within the flame zone may be cooled blow the polymer combustion temperatures, at least to some degree. Additionally, the lower temperature can subsequently slow the pyrolysis rate of polymers. Such endothermic reaction is known to act as a heat sink. Usually, metal hydroxides and metal carbonates act as flame retardant additives primarily based on this mechanism.

3. Char-forming flame retardants: this is the condensed phase mechanism. Flame retardants can cause char formation at the surface of the polymer by binding up the polymer as non-pyrolyzable carbon (char, more specifically) through chemical transformation of the degraded polymer chain, like crosslinking. Additionally, charring could be promoted by catalysis or oxidative dehydrogenation. Char formation can negatively affect the thermal decomposition of the polymer and exhibit resistance to combustion from several aspects. Char is produced at the expense of other reactions that may form combustible volatile

fragments, which may finally limit the total amount of gaseous fuel volatile released to support polymer combustion. Additionally, once an adherent and stable char layer is formed on the surface of a polymer, this char layer can act as a physical barrier of mass transfer from the condensed phase to the gas phase, and simultaneously an insulator of heat transfer from the flame to underlying polymer, which may make further thermal decomposition process more difficult [40]. However, if the char layer formed is of low quality, for example, it has cracks, the char layer may not be effective enough to retard heat transfer from the flame to the polymer and diffusion of combustible materials under the layer to the flame. Usually, intumescent additives and nanocomposites act as flame retardants and mainly function as this mechanism describes.

Some flame retardants, like aluminum hydroxides, can operate exclusively through a physical mode of action. However, no single flame retardants can function exclusively in a chemical model of action. Understandably, chemical reaction is always accompanied by corresponding physical reactions. Similarly, chemical mechanism is always accompanied by one or more physical mechanisms, for instance, the endothermic decomposition of the flame retardants [53]. An effective cooperation of several different mechanisms may have synergistic effect on the flame retardancy, with using a new flame retardant system that is developed based on a designated combination of different flame retardant additives. Namely, the improvement of flame retrdancy is larger than that is assumed simply from addition of the separate effects of each kind of flame retardant.

4.2 Selection Criteria of Flame Retardants

There are no flame retardants that can universally work for all polymers. Namely, different polymers may need different types of flame retardant systems to achieve the optimum flame retardancy performance. One kind of flame retardant may only improve a particular aspect of

how the polymer responses in a fire condition. Namely, one kind of flame retardant can aid the polymer to pass a certain regulatory test, but may not pass another different fire test. The flame retardants must be carefully identified and selected to match each type of polymer in a specific fire risk scenario. More specifically, the criteria for the selection of flame retardants are usually based on [17]:

- The efficiency of a particular type of flame retardant in a particular polymer system;

- Thermal stability at processing temperatures and processing conditions of the polymer;

- Compatibility and the ability to preserve valuable physical properties;

- The cost-performance trade-off;

- Low tendency to bleed out or to evaporate;

- Color-less and odorless;

- Resistance to ageing and hydrolysis;

- No corrosion of equipment;

- Sustainability and recyclability;

- Ecological impact of the flame retardant materials and no toxicity.

In many cases, the existing traditional flame retardants mentioned earlier cannot fully meet the criteria above. For example, halogen-containing flame retardants are being phased out in their utility due to their proven or suspected health and environmental concerns; the application of aluminum trihydrate and magnesium hydroxides requires so high loading rate of the additives within the polymer to achieve an optimum level of flame retadancy that end products are characterized as high density, low flexibility, and low mechanical properties; and intumescent systems are relatively expensive and electrical requirements can limit the use of this kind of flame retardant polymers [54]. In this condition, polymer nanocomposite has emerged in the field of flame retardancy because it has the potential to eliminate or avoid the disadvantages of traditional flame retardant systems, at least to some degree.

4.3 Polymer Nanocomposites

Polymer nanocomposite is a new class of flame retardant technology. Compared to traditional flame retardant systems, polymer nanocomposites are environmentally friendly, highly efficient, and capable of imparting polymer's other properties [7]. By definition, polymer nanocomposites are polymer matrix reinforced with nanometric particles that are uniformly dispersed so that the majority of the polymer is all interfacial polymer, which can significantly increase the interfacial area between the polymer and nanometric particles. This phenomenon is clearly different from traditional polymer composite in which the fillers or fibers are quite large in size and the interfacial polymer is only a small portion of the whole polymer [4]. The immense interior interfacial area within the polymer could enable a considerable reduction of the loading rate of the nanoparticles to achieve an acceptable level of flame retardancy. For example, polymer-layered silicate nanocomposites have been found to possess noticeably enhanced properties even at a very low concentration of silicate, usually inferior to 5 wt%, in the aspect of thermal stability, gas barrier properties, and flame retardancy [14].

In general, polymer nanocomposites primarily function in the condensed phase to improve flame retarandcy. In fire conditions, the mass loss rate of the polymer is decreased by the formation of a nanoparticle-rich fire protection barrier. Due to the reduction of fuel mass supply, the heat release rate and flame growth are also lowered correspondingly, especially the peak heat release rate during the combustion process. However, the total heat release of the polymer nanocomposite remains almost constant. Namely, the total heat release of the polymer nanocomposite is just spread out over a longer burning time so that the burning process is less intensive. Although polymer nanocomposite indeed exhibits certain property of retarding flame growth, polymer nanocomposite by itself is still not enough to pass regulatory tests. But with the low base flammability of polymer nanocomposite, the incorporation of traditional flame retardant additives can further enhance its flame retardancy to pass the regulatory tests more easily. More

specifically, the combination of a small amount of traditional flame retardants with polymer

nanocomposite can achieve the same acceptable level of fire safety as the one provided by

traditional polymer but of an extremely high loading of flame retardant additives. Depending on

the specific dimensions of these nanoscale traditional flame retardant particles, they can be

roughly divided into three groups [14, 16]:

1. 2 D nanoparticles: only one dimension of the particle is within nanometer range. The

   filler is presented in the form of layer or sheet, such as nanoclay (layered silicate), which

   is one to a few nanometers thick but hundreds or thousands of nanometers wide and long.

2. 1D nanoparticles: two dimensions of the particle are within nanometer range and the third

   dimension is larger. The filler is presented in the form of fiber or elongated structure,

   such as carbon nanotubes, carbon nanofibers, or cellulose whiskers.

3. 0 D nanoparticles: all of the three dimensions are within nanometer range. The filler is

   presented in the form of isodimensional nanoparticles, such as spherical silica

   nanoparticles, nanometric titanium oxide, nanoscale ferric oxide, and polyhedral

   oligosilsesquioxane (POSS).

In the 2D nanoparticles, the polymer nanocomposites composed of clay or layered silicates, also

named as polymer-layered silicate nanocomposites, have been broadly investigated probably due

to the fact that the raw materials of clay are widely available and cost effective, and the study of

their intercalation chemistry has established the fundamental knowledge for commercial

application. To achieve a fine dispersion of the nanoclay within the polymer matrix, organically

modified nanoclays are often used [16]. However, thermal instability issues are big concerns

associated with the organic treatment on the clay surface, which limit the types of polymers that

the clay can be put in [55, 56, 57]. Usually the poor dispersion of the nanoclay and the

decomposition of the organic surfactant on the clay limit the wide application of nanoclay to

flame retardant polymer nanocomposites [7].

Among the 1D nanoparticles, carbon nanotubes (CNTs), potentially regarded as an alternative to nanoclay or layered-silicate, are the most widely investigated nanofibrous materials, because the acceptable level of flame retardancy can be achieved even with a much lower loading rate of nanotubes (1-2 wt%) due to their high aspect ratio, which can form a relatively uniform protective network without any cracks or gaps [7]. Carbon nanofibers are another type of 1D nanoparticles. However, few reports of the flame retardant performance of carbon nanofibers have been available because the formation of carbon nanofibers is of low efficiency when directly mixing them with the polymers [58] . Moreover, carbon nanofibers are not as efficient as carbon nanotubes, but carbon ninofibers are much more cost-effective [7]. Although carbon nanotubes and carbon nanofibers do not have the same thermal instability problem as nanoclay, poor interface with many polymers, which makes it difficult to produce desired nanocomposite structure, tends to be another limitation of their wide application, besides the high cost of them.

In 0 D nanoparticles, nanometric titanium oxide, nanoscale ferric oxide, POSS, and spherical silica nanoparticles are all relatively new subjects. Some investigations have been done on them, in which they all show their potential as nanofillers within flame retardant polymer nanocomposites.

For spherical silica nanoparticles, due to the formation of tightly packed silica particles in various polymers that significantly reduce both heat-bound and loosely bound polymer chains around the particles, the thermal stability of nanosilica-filled polymer nanocomposites can be improved, and subsequently flammability properties [59]. However, in previous research by Kashiwagi, it indicates that the overall flame retardancy of nanoscale silica particles appears to be less efficient than that of silicate-layered particles [15] . The relatively low efficiency of nanoscale silica particles is caused by the failure of formation of network-structured protective layer that covers the entire polymer nanocomposite surface during gasification in a fire condition. One potential method of forming a desired *in-situ* silica network during gasification is to enhance the formation

of crosslinks among the particles by appropriate surface treatment of nanoscale silica particles.

However, few studies have addressed this field [53].

CHAPTER V

EXPERIMENTAL

Poly (methyl methacrylate) (PMMA), with methyl methacrylate (MMA) as the monomer, is the polymer selected in this study. Among all polymers, PMMA is a kind of extensively used thermoplastic in the family of poly (acrylic ester)s due to its desirable properties, including exceptional optical clarity, good moldability, protection against ultraviolet radiation, high strength, and excellent dimensional stability [60, 61]. However, the biggest concern pertaining to PMMA is its low heat resistance, poor thermal stability, and high flammability with LOI of 18 [62]. PMMA nanocomposite also has the potential to improve thermal properties significantly and mechanical properties as well, with the addition of a small loading rate of inorganic flame retardant particles.

However, taking it into account that the surface of nanoscale inorganic particles is hydrophilic, but on the contrary the polymer matrix is hydrophobic, obviously these two components are not compatible in nature, which will result in weak interfacial interaction between them if they are directly mixed together to form polymer nanocomposites [63]. Additionally, due to the immense surface area of nanoscale inorganic particles and corresponding high surface energy, these nanoscale particles are easy to agglomerate and can hardly be finely dispersed within the polymer matrix to produce optimum nanocomposites if without any special operations. Consequently,

surface treatment of nanoscale inorganic particles emerges as a widely applicable technology to overcome the deficiencies described above. Generally, surface treatment of inorganic particles means to create organic coatings over the particles, which can be achieved by utilizing physical and chemical interactions between the particles and the surface treatment agents [64]. Coupling agent treatment is a kind of chemical method, and coupling agents contain reactive groups to form strong covalent bond between inorganic particles and organic matrix. 3-aminopropyltriethoxysilane (KH 550) and 3-methacryloxypropyltrimethoxysilane (KH 570) are two types of saline coupling agents. Their molecular formulas are listed below [65]:

$$NH_2(CH_2)_3Si(OMe)_3 \qquad\qquad (KH\ 550)$$

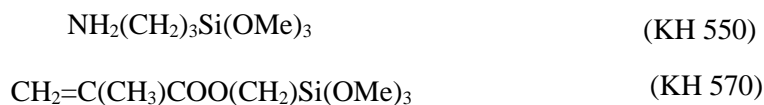$$CH_2=C(CH_3)COO(CH_2)Si(OMe)_3 \qquad (KH\ 570)$$

Fig. 7 The Molecular Formulas of Saline Coupling Agents.

Compared with nanoclay or silicate-layered particles, nanoscale silica particle is a relatively new type of nanofiller in flammability studies of nanocomposites, and very limited research has been done on it. Although previous research indicates that the overall flame retardancy of nanoscale silica particles appears to be less efficient than that of silicate-layered particles, one possible approach to further improving the thermal stability and subsequently flammability of polymer nanocomposites is also identified that enhancing the formation of crosslinks among the particles by appropriate surface treatment of nanoscale silica particles, may promote the formation of *in-situ* silica network-structured protective layer covering the polymer nanocomposite decomposing surface [53].

Moreover, the flame retardant mechanism of polymer nanocomposites mainly functions in the condensed phase and a strong correlation exists between char yield and fire resistance of polymers in fire conditions [66]. When exposed to a fire, commonly, linear PMMA

depolymerizes to its constituent monomers and almost little carbonaceous is left to yield char, which attributes, at least partially, to the low flame retardancy of PMMA [66]. However, it is found that PMMA by itself tends to yield more char and internal mass transfer can be noticeably reduced if its molecule structure is altered to crosslinked PMMA rather than linear PMMA [67]. As the molecular structure of KH 570 shows, when nanoscale silica particles are surface treated with KH 570, many vinylidene groups presented as $RC=CH_2$, are also introduced to the nanoparticle surface. These vinylidene groups can participate in free-radical polymerization, become part of polymer chain, and finally create nanosilica-based crosslinked polymer nanocomposites [68]. Namely, KH 570 can act not only as the surface treatment coupling agent, but also as the crosslinking agent. However, KH 550 only plays the role of coupling agent, and do not involve in polymerization reactions. Moreover, because MMA has the similar functional groups to KH 570, polymerization is more likely to happen for MMA than other dissimilar monomers, which further makes PMMA a good polymer candidate for this study.

It is necessary to state clearly that it is Logan C. Hatanaka and Lubna Ahmed from Texas A&M University who made the test specimens. The detailed information of materials, synthesis process, and sample preparation is presented below.

5.1 Materials

Methyl methacrylate (MMA) and 1,1'-Azobis(cyclohexanecarbonitrile) (ABCN) were used as the monomer and initiator, respectively. Both the monomer and initiator were obtained from Polysciences. Two kinds of nanoscale silica particles with different surface treatment agents, namely KH 550 and KH 570, were collected from US Nano. The average diameter ranged between 20 and 30 nm. Silica surface treated with KH 570 was used for crosslinking nanoscale silica particles with the polymer to form crosslinked PMMA nanocomposites, while KH 550 was

used to produce the non-crosslinked PMMA nanocomposite products, also known as linear PMMA nanocomposites.

5.2 Synthesis

The monomer MMA was placed in a glass reaction vial with a silicone septum on top. Surface modified nanofillers were added to the monomer under magnetic stirring. The amount of the filler varied depending upon the loading rate of nanofillers within the nanocomposites. For this study, 1, 2 and 4 wt% of silica-containing PMMA nanocomposites were prepared. The stirring continued for half an hour followed by sonication for another half an hour at room temperature. The sonication procedure aided in de-gasification of any dissolved oxygen and enhanced mixing. After sonication, the initiator ABCN was added to 0.2 wt% of the MMA. To further remove dissolved oxygen, the solution was inerted by bubbling nitrogen gas through it for about ten minutes. The solution was continuously stirred while the inerting process took place. After the inerting process, the reaction vial was submerged in an oil bath maintained at a temperature of 70 ± 1 °C while the stirring continued.

5.3 Sample Preparation

A method from literature was used to build a mold to prepare 100 mm×10 mm×5 mm samples for cone calorimeter analysis [69]. Two glass plates were put in parallel with silicone tubing in the middle. The wall thickness of the silicone tube determined the sample thickness. The glass plates with the silicone tubing in-between were clamped to keep the mold structure together. The polymerization solution was put in the hollow space created in the mold and then the clamped mold was sealed at the top with another length of silicone tubing. The mold was then placed in a large oil bath for curing for 24 hours at 70 ± 1 °C while the stirring continued. After the curing process was complete, the glass plates were removed and the solid mold was cut into the samples

with a dimension of 100 mm×100 mm×5 mm. By using this mold and procedure, neat PMMA, 1, 2 and 4 wt% silica crosslinked and non-crosslinked PMMA samples were all prepared.

5.4 Cone Calorimetric Measurements

As mentioned earlier, cone calorimeter is a well-known bench-scaled instrument for testing of fire properties. While a single parameter is not enough to represent the fire scenario, a cone calorimeter can aid in the prediction of the material burning behavior quite decently. Cone calorimeter is able to provide some parameters for fire analysis including, but not limited to, heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), time to ignition (t_{ign}), mass loss rate (MLR), average specific mass loss rate (MLR_{ave}), smoke production, specific extinction area (SEA), and mean specific extinction area (SEA_m), effective heat of combustion, mean CO_2 yield, and mean CO yield [44].

A series of samples were tested by using the cone calorimeter, including neat PMMA samples, 1, 2, and 4 wt% silica non-crosslinked and crosslinked samples. All samples were tested under the standard of ASTM E 1354 by the cone calorimeter manufactured by Fire Testing Technology Limited (FTT). During the testing, these samples were all evaluated in a horizontal orientation and directly exposed to a heater with a heat flux of 50 kW/m² [49]. The unexposed surfaces of these samples were wrapped in aluminum foil prior to testing, the samples were placed in retainer frame, and a thin wire cross was placed on the exposed surface of those samples to prevent the samples from bucking before burning. In addition, the ambient temperature was set from 20.2 °C to 20.9 °C, the ambient pressure was set from 97.994 kPa to 98.148 kPa, and the relative humidity was in the range of 27% to 28%.

CHAPTER VI

RESULTS AND DISCUSSION

The testing results are presented in Table 1. In the following comparison, neat PMMA samples will be used as the baseline to assess the fire behavior of other samples in the aspects of t_{ign}, HRR, PHRR, average HRR, THR, MLR, MLR_{ave}, SEA_m, effective heat of combustion, mean CO yield, maximum average rate of heat emission (MARHE), and flame spread b value.

Table 1. Cone Calorimeter Results of All Samples.

Sample	t_{ign} (s)	PHRR (kW/m^2)	MLR_{ave} (g/s·m^2)	THR (MJ/m^2)	SEA_m (m^2/kg)
Neat PMMA	28	781	24.9	89.3	144
1 wt% Silica Non-crosslinked	23	644	20.7	93.1	154
1 wt% Silica Crosslinked	11	637	18.9	86.2	143
2 wt% Silica Non-crosslinked	21	503	18.2	80.1	152
2 wt% Silica Crosslinked	10	503	16.1	90.7	163
4 wt% Silica Non-crosslinked	14	455	17.0	73.9	162
4 wt% Silica Crosslinked	12	470	16.8	82.4	164

Sample	Effective heat of combustion (MJ/kg)	Mean CO yield (kg/kg)	MARHE (kW/m^2)	Average HRR (kW/m^2)	b (m^2/kg)
Neat PMMA	24.0	0.0116	466	363	2.52
1 wt% Silica Non-crosslinked	24.0	0.0120	416	305	1.98
1 wt% Silica Crosslinked	24.2	0.0114	417	282	1.79
2 wt% Silica Non-crosslinked	24.3	0.0100	359	225	1.19
2 wt% Silica Crosslinked	24.3	0.0103	373	229	1.27
4 wt% Silica Non-crosslinked	24.0	0.0112	331	269	1.63
4 wt% Silica Crosslinked	24.8	0.0111	341	242	1.39

6.1 Main Flame Retardant Mechanism

Flame retardants can have totally different chemical structures, but they function mainly through three most common mechanisms: gas phase flame retardants, endothermic flame retardants, and condensed phase flame retardants [4, 17]. For gas phase flame retardants, the combustion process in the gas phase will be changed to consume highly reactive free hydrogen and hydroxyl radicals, so that the main combustion product will be changed as will, like the yield of CO_2. For endothermic flame retardants, they will act as a heat sink to cool the solid polymer and release inert gas to dilute combustible fuel in the gas phase, so that commonly the effective heat of combustion will be lowered. For all neat PMMA samples and silica-containing PMMA samples, the mean effective heat of combustion (calculated heat release rate divided by measured mass loss

rate) is almost constant and falls within the range of 24±0.8 MJ/kg, which is consistent with the research by Kashiwagi, who indicates that the specific heat of combustion is 24±2 MJ/kg for all PMMA and silica-containing PMMA samples [15]. Consequently, considering the unchanged values of mean effective heat of combustion and mean CO_2 yield (not shown) for all samples, it is reasonable to state that the main flame retardant mechanism of silica-containing PMMA samples is the chemical and physical processes in the condensed phase. Moreover, from previous research, polymer nanocomposites mainly function in the condensed phase to retard flame, in which nanoparticles will accumulate near the polymer burning surface to form a nanoparticle-rich protective layer as shown in Fig. 8 [35, 36, 37]. For silica-containing PMMA samples, this nanoparticle-rich protective layer is composed of nanoscale silica particles. More importantly, given the physical and chemical properties of nanoscale silica particles and the purpose of introducing the crosslinking structure into polymers, the statement of condensed phase mechanism is solidly evident.
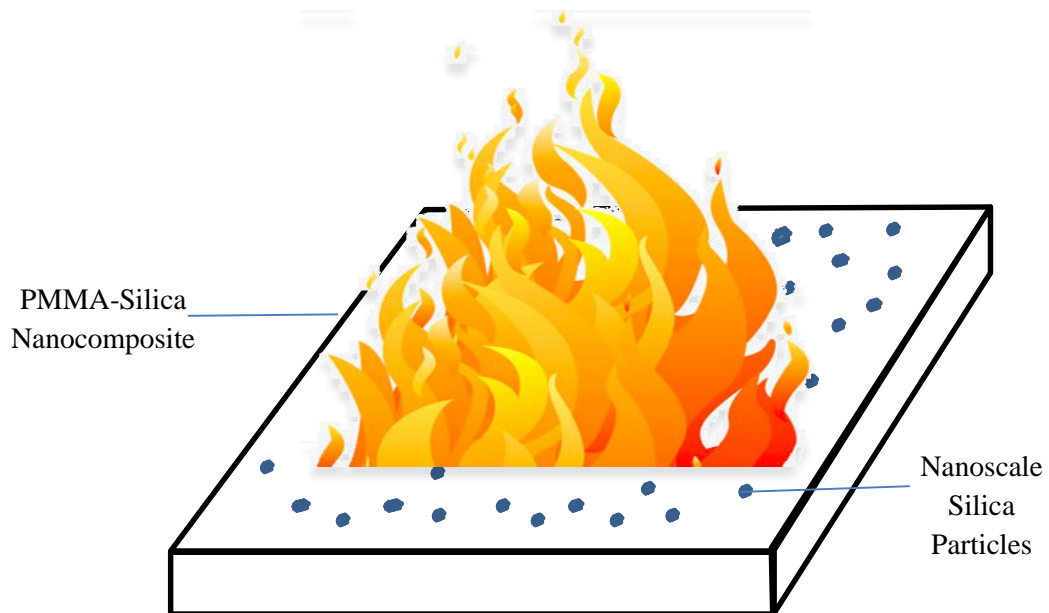

Fig. 8 Schematic of Flame Retardant Mechanism (not Scaled).

6.2 Time to Ignition

The parameter of time to ignition (t_{ign}) is closely related to the ignitability of materials. The lower value of time to ignition, the more ignitable the testing materials are, when tested in the same fire scenario [70]. Time to ignition, t_{ign}, can be precisely expressed as [42]:

$$t_{ign} = t_{py} + t_{mix} + t_{chem}$$

Where:

t_{py} =heating time for the solid to reach pyrolysis temperature;

t_{mix} =diffusion or transport time needed for the flammable fuel and oxygen to reach the ignition pilot;

t_{chem} =time needed for the flammable mixture to proceed to combustion once at the pilot.

However, for solid materials, usually, compared with t_{py}, t_{mix} and t_{chem} are so quick and negligible [42]. Time to ignition is closely related to the pyrolysis temperature of the solid material to produce sufficient volatiles at the lower flammable concentration, if the radiant heat flux is the same. From Table 1, at the same mass concentration of silica within the test range in this research, the crosslinked samples have lower t_{ign} than the non-crosslinked samples, indicating that the crosslinked samples are a little easier to ignite than the non-crosslinked samples. Namely, the pyrolysis temperature of crosslinked samples is lower than that of non-crosslinked samples, especially at a lower concentration of silica. Moreover, all t_{ign} data of silica-containing PMMA samples are lower than that of neat PMMA samples, meaning that silica-containing PMMA samples are easier to ignite and tend to decompose at a relatively lower temperature than neat PMMA samples. This observation reflects that silica-containing flame retardants may negatively affect the parameter of t_{ign}, which can be further confirmed in Figs. 9-13. The curves of heat release rate of silica-containing PMMA samples suddenly start to rise earlier than neat PMMA

samples. However, such a disappointing observation is consistent with previous research, in which it is found that little influence is identified on the thermal decomposition temperature, and t_{ign} is not improved for most polymer nanocomposites [4]. Even for some polymer nanocomposites, t_{ign} is decreased, like this current research. Nevertheless, only with the poor performance of ignitibility, it is hard to draw the conclusion that silica-containing PMMA samples have bad flame retardancy, because the real meaning of flame retardancy is that one or several of fire risks can be under control in a specific fire scenario, not only ignitability.

One possible explanation to this disappointing observation is that the organic coupling agents used in the research, more specifically, KH 550 and KH 570, tend to decompose at a relatively low temperature and initiate the flame much earlier than neat PMMA samples. Due to the lower t_{ign} of crosslinked samples than non-crosslinked samples, possibly KH 570 is easier to decompose than KH 550. Another possible reason is that the pathway of heat adsorption into PMMA nanocomposites and thermal decomposition is changed. However, PMMA nanocomposite degrades to give only monomers [71]. Considering there is no change in the thermal degradation pathway and only monomer is produced, the second reason may not be reasonable enough to explain the early time to ignition [72].

6.3 Heat Release Rate

Heat release rate (HRR) is defined as the mass loss rate of the material times its heat of combustion [44]. HRR is the critical fire reaction property because it is the driving force for flame spread and also controls other reaction properties, like the yield of CO and CO_2, and the decomposition reaction [73]. In the cone calorimeter, HRR is calculated from the oxygen concentration in the flue gasses based on the general principle that the heat released from a wide range of organic fuels is proportional to the oxygen consumed during combustion [44]. More specifically, for the complete combustion of conventional organic fuels, 13.1 kJ of heat energy is

released for the consumption of per gram of oxygen, with an accuracy of ± 5% or better [74].

The peak heat release rate (PHRR) is the maximum amount of heat liberated by a material during the combustion process. It often occurs over a very short period of time (less than a few seconds). The PHRR is considered to be a critical property controlling the maximum temperature and flame spread rate [75]. Compared with neat PMMA samples, all silica-containing PMMA samples are observed to have lower values of PHRR. As shown in Figs. 9-13, the peak of the heat release rate curve of neat PMMA samples is much higher than other silica-containing PMMA samples. Moreover, the good reduction of PHRR confirms the formation of silica-containing PMMA nanocomposites, rather than microcomposites [76]. Additionally, from Table 1, at the same mass concentration of silica, there is no significant difference between non-crosslinked samples and crosslinked samples in the aspect of PHRR.
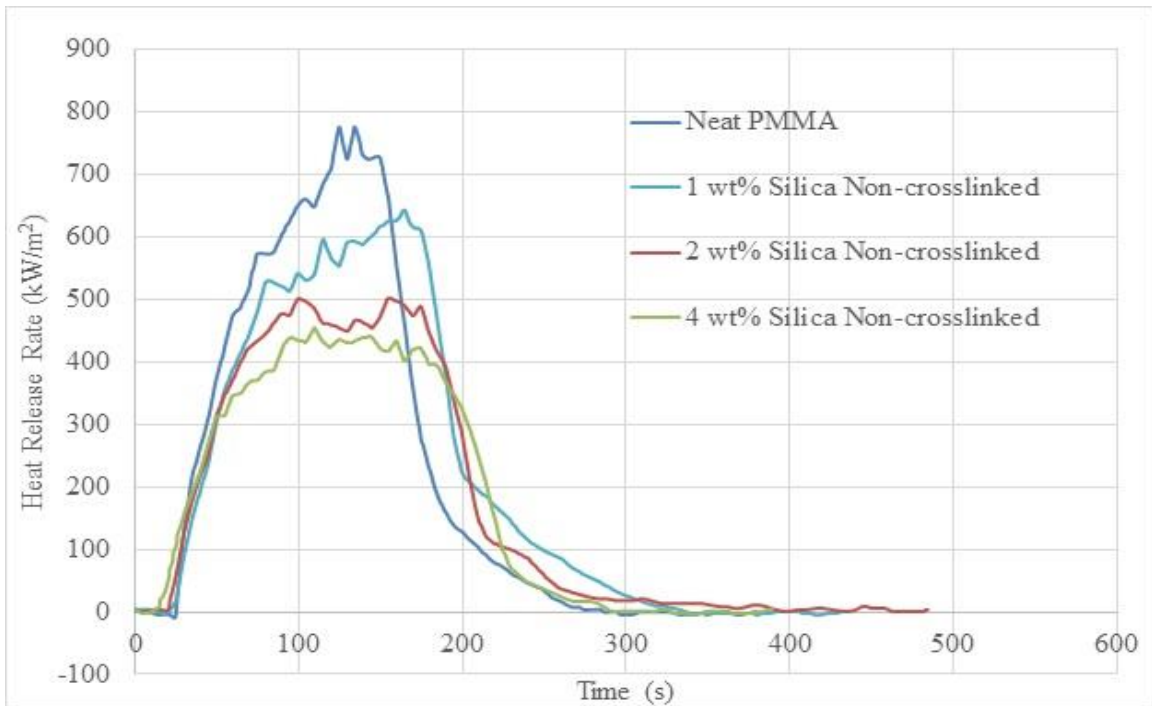

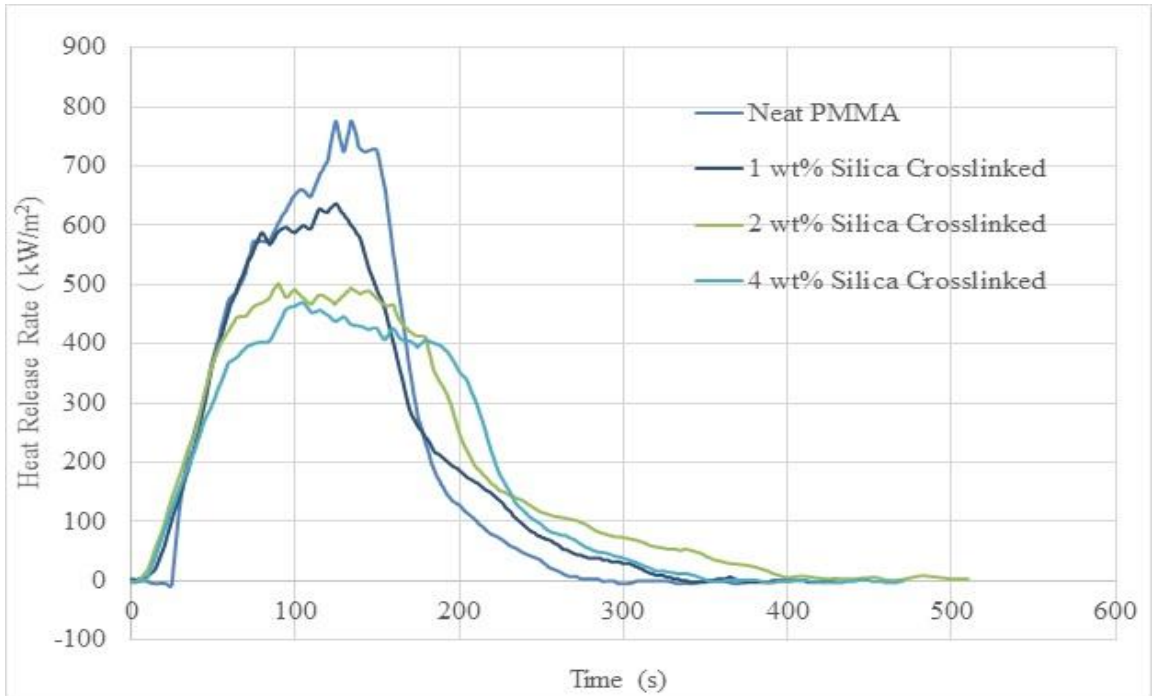Fig. 9 Heat Release Rates of Non-crosslinked Samples.

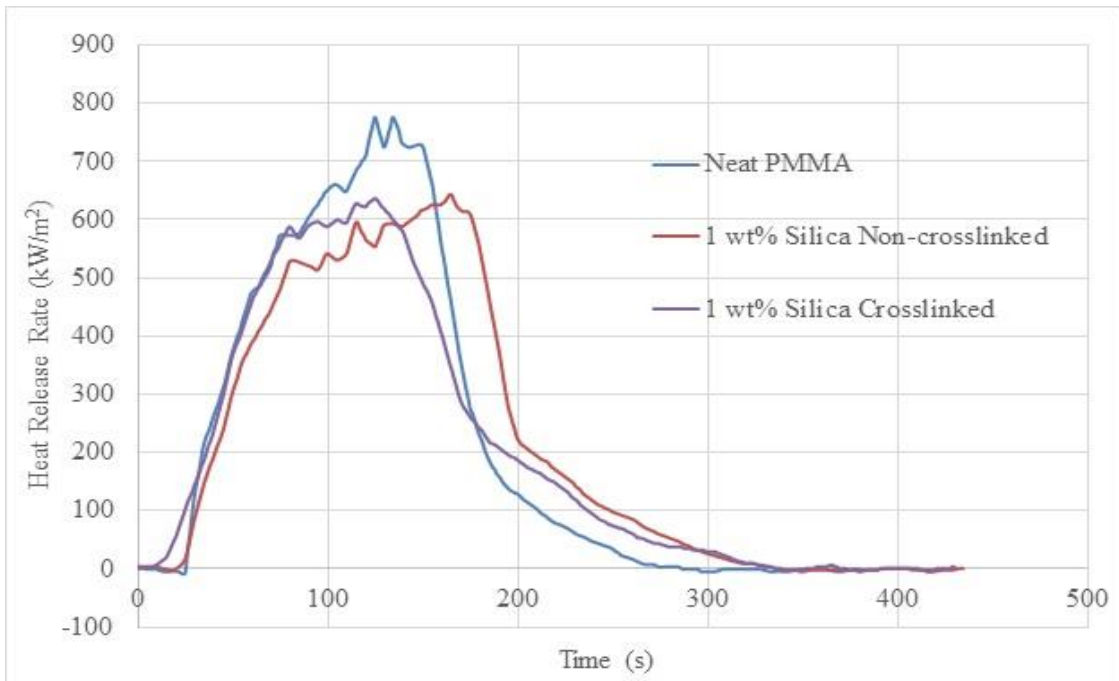Fig. 10 Heat Release Rates of Crosslinked Samples.

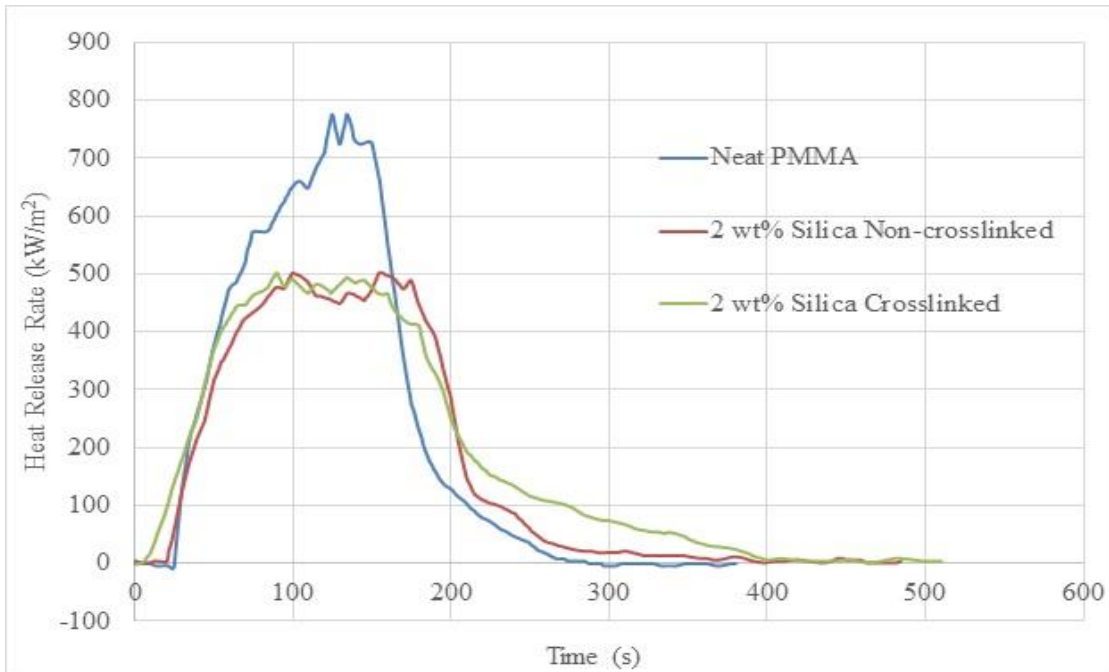Fig. 11 Heat Release Rates of 1 wt% Silica Samples.

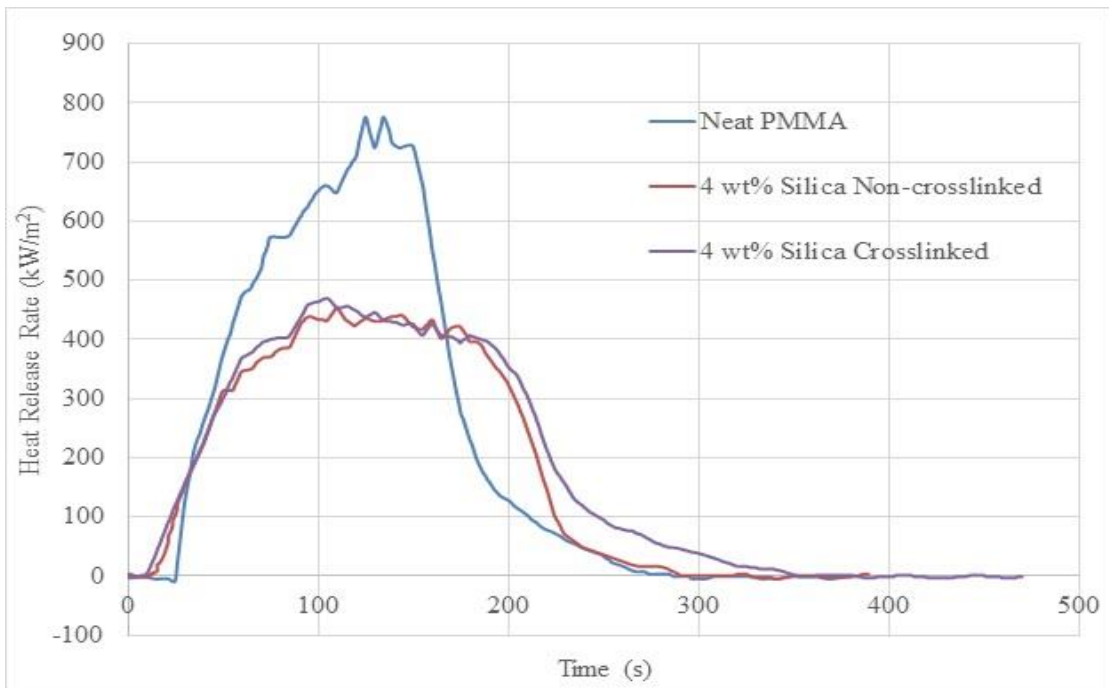Fig. 12 Heat Release Rates of 2 wt% Silica Samples.

Fig. 13 Heat Release Rates of 4 wt% Silica Samples.

For all silica-containing PMMA samples, the initial sharp increase of HRR is very similar to that of neat PMMA samples, but after the burning goes on, HRR does not go as high as neat PMMA samples, and even becomes relatively stable in some period of time, as shown in Figs. 9 and 10. Namely, the flame retardanny of silica-containing PMMA samples only takes effect with preceding burning. This observation agrees well with the statement about main flame retardant mechanism, because the condensed phase mechanism need to be activated by the burning of polymer [53].

From Figs. 12 and 13, the trends of the heat release rate curves are very similar at the same mass concentration of silica, 2 and 4 wt% silica respectively, which means there is no significant difference between crosslinked samples and non-crosslinked samples at the same mass concentration of silica in the aspect of enhancing char layer formation to retard flame. However, from Fig. 11, the trend of heat release rate curve of 1 wt% silica crosslinked samples is different from 1 wt% silica non-crosslinked samples. Although PHRR of 1 wt% silica crosslinked samples appears not only earlier than 1 wt% silica non-crosslinked samples, but also a little earlier than neat PMMA samples, the average HRR of 1 wt% silica crosslinked samples is smaller. That is, the intensity of combustion of 1 wt% silica crosslinked samples is reduced more by the formation of crosslinked PMMA, which is designated to produce more stable nanosilica-containing char layer to protect unburned PMMA under it. However, this observation is not so evident for 2 wt% and 4 wt% silica-containing PMMA samples. Namely, at the relatively high concentration of silica, crosslinked PMMA samples do not show the tendency of forming better char layer to retard flame than non-crosslinked PMMA samples. Possibly, the high concentration of nanoscale silica particles does not contribute much to, or even negatively affect the formation of crosslinked PMMA, due to the unavoidable agglomerate of nanoscale silica particles. For the low concentration of nanoscale silica particles, crosslinking appears to contribute more to char formation to protect polymer, due to the relative lack of nanoscale silica particles, which are

actually only loosely isolated on the decomposing polymer surface and cannot form network-structured protective layer.

With the addition of silica-containing flame retardants in PMMA samples, the total heat release (THR) of silica-containing PMMA samples tends to decrease a little. The THR of non-crosslinked samples seems to decrease a little more at a higher mass concentration of silica. This observation reflects that crosslinked samples are more completely burned than non-crosslinked samples [76]. When plotting heat release rate and corresponding burning time on two axes, the total integrated area under the HRR curve over the test period can be represented as the total heat release. Therefore, from Figs. 11, 12, and 13, the observations shown above can be confirmed by comparing the areas under the HRR curves. Namely, the silica-containing PMMA samples either have visually almost the same area as neat PMMA samples, or have a smaller area than neat PMMA samples. At a high mass concentration of silica within the experimental range, non-crosslinked samples have a little smaller area than crosslinked samples. Compared with neat PMMA samples, silica-containing PMMA samples tend to yield char at the expense of flammable volatiles, and within PMMA nanocomposites combustible polymer is replaced with noncombustible nanoscale silica particles, which may combine together to explain the reduction of THR. For 2 wt% and 4 wt% silica-containing PMMA samples, the flame duration time of crosslinked samples is longer than non-crosslinked samples, in which crosslinked samples have more chance to burn more completely and release more heat, although more char tends to be yielded by crosslinked samples.

Besides the fact that even at the same mass concentration of silica, non-crosslinked samples and crosslinked samples have different fire behaviors, the different mass concentrations of silica generate different effects on the fire behavior of those tested samples as expected. As shown in Figs. 9 and 10, with the increase of the mass concentration of silica in those PMMA samples from neat PMMA to 4 wt% silica, PHRR of those crosslinked and non-crosslinked samples decreases

gradually. For example, neat PMMA samples have the highest PHRR of 781 kW/m^2, and 4 wt% silica non-crosslinked samples have the lowest PHRR of 455 kW/m^2 among the non-crosslinked samples, which is 42% lower than that of neat PMMA samples. Similarly, 4 wt% silica crosslinked samples have the lowest PHRR of 470 kW/m^2 among the crosslinked samples, which is 40% lower than that of neat PMMA samples. Actually, compared with 13 wt% nanoscale silica particles and a roughly 50% reduction of PHRR in Kashiwagi's study, 4 wt% silica crosslinked and non-crosslinked samples are highly efficient in this current study [15]. With the increase of mass concentration of silica in PMMA samples within the experimental range, adversely non-crosslinked samples tend to decrease their THR uniformly and 4 wt% silica non-crosslinked samples have the lowest THR of 73.9 MJ/m^2, which is 17% lower than that of neat PMMA samples. However, with the increase of mass concentration of silica in PMMA samples within the experimental range, THR of crosslinked samples does not change uniformly. 2 wt% silica crosslinked samples have the highest THR of 90.7 MJ/m^2, and 4 wt% silica crosslinked samples have the lowest THR of 82.4 MJ/m^2, but the difference between them is not as big as what has been observed among non-crosslinked samples.

6.4 Mass Loss Rate

Mass loss rate (MLR) is closely related to how fast the sample is consumed during the combustion process. In cone calorimeter test, MLR$_{ave}$ is calculated over period starting when 10% of the ultimate specimen mass loss has occurred and ending at the time when 90% of the ultimate specimen mass loss has occurred [45]. Generally, with the embedding of nanoscale silica particles into PMMA samples, MLR$_{ave}$ can be reduced, for both crosslinked and non-crosslinked samples, which is consistent with average HRR. But the reduction effects on MLR$_{ave}$ are different for crosslinked and non-crosslinked samples respectively, as expected, due to the different pathways of protective layer formation. For example, the lowest MLR$_{ave}$ of the crosslinked samples is 2 wt% silica samples of 16.1 g/(s·m^2), but the lowest MLR$_{ave}$ of the non-crosslinked samples is 4

wt% silica samples of 17.0 g/(s·m²). As shown in Figs. 14 and 15, the slope of mass loss of neat

PMMA samples is steeper than that of silica-containing PMMA samples during the combustion

process, for both crosslinked and non-crosslinked samples. Compared to neat PMMA samples,

for non-crosslinked samples, the formation of protection layer most likely enhanced by nanoscale

silica particles, acts as the protective shield to reduce mass transport to the incident flame.

Moreover, as shown in Table 1, at the same mass concentration of silica within the test range,

MLR_{ave} of crosslinked samples is a little smaller than that of non-crosslinked samples, which

means that the crosslinked samples have less intensive combustion process than the non-

crosslinked samples. Compared with non-crosslinked samples, besides nanoscale silica particles,

crosslinked samples seem to have lower MLR_{ave} due to the existence of crosslinking of polymer
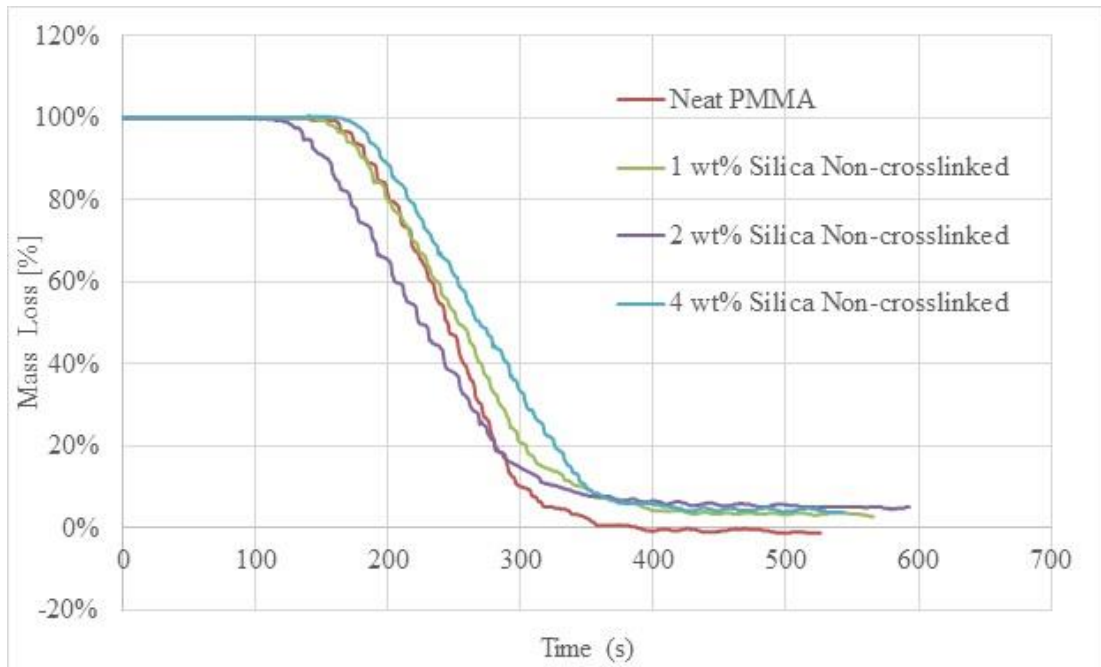
chains to further enhance char formation.

Fig. 14 Mass Loss of Non-crosslinked Samples.

One interesting observation is that the mass of neat PMMA samples was completely burned, and

almost no residue was left. However, for silica-containing PMMA samples, there was a small

quantity of black residue left, which means that the samples were not completely burned, due to the fact that nanoscale silica particles are inherently hard to burn. Moreover, the black residue is another important evidence of char formation.
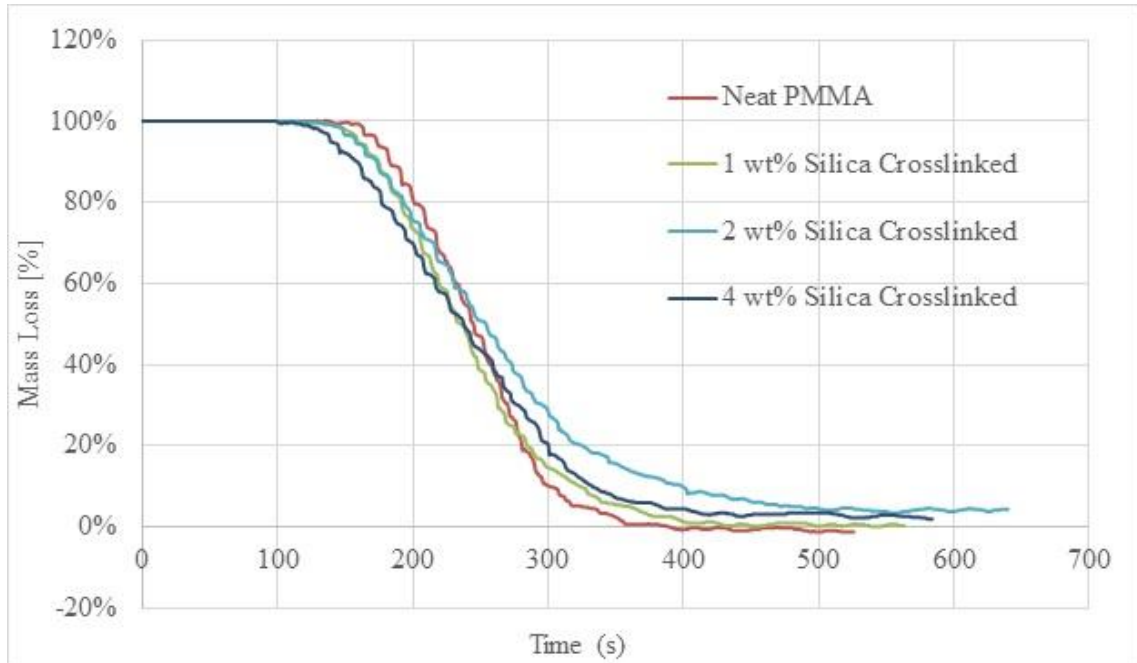

Fig. 15 Mass Loss of Crosslinked Samples.

6.5 Smoke Property

In principle, specific extinction area (SEA) is determined as the product of the extinction coefficient and the volumetric flow rate, divided by the mass loss rate of tested sample [77]. It represents the effective optical obscuring area generated by 1 kg of mass loss of specimen. Specific extinction area is used to assess how much soot in smoke is released from the combustion of different samples [78]. With the addition of silica-containing flame retardants into PMMA samples, the value of SEA_m of most silica-containing PMMA samples was increased. Namely, the soot release of those samples was higher, which will induce optical obscurity and reduce visibility, than neat PMMA samples, but except 1 wt% silica crosslinked samples, which

have almost the same SEA$_m$ value as neat PMMA samples. Additionally, from the cone

calorimeter test reports, the mean CO yield (kg/kg) remained almost the same for all neat PMMA

samples and silica-containing PMMA samples. Overall, there is no significant difference

observed between neat PMMA samples and silica-containing PMMA samples on SEA and CO

yield. This observation further demonstrates that the improved flame retardancy performance is

not caused by a process in the gas phase, but actually a modification of the thermal

decomposition process in the condensed phase [14].

6.6 Comprehensive Evaluation of Flame Retardancy

6.6.1 Fire Development and Spread

The average rate of heat emission (ARHE) is defined as the cumulative heat emission divided by

time. Its peak value is the maximum average rate of heat emission (MARHE), which is a

parameter included in the cone calorimeter test report to predicate the propensity for fire

development under real conditions [79]. Generally, all silica-containing PMMA samples have

smaller MARHE values than neat PMMA samples, and all non-crosslinked samples have smaller

MARHE values than crosslinked samples especially at the high mass concentration of nanoscale

silica particles. The MARHE values of all silica-containing PMMA samples decrease with the

increase of the loading rate of nanoscale silica particles.

To predicate the propensity of fire spread, Cleary and Quintiere proposed another parameter b

expressed as [80]:

$$b = 0.01\dot{q}''_{avg} - 1 - \frac{t_{ign}}{t_b}$$

Where:

$\dot{q}''_{avg}$: average heat release rate (kW/m^2) at a 50 kW/m^2 irradiance;

t_{ign} : time to ignition(s);

t_b : duration of flaming from time to ignition to time to flame out.

If b is less than 0.4, the material shows negligible propensity to spread fire [80]. Those materials of higher values of b, show increased hazards of fire spread in full-scale application. Generally, nanoscale silica particles indeed retard fire spread for all silica-containing PMMA samples, and reduce their fire hazards in full-scale application. Among all silica-containing PMMA samples, 2 wt% silica samples have the best potential to control fire spread, rather than 4 wt% silica samples.

6.6.2 Fire Retardancy Performance

The lower value of PHRR, the lower the maximum temperature and flame spread rate of the tested sample is in cone calorimeter. The lower value of THR, the smaller the fire load of the tested sample is, which characterizes the propensity of the tested sample to produce a shorter-duration fire [81]. The lower value of MLR$_{ave}$, the longer the time the tested sample can burn, if the tested samples are of the same mass and the same exposed area. To comprehensively evaluate the fire retardancy performance of tested samples, an approach is proposed to plot PHRR in units of kW/m^2 on one axis, which represents the character of causing fast flame spread rate, and plot THR·MLR$_{ave}$ in units of kg kW/m^4 on the other axis, which represents the character of causing long-duration fires. The tested samples near the origin point (0, 0) have the most expected and successful fire retardancy performance. Adversely, those tested samples, which lie far from the origin point, have relatively worse fire retardancy performance when exposed to the same fire scenario.

By plotting PHRR (kW/m^2) and THR·MLR$_{ave}$ (kg kW/m^4) on two axes as shown in Fig. 16, the tested samples are ranked as follows: neat PMMA samples, 1 wt% silica non-crosslinked

samples, 1 wt% silica crosslinked samples, 2 wt% silica crosslinked samples, 2 wt% silica non-crosslinked samples, 4 wt% silica crosslinked samples, 4 wt% silica non-crosslinked samples. Consequently, when PHRR, THR, and MLR_{ave} are comprehensively considered, 4 wt% silica non-crosslinked samples have the best fire retardancy performance, followed by 4 wt% silica crosslinked samples. As expected, neat PMMA samples have the worst fire retardancy performance.
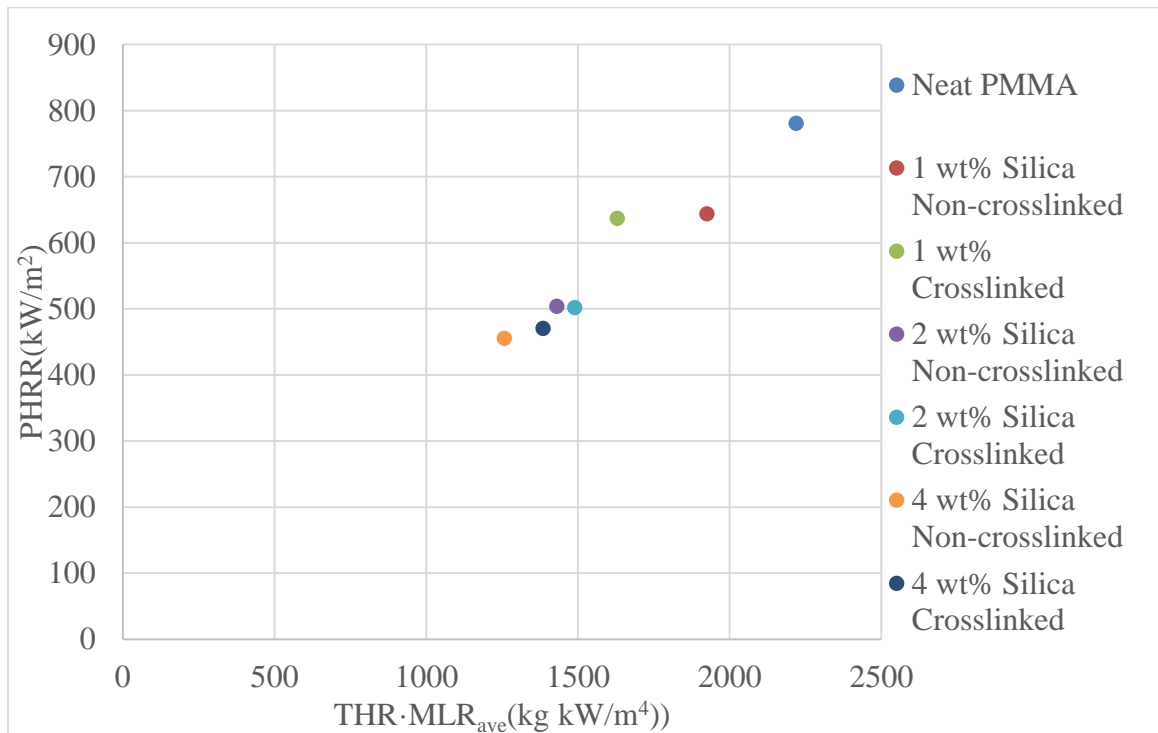

Fig. 16 Fire Retardancy Performance Evaluation.

CHAPTER VII

CONCLUSION

Through comprehensively considering heat release rate, total heat release, and mass loss rate, it is found that the best flame retardancy performance can be achieved by 4 wt% silica non-crosslinked PMMA samples, followed by 4 wt% silica crosslinked PMMA samples. Neat PMMA samples have the worst flame retardancy performance compared with other silica-containing PMMA samples. This observation suggests that flame retardant properties can be significantly improved by embedding a small amount of nanoscale silica particles into the poly (methyl methacrylate) matrix to form polymer nanocomposites, for both crosslinked and non-crosslinked nanocomposites. The additional analysis of heat release rate, effective heat of combustion, specific extinction area, and the yield of CO and CO_2, tends to demonstrate that the improvement in flame retardancy performance is caused by the modification of the thermal decomposition and combustion process in the condensed phase. Namely, silica-containing flame retardants can form one nanosilica-rich protective layer during combustion to protect the polymer matrix from further thermal decomposition, and hence improve the fire retardancy performance, which can further be promoted by crosslinking polymer chains especially at the low concentration of nanoscale silica particles. For the low concentration of nanoscale silica particles, crosslinking appears to contribute more to char formation to protect polymer, due to the relative lack of nanoscale silica particles, which actually are only loosely isolated on the decomposing polymer surface and cannot form network-structured protective layer. For the high concentration of nanoscale silica particles, the contribution of crosslinking to fire retardancy is limited by the formation of nanosilica-rich protective layer. However, silica-containing flame retardants may negatively

affect the fire behavior of PMMA samples in the aspect of ignitability and soot production to induce obscurity and reduce visibility. Moreover, the mass concentration of nanoscale silica particles in PMMA nanocomposite also has some effects on the flame retardancy. Consequently, the combination of nanoscale silica particles with the modification of the internal structure of the polymer nanocomposites (i.e., crosslinked and non-crosslinked) would be a potential way to improve their flame retardancy performance.

REFERENCES

1. Roshan, J.P. and Wang, Q. *Prediction of properties and modeling of fire behavior of polyethylene using cone calorimeter*. Journal of Loss Prevention in the Process Industries, 2015. 41: p. 1–8.

2. Visakh, P.M. and Arao, Y. Flame Retardants (Polymer Blends, Composites and Nanocomposites), Springer. 2015.

3. Mngomezulu, M.E., John MJ, Jacobs V, Luyt AS. *Review on flammability of biofibres and biocomposites*. Carbohydrate Polymers, 2014. 13(111): p. 149-182.

4. Morgan, A.B. and Gilman, J.W. *An overview of flame retardancy of polymeric materials: application, technology, and future directions*. Fire and Materials, 2013. 37(4): p. 259-279.

5. Betts, K.S. *New thinking on flame retardants*. Environmental Health Perspectives, 2008. 116(5): p. A210.

6. Wang, Q. *Polymer nanocomposite: a promising flame retardant*. Journal of Materials Science and Nanotechnology, 2011. 1(2): p.1.

7. Zhao, Z., Gou, J., Bietto, S., Ibeh, C., Hui, D. *Fire retardancy of clay/carbon nanofiber hybrid sheet in fiber reinforced polymer composites*. Composites Science and Technology, 2009. 69(13): p.2081-2087.

8. Pandey, P., Anbudayanidhi, S., Mohanty, S., Nayak, S.K. *Flammability and thermal characterization of PMMA/clay nanocomposites and thermal kinetics analysis*. Polymer Composites, 2012. 33(11): p. 2058-2071.

9. Iji, M., Serizawa, S. *Silicone derivatives as new flame retardants for aromatic thermoplastics used in electronic devices*. Polymers for Advanced Technologies, 1998. 9(10-11): p. 593-600.

10. Kashiwagi, T., Gilman, J.W., Butler, K.M., Harris, R.H., Shields, J.R., Asano, A. *Flame Retardant Mechanism of Silica Gel/Silica*. Fire and Materials, 2000. 24: p. 277-289.

11. Lu, S.Y., and Hamerton, I. *Recent developments in the chemistry of halogen-free flame retardant polymers.* Progress in Polymer Science, 2002. 27(8): p. 1661-1712.

12. Nie, S., Peng, C., Yuan, S., Zhang, M. *Thermal and flame retardant properties of novel intumescent flame retardant polypropylene composites.* Journal of Thermal Analysis and Calorimetry. 2013. 113(2): p. 865-871.

13. Zhang, S. and Horrocks, A.R. *A review of flame retardant polypropylene fibres*. Progress in Polymer Science, 2003. 28(11): p. 1517-1538.

14. Alexandre, M. and Dubois, P. *Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials*. Materials Science and Engineering: R: Reports, 2000. 28(1): p. 1-63.

15. Kashiwagi, T., Morgan, A.B., Antonucci, J.M., VanLandingham, M.R., Harris R.H., Awad, W.H., Shields, J.R. *Thermal and flammability properties of a silica–poly (methylmethacrylate) nanocomposite.* Journal of Applied Polymer Science, 2003. 89(8): p. 2072-2078.

16. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.M., Dubois, P. *New prospects in flame retardant polymer materials: from fundamentals to nanocomposites.* Materials Science and Engineering: R: Reports, 2009. 63(3): p. 100-125.

17. Bourbigot, S. and Le Bras, M. Chapter 5: Flame Retardant Plastics. Plastics Flammability Handbook - Principles, Regulations, Testing, and Approval (3rd Edition). 2004. p. 133-172.

18. Babrauskas, V. and Peacock, R.D. *Heat release rate: the single most important variable in fire hazard*. Fire Safety Journal, 1992.18(3): p. 255-272.

19. Bourbigot, S. and Duquesne, S. *Fire retardant polymers: recent developments and opportunities.* Journal of Materials Chemistry, 2007. 17(22): p. 2283-2300.

20. Grand, A.F. and Wilkie, C.A. (eds). Fire Retardancy of Polymeric Materials. Marcel Dekker, Inc. 2000. ISBN0-8247-8879-6.

21. Georlette, P.I. Applications of Halogen Flame Retardants. Fire Retardant Materials, Woodhead Publishing Cambridge. 2001. p. 264-292.

22. Murphy, J. *Flame retardants: trends and new developments*. Plastics, Additives and Compounding, 2001. 3(4): p. 16-20.

23. Lewin, M. Physical and Chemical Mechanisms of Flame Retarding of Polymers. Special Publication-Royal Society of Chemistry. 1998. 224(1): p. 3-32.

24. Levchik, S.V. and Weil, E.D. *A review of recent progress in phosphorus-based flame retardants.* Journal of Fire Sciences, 2006. 24(5): p. 345-364.

25. Pawlowski, K.H. and Schartel, B. *Flame retardancy mechanisms of triphenyl phosphate, resorcinol bis (diphenyl phosphate) and bisphenol A bis (diphenyl phosphate) in polycarbonate/acrylonitrile–butadiene–styrene blends*. Polymer International, 2007. 56(11): p. 1404-1414.

26. Braun, U., Balabanovich, A.I., Schartel, B., Knoll, U., Artner, J., Ciesielski, M., Döring, M., Perez, R., Sandler, J.K., Altstädt, V., Hoffmann, T. *Influence of the oxidation state of phosphorus on the decomposition and fire behavior of flame-retarded epoxy resin composites*. Polymer, 2006. 47(26): p. 8495-8508.

27. Braun, U., Bahr, H., Sturm, H., Schartel, B. *Flame retardancy mechanisms of metal phosphinates and metal phosphinates in combination with melamine cyanurate in glass‐fiber reinforced poly (1, 4‐butylene terephthalate): the influence of metal cation*. Polymers for Advanced Technologies, 2008. 19(6): p. 680-692.

28. Schartel, B., Kunze, R., Neubert, D., Braun, U. *Mechanistic studies on PA-66 fire retarded with red phosphorus.* Recent Advances in Flame Retardancy of Polymeric Materails, 2002. 13: p. 93-103.

29. Green, J. *Mechanisms for flame retardancy and smoke suppression-A review*. Journal of Fire Sciences, 1996. 14(6): p. 426-442.

30. Hull, T.R., Witkowski, A., Hollingbery, L. *Fire retardant action of mineral fillers*. Polymer Degradation and Stability, 2011. 96(8): p. 1462-1469.

31. Le Bras, M., Bourbigot, S., Camino, G., Delobel, R., editors. Fire Retardancy of Polymers: The Use of Intumescence. Elsevier. 1998.

32. Le Bras, M., Bourbigot, S., Revel, B. *Comprehensive study of the degradation of an intumescent EVA-based material during combustion.* Journal of Materials Science, 1999. 34(23): p. 5777-5782.

33. Camino, G., Costa, L., Luda, M.P. *Mechanistic aspects of intumescent fire retardant systems*. Macromolecular Symposia, 1993. 74(1): p. 71-83.

34. Aslin, D.C. *The design and development of intumescent coatings for structural fire protection*. Journal of the Oil and Colour Chemists' Association, 1989. 72(5): p. 176-190.

35. Zhu, J., Uhl, F.M., Morgan, A.B., Wilkie, C.A. *Studies on the mechanism by which the formation of nanocomposites enhances thermal stability*. Chemistry of Materials, 2001. 13(12):p. 4649-4654.

36. Gilman, J.W., Jackson, C.L., Morgan, A.B., Harris, R., Manias, E., Giannelis, E.P., Wuthenow, M., Hilton, D., Phillips, S.H. *Flammability properties of polymer-layered-*

silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chemistry of Materials, 2000.12(7): p. 1866-1873.

37. Gilman, J.W., Harris, R.H., Shields, J.R., Kashiwagi, T., Morgan, A.B. *A study of the flammability reduction mechanism of polystyrene－layered silicate nanocomposite: layered silicate reinforced carbonaceous char.* Polymers for Advanced Technologies, 2006. 17(4): p.263-271.

38. Kashiwagi, T. *Polymer combustion and flammability—role of the condensed phase*. Symposium (International) on Combustion, 1994. 25(1): p. 1423-1437.

39. Beyler, C.L. and Hirschler, M.M. Thermal Decomposition of Polymers. SFPE Handbook of Fire Protection Engineering. 2002. 2: p. 110-131.

40. Grand, A.F., Wilkie, C.A., editors. Fire Retardancy of Polymeric Materials. CRC Press. 2000.

41. UL-94, Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. 2016 Edition.

42. Quintiere, J. Fundamentals of Fire Phenomena. Wiley, 2006.

43. Camino, G., Costa, L., Casorati, E., Bertelli, G., Locatelli, R. *The oxygen index method in fire retardance studies of polymeric materials*. Journal of Applied Polymer Science, 1988. 35(7): p.1863-1876.

44. Lindholm, J., Brink, A., Hupa, M. *Cone calorimeter—a tool for measuring heat release rate*. Åbo Akademi Process Chemistry Centre, Finland. 2009.

45. Hurley, M.J., Gottuk, D.T., Hall Jr, J.R., Harada, K., Kuligowski, E.D., Puchovsky, M., Watts Jr, J.M., Wieczorek, C.J., editors. SFPE Handbook of Fire Protection Engineering. Springer, 2015.

46. Schartel, B. and Hull, T.R. *Development of fire retarded materials－Interpretation of cone calorimeter data*. Fire and Materials, 2007. 31(5): p. 327-354.

47. Hull, T.R., Wills, C.L., Artingstall, T.A., Price, D.E., Milnes, G.J. *Mechanisms of smoke and CO suppression from EVA composites.* Fire Retardancy of Polymers: New Applications of Mineral Fillers. Royal Society of Chemistry, London. 2005. p. 372-385.

48. Weil, E.D., Patel, N.G., Said, M.M., Hirschler, M.M., Shakir, S. *Oxygen index: correlations to other fire tests*. Fire and Materials, 1992. 16(4): p.159-167.

49. Morgan, A.B. and Bundy, M. *Cone calorimeter analysis of UL-94 V-rated plastics*. Fire and Materials, 2007. 31(4): p. 257-283.

50. Lyon, R.E., Takemori, M.T., Safronava, N., Stoliarov, S.I., Walters, R.N. *A molecular basis for polymer flammability.* Polymer, 2009. 50: p. 2608–2617.

51. Kandare, E., Chukwudolue, C., Kandola, B.K. *The use of fire retardant intumescent mats for fire and heat protection of glass fibre-reinforced polyester composites: Thermal barrier properties.* Fire and Materials, 2010. 34(1): p. 21-38.

52. Troitzsch, J.H. *Overview of flame retardants.* Chemistry Today. 1998. p.16.

53. Morgan, A.B., Wilkie, C.A., editors. Flame Retardant Polymer Nanocomposites. John Wiley & Sons. 2007.

54. Beyer, G. *Nanocomposites: a new class of flame retardants for polymers.* Plastics, Additives and Compounding, 2002. 4(10): p. 22-28.

55. Xie, W., Gao, Z., Pan, W.P., Hunter, D., Singh, A., Vaia, R. *Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite*. Chemistry of Materials. 2001. 13(9): p. 2979-2990.

56. Dharaiya, D. and Jana, S.C. *Thermal decomposition of alkyl ammonium ions and its effects on surface polarity of organically treated nanoclay*. Polymer, 2005. 46(23): p. 10139-10147.

57. Shah, R.K. and Paul, D.R. *Organoclay degradation in melt processed polyethylene nanocomposites*. Polymer, 2006. 47(11): p. 4075-4084.

58. Zammarano, M., Krämer, R.H., Harris, R., Ohlemiller, T.J., Shields, J.R., Rahatekar, S.S., Lacerda, S., Gilman, J.W. *Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation*. Polymers for Advanced Technologies, 2008. 19(6): p. 588-595.

59. Tsagaropoulos, G. and Eisenburg, A. *Direct observation of two glass transitions in silica-filled polymers. Implications to the morphology of random ionomers*. Macromolecules, 1995. 28(1): p. 396-398.

60. Li, Y., Zhao, B., Xie, S., Zhang, S. *Synthesis and properties of poly (methyl methacrylate)/montmorillonite (PMMA/MMT) nanocomposites*. Polymer International, 2003. 52(6): p. 892-898.

61. Pandey, P., Anbudayanidhi, S., Mohanty, S., Nayak, S.K. *Flammability and thermal characterization of PMMA/clay nanocomposites and thermal kinetics analysis*. Polymer Composites, 2012. 33(11): p. 2058-2071.

62. Laachachi, A., Cochez, M., Ferriol, M., Leroy, E., Cuesta, J.L., Oget, N. *Influence of Sb_2O_3 particles as filler on the thermal stability and flammability properties of poly (methyl methacrylate) (PMMA).* Polymer Degradation and Stability, 2004. 85(1): p.641-646.

63. Hong, R.Y., Fu, H.P., Zhang, Y.J., Liu, L., Wang, J., Li, H.Z., Zheng, Y. *Surface-modified silica nanoparticles for reinforcement of PMMA*. Journal of Applied Polymer Science, 2007. 105(4): p. 2176-2184.

64. Rong, M.Z., Zhang, M.Q., Ruan, W.H. *Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review*. Materials Science and Technology, 2006. 22(7): p. 787-796.

65. Li, X., Cao, Z., Zhang, Z., Dang, H. *Surface-modification in situ of nano-SiO_2 and its structure and tribological properties*. Applied Surface Science, 2006. 252(22): p. 7856-7861.

66. Lomakin, S.M., Brown, J.E., Breese, R.S., Nyden, M.R. *An investigation of the thermal stability and char-forming tendency of cross-linked poly (methyl methacrylate).* Polymer Degradation and Stability, 1993. 41(2): p. 229-243.

67. Nyden, M.R., Forney, G.P., Brown, J.E. *Molecular modeling of polymer flammability: application to the design of flame-resistant polyethylene.* Macromolecules, 1992. 25(6): p. 1658-1666.

68. Hatanaka, L.C., Ahmed, L., Sachdeva, S., Wang, Q., Cheng, Z., Mannan, M.S. *Thermal degradation and flammability of nanocomposites composed of silica cross-linked to poly (methyl methacrylate)*. Plastics, Rubber and Composites, 2016. 45(9): p. 375-381.

69. Sandler, S. Polymer Synthesis. 2nd ed. Academic Press. 1991.

70. NFPA 272. Standard Method of Test for Heat and Visible Smoke Release Rates for Upholstered Furniture Components or Composites and Mattresses Using an Oxygen Consumption Calorimeter. 2003 version.

71. Cullis, C.F. and Hirschler, M.M. The Combustion of Organic Polymers. Oxford Science Publications. 1981.

72. Jash, P. and Wilkie, C.A. *Effects of surfactants on the thermal and fire properties of poly (methyl methacrylate)/clay nanocomposites*. Polymer Degradation and Stability, 2005. 88(3): p. 401-406.

73. Mouritz, A.P., Mathys, Z., Gibson, A.G. *Heat release of polymer composites in fire*. Composites Part A: Applied Science and Manufacturing, 2006. 37(7): p. 1040-1054.

74. Huggett, C. *Estimation of rate of heat release by means of oxygen consumption measurements.* Fire and Materials, 1980. 4(2): p. 61-65.

75. Mouritz, A.P. and Gibson, A.G. *Fire properties of polymer composite materials*. Springer Science & Business Media. 2007.

76. Wang, D., Echols, K., Wilkie, C.A. *Cone calorimetric and thermogravimetric analysis evaluation of halogen-containing polymer nanocomposites*. Fire and Materials, 2005. 29(5): p. 283-294.

77. Myllymäki, J. and Baroudi, D. *Prediction of smoke production and heat release by convolution model*. VTT TIEDOTTEITA. 1999.

78. Barakat, M., Souil, J.M., Breillat, C., Vantelon, J.P., Knorre, V., Rongère, F.X. *Smoke data determination for various types of fuel*. Fire Safety Journal, 1998. 30(3): p. 293-306.

79. Sacristán, M., Hull, T.R., Stec, A.A., Ronda, J.C., Galià, M., Cádiz, V. *Cone calorimetry studies of fire retardant soybean-oil-based copolymers containing silicon or boron: Comparison of additive and reactive approaches.* Polymer Degradation and Stability, 2010. 95(7): p. 1269-1274.

80. Cleary, T.G. and Quintiere, J.G. *A framework for utilizing fire property tests*. Fire Safety Science, 1991. 3: p. 647-656.

81. Petrella, R.V. *The assessment of full-scale fire hazards from cone calorimeter data*. Journal of Fire Science, 1994. 12(1): p.14–43.

VITA

Ruiqing Shen

Candidate for the Degree of

Master of Science

Thesis: CONE CALORIMETER ANALYSIS OF FLAME RETARDANT POLY (METHYL METHACRYLATE)-SILICA NANOCOMPOSITES

Major Field: Chemical Engineering

Biographical:

Education:

Completed the requirements for the Master of Science in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma in December, 2016.

Completed the requirements for the Bachelor of Science in Fire Protection and Safety Technology at Oklahoma State University, Stillwater, Oklahoma in 2015.

Experience:

Graduate Teaching Assistant at FPST, Oklahoma State University, Stillwater, Oklahoma (August-December, 2015-2016).