SYSTEMATIC ANALYSIS OF FLAMMABILITY REDUCTION OF POLYMER NANOCOMPOSITES

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Abstract: Polymeric materials are widely used around the world along with high fire hazards due to their flammability. With wide applications of nanotechnology, researchers are currently focusing to develop polymer nanocomposites to enhance their performance in flammability reduction. These flame retardant polymer nanocomposites reduce the ignition time but when applied in proper composition they could reduce the peak heat release rate (PHRR) significantly. With an increasing emphasis on this research area, a database is required to record all the formulations and performance of flame retardant polymer nanocomposites. In this paper, major cone calorimeter test parameters such as ignition time, peak heat release rate, total heat release, were recorded from available literature for polymers including polymethyl methacrylate (PMMA), polypropylene (PP), polystyrene (PS), and polyethylene (PE). Judging by the highest reduction (%) of PHRR, the best formulations of flame retardant polymer nanocomposite have been identified and listed. Ranges of PHRR reduction (%) of different formulations for individual polymers were determined. This review will provide insights to select and/or develop best formulations for flame retardants polymers in the future research.

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INTRODUCTION

Polymers especially thermoplastics are widely used as construction materials in various sectors of industries. The production and consumption of thermoplastics materials boomed right after the end of World War II. A new era started as these polymeric materials started to replace the traditional materials because of their low cost. Plastics are widely used in electrical industries to exploit the properties of insulation, durability, flexibility and robustness. Plastics also have been widely used in the building industries to provide piping, roofing, insulation, flooring etc. Other major industries where plastics are used are packaging, automotive, military, domestic and commercial furniture fittings, textile, plastic reinforced glass industries etc. Other than the mentioned industries, plastics are finding their application in novel applications too. Anthony et al. studied the applications and societal benefits of plastics [1]. According to this study, global demand for plastic materials is increasing day by day. In 2006, the global demand for plastics was 49.5 million metric tons. Polypropylene (PP), polystyrene (PS), polymethyl methacrylate (PMMA), high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) are the most widely used plastics. Global market demand for these plastic materials is shown in figure 1.

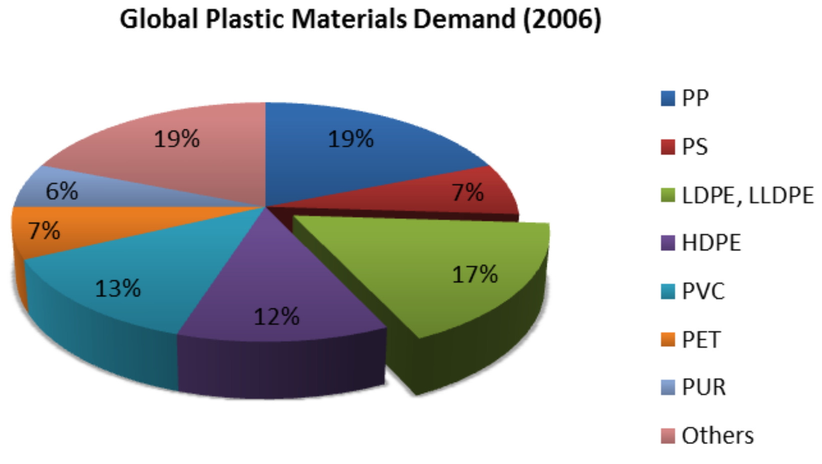

Figure 1. World Plastic Materials Demand [1]

Even though the increasing demand for polymeric materials are generating billions of dollars globally, as these materials are taking over conventional construction materials; application of polymeric materials has raised questions regarding their fire hazard. One of the major drawbacks of plastic materials is that they are highly flammable and they decompose easily in fire conditions. According to the National Fire Protection Association (NFPA) US fire statistics, thermoplastics are responsible for 29400 fire incidents, which have resulted in 280 causalities, 1160 injuries and property damage as high as 0.7 billion dollars. Ahrens also claimed that in a household fire the first item to be ignited is more likely to be polymeric materials [2]. According to Ahrens, the number of deaths due to fire is decreasing since 1980s to present day. This could be the result of strong legislations and emphasizing on research programs to develop new processes and technologies to increase the flame retardant performance of polymeric materials.

Thermoplastics could be classified into three major types. They are commodity and engineering plastics, specialty plastics and research plastics. Lyon et al. has listed these plastics according to their costs and related fire hazard [3, 4]. Research and specialty plastics are inherently flame retardant, but these plastics are not cost effective. Whereas commodity and engineering plastics such as PP, PMMA, PS, PE, NYLON 66, PVC etc. are highly flammable but their production cost is much lower than that of specialty and research plastics. Incorporation of flame retardants with polymers could be useful as they reduce the flammability of polymers. Flame retardant additives are chemical compounds which are added into the polymeric matrix either by blending or by chemical reaction with the polymer. The major advantage of using flame retardant additives is that they enhance the fire properties of the polymers. Global demand for fire retardant materials is increasing in accordance with plastic production. According to a market study carried out by Ceresana Consulting group, global demand for fire retardant materials at 2013 was 2 million metric tons, of which 28% of the FR was consumed in North America alone [5] . Construction sector is the major field where FR are most used with polymers. Recent boom in electronics industries has increased the demand for FR materials, especially in Asia pacific zone. Countries like China, Japan and India are leading manufacturing businesses. It has been reported that global market for FR materials is increasing by 5% annually and the predicted revenue from this sector will be 7.15 billion us dollars. Many commercial FR based on aluminum hydroxide (ATH), organo-phosphorous, halogenated etc. are widely used today. Halogen and phosphorous based FRs are proven old technology. Global consumption (% of total volume of production) of various FR could be depicted from figure 2.

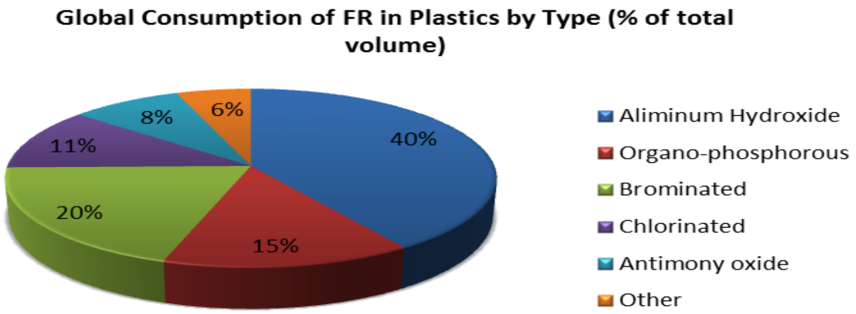

Figure 2. Global Consumption of Fire Retardants by Types

History of using flame retardant materials goes back to early stage of 1900s. Halogenated and phosphorous based fire retardants are old technology. Mechanism of these two types of polymers is well known and could be found in published literature. To understand how flame retardant materials work, basic idea about thermal decomposition of polymer material is required. Mechanisms for thermal decomposition of polymers and flame retardant action are explained extensively in many literatures [6]. In this study, chemical and physical processes of thermal decomposition of polymeric materials have been discussed, followed by the fundamentals of flame retardant materials. Morgan et al. classified all the flame retardants into three types. They are gas phase flame retardants, endothermic flame retardants and char forming flame retardants [7]. Morgan also identified the six major flame retardants e.g. halogenated FR, phosphorous based FR, mineral filler FR, intumescent flame retardant (IFR), inorganic FR and nanocomposites. Detailed mechanisms of the mentioned FR's mode of action could be found elsewhere.

Halogen based flame retardants have been widely used as flame retardant materials. Major disadvantage for using halogenated FR is that they generate toxic vapor which are not environment friendly. Thus, other flame retardant which do not have adverse effect on environment and human exposure, are replacing halogen based FRs. Nanofillers are the newest technology which was first introduced during early 1970s; could be a prospective solution to replace halogen based fire retardants. Flame retardant polymer nanocomposites reduce the flammability of virgin polymer significantly. The fire performance of the polymers could be enhanced even more by using nanofillers along with traditional, commercial or modified flame retardants. Besides, to achieve the same level of PHRR reduction, the amount of commercial FR required is much less when they are used along with nano fillers. This is why research field in polymer nanocomposite is dynamic.

This paper is to study the fire performance of different type of flame retardants and to find out the best formulations of flame retardant polymer nanocomposites which lead to maximum reduction of peak heat release rate (PHRR). Cone calorimeter test results have been recorded from different peer reviewed journal papers to evaluate polymer nanocomposites' fire performance. Polymers of interest are PMMA, PS, PP and PE. Andrady studied the applications and societal benefits of polymers (aka plastics) [1]. The author mentioned that the selected four polymers are the most widely produced and consumed polymers in the world. These four polymers meet more than 60% of the global demand for plastics. Especially, PE meets 29% of the total demand for polymeric materials. Since 1970s researchers from different countries started testing fire performances of these polymers after incorporating flame retardant materials into the polymer matrix.

PHRR is considered as the most significant parameter in evaluation of fire performance of polymers. Polymer with high heat release rate possess greater fire hazard. Interestingly, for polymer nanocomposites, the PHRR is significantly less than that of the virgin polymer. Though, nano particles cannot help extinguish the fire, but rather it delays the process. Propagation of fire is slowed down due to reduced heat release rate from the polymers. Nanocomposite polymers show no tendency for dripping and produce less smoke than pure polymer. These positive features could be a life saver. Delayed fire growth helps fire safety equipment to activate at early stage and fire fighters would get enough time to control the fire scenario. Ignition time is another important parameter in fire performance evaluation. When a polymer is heated, the polymer chain breaks up to produce volatile flammable products. These vapor products start to burn in presence of oxygen when they reach their lower flammability limit (LFL). The time it takes to start an ignition over polymer surface is termed as ignition time (T_{ig}). Generally, decrease in ignition time of polymer nanocomposites is observed from the original value. This holds true for PS, PP and PE. Interestingly, ignition time often increases for PMMA. This is one of the findings which is discussed later.

To understand the research progress in the field of fire retardants so far since 1970s, a database for different nanocomposite formulations is required. Many review articles had been published, which are discussed at literature review section. All these publications mainly focus on the basic mechanisms of different types of fire retardants. Literature to show the progress in this field statistically is not available. In this paper, recent developments of this dynamic field of research is presented by building a database for parameters including ignition time, time to PHRR , PHRR, total heat release (THR) and LOI (limiting oxygen index). Based on percentage reduction in PHRR, best formulations were identified. All polymer nanocomposites were sorted out according to their fire performance. Best compositions which could reduce PHRR for more than 80% of the original value are shown in results and discussion chapter. All the data recorded for this study are attached at appendix section.

This study would be helpful for current and future researchers interested in this field. This paper consists of literature review, basics of thermal degradation of polymers, flame retardant fundamentals and a database providing critical fire testing data for different polymer nanocomposites. Prospective researchers would get a quick glance to realize the recent developments and idea about future work scope. As, combination of FRs successfully applied in one particular polymer could be a prospective formula for other polymers. This literature overview report is unique in a sense that it not only provides a cone calorimeter data base for selected polymers, but also these data have been systematically organized for researchers to pick the best combinations of FR materials which could be investigated for other polymers.

CHAPTER II

REVIEW OF THE LITERATURE

In a recent feature article, Bourbigot (2007) discussed recent developments and opportunities in the research field of nanocomposite polymers which have improved fire performance [8]. According to this review paper, flammability of polymers could be reduced in three ways. Such as, (i) using inherently flame retardant materials (ii) chemical modification of polymers and (iii) adding flame retardants into the polymer. Difficulty in manufacturing process of inherently flame retardant polymers is reflected in their cost. Thus, application of this type of special polymers is limited to sophisticated applications (e.g. defense industry). Fire retardant type monomers could be copolymerized with the polymer to reduce the flammability of the polymer. Both inherently flame retardant polymers and chemically modified polymers have tendency for low flammability. Bourbigot also reported that these two mentioned techniques have shown great prospect, but due to high manufacturing cost the application is limited today. On the other hand, incorporation of fire retardant materials with polymers is quite popular, simply because of fewer complications in manufacturing process.

Flame retardant materials reduce the flammability of polymers by interrupting the ability of polymers to attain self-sustained combustion cycle. Details about self-sustained combustion are discussed on later chapter. This cycle is the process how polymers burn after being ignited by an external heat source and the cycle continues till an element from the fire triangle is diminished. Hirshler et al. (2008) concisely explained the chemical and physical processes involved in the thermal decomposition of polymeric materials [6]. He explained how polymer chains break down by chain-scission mechanism when heat is applied to the polymer surface. Chain-scission mechanism is significant because flammability of polymer is dependent on it. Random or end-chain scission generates more volatile vapor products than cross-linking scission mechanism. Hirschler also mentioned that, fire retardants active in condensed phase promotes cross-linked polymer chain scission, which promotes formation of carbonaceous char layer on the polymer surface exposed to external heat. There is other type of fire retardants which depletes oxygen by radical scavenging mechanism. Understanding of the thermal decomposition of the polymers is important to realize fire retardant's mode of action. General classification of fire retardants and their general mode of action in fire scenarios have been explained by G.J. van Esch (1997) [9].

Even though, flame retardant materials reduce flammability of polymers, but use of halogen based fire retardants will become obsolete in near future for environmental scrutiny. Lu et al (2002) mentioned the use of phosphorous, boron, silicon, nitrogen containing monomers could be copolymerized to make any polymer inherently flame retardant [10]. But, industries are always eager to grab the easier and cost effective solutions. Application of nanofillers as fire retardants has shown great promise. Gilman et al. (1997) reported that nanoparticles of montmorillonite (MMT) clay could significantly reduce the peak heat release rate at relatively low loading [11]. However, incorporation of MMT alone cannot improve test results of other fire testing standards and regulations (UL 94 V and LOI etc.). This problem could be solved by using nanofillers and other types of conventional fire retardant materials together. Chigwada et al. (2003) investigated the synergism between conventional flame retardants and organically-modified clays [12]. From his investigation, it was found that for 3% (wt %) loading of clay in PS, % reduction in PHRR was 57%, whereas 15% (wt%) tricresylphosphate (TCP) reduced the PHRR by only 21%. Interestingly, when 15% TCP and 3% clay were combined together with PS, the PHRR was reduced to 65% and the polymer nanocomposites passed other fire tests also. This phenomenon holds true for other polymers also.

Blumstein et al. (1965) first investigated the thermal stability of PMMA –MMT polymer nanocomposite [13, 14]. He reported that, PMMA intercalated within clay has enhanced fire performance due to chemical structure and limited thermal motion. Recently, Sahoo et al. (2007) reported that PMMA-MMT nanocomposite are biodegradable, where as pure PMMA is not. Hydrophilic nature of MMT is favorable for the growth of bacteria *B. cereus* [15]. Recently, several groups have been working relentlessly to organically modify MMT. Organically modified MMT has shown great prospects in reducing flammability [16-18]. Similar published works based on organically modified clay PS, PP and PE nanocomposites also showed a tendency of enhanced fire performance, which meets UL 94V test.

From literature review it is noted that, layered double hydroxide and intumescent flame retardants are most popular after clays. Concept of intumescence is old idea, but pioneering work by Camino et al. (1988) revitalized the idea of intumescence and applied it in polymers as fire retardant [19]. In a recent study, carried out by Lu et al. (2010) showed that flammability of PS could be reduced significantly when clay, multiwalled carbon nanotube (MWNT) or metal oxide (Fe_2O_3) nanoparticles are used with IFR. Loading amount of IFR is generally 30% (wt%), adding 2% clay with 18% IFR is capable of reducing the PHRR by 73% [20]. This feature of IFR is applied to reduce flammability for most of the polymers.

Layered double hydroxides (LDH) are hydrocalcite like compounds. These are basically anionic clays, which are inexpensive and environment friendly. When LDHs are incorporated with polymer matrix; mechanical, thermal and fire retardant properties of the polymer matrix is greatly enhanced. Thus, in last two decades researchers have investigated effect of LDHs as fire retardant material. Mg-Al LDH and Zn-Al LDH are most widely studied LDH system. Only few literatures are available for the studies featuring the effect of other LDH systems. The general formula of LDH is $[M^{2+}_{1-x}M^{3+}(OH)_2][A^{n-}_{x/n}].mH20$, where M^{2+} is a divalent metal cation (e.g Mg^{2+},Ca^{2+},Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}etc.) and M^{3+} is a trivalent cation (e.g Al^{3+}, Co^{3+}. Ni^{3+}, Fe^{3+} etc.). And A^{n-} is a charge balancing anion (NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-} etc.). Researchers have varied the cations and anions to investigate the effect on fire properties of the polymer nanocomposites. Matusinovic et al. (2013) varied the divalent metals (Zn, Mg, Ca) in a benzoic acid modified LDH to study the effects of nanodisperson in PS and PMMA polymer matrix [21]. Dispersion plays a key role in performance of fire flame retardants. Matusinovic reported that polar nature of PMMA led to well nanodispersed LDH within the polymer matrix, which is reflected by enhanced fire performance showed by all three (Zn-Al, Mg-Al, Ca-Al) LDHs. But, for non-polar polymer like PP, achieving nanodispersed LDH in PP matrix is considered to be hard. Charles et al. (2009) used PP-graft-maleic anhydride to predisperse oleate containing (organically modified) LDH; results observed were promising as PP-g-MA helps to disperse nanofillers.

Application of carbon nanotubes has also drawn attraction recently. Kashiwagi (2002) first investigated the fire performance of polypropylene carbon nanotube nanocomposites [22]. Only 2% (wt %) MWNT dispersed in PP reduced the PHRR by more than 50%. Su et al. (2004) carried out a similar work which also supports Kashiwagi’s claims. Advantage of using CNT is that their dispersion is not dependent on the polar nature of polymers plus they require less loadings than other nanofillers. Enhanced thermal stability and reduced flammability could be achieved by combining MWNT with IFR [23], functionalizing CNTs by grafting on IFR [24]. Hai-Yun Ma (2008) grafted a novel IFR containing phosphorous-nitrogen into carbon nanotubes and incorporated them in PS. He reported that functionalized CNTs have similar effects as normal CNT. Morgan et al. (2010) incorporated vapor grown carbon nanofibers (VGNCF) with PP and PE and investigated their fire performance [25]. According to the author, VGNCF could enhance fire performance by reducing PHRR, but only drawback of using VGNCF is increased smoke production.

Nano particles of metal oxides are also used to reduce flammability of polymers. Nanoparticles of titanium oxide (TiO_2), alumina (Al_2O_3), antimony oxide (Sb_2O_3), iron (ii) oxide (Fe_2O_3), cerium dioxide (CeO_2) are also known for reducing flammability. PHRR reduces greatly when these nanoparticles are used with conventional fire retardants or other nanofillers such as phosphorous based FR [26-28] , clays [29] etc.

Aim of this study is to systematically analyze the flammability reduction of polymer nanocomposites. From literature review, four major effects were observed. First, nanocomposites reduce the PHRR. When they are used alone, they cannot meet other regulatory tests. But combination of nanofillers and conventional flame retardants not only reduces the flammability but also meets other regulatory tests. Second, in most cases ignition time decreases except for PMMA. However, for PS, PP and PE nanocomposites this observation is common. Third, total heat release rate stays almost constant which explains that nanocomposites do not extinguish the fire, they just delays the burning process. And fourth, nanodispersed particles can reduce PHRR greatly. Nano dispersion depends on the polymerization process. Heat release rate reduction is considered as the most significant parameter, as it governs the fire spread. In this study, cone calorimeter data has been recorded from published papers to see if these four observations hold true for PMMA, PS, PP and PE. Previous studies have mainly focused on the recent advancements and basic mechanisms of different types of fire retardants. In this study, a database was created first by recording cone calorimeter data (e.g. ignition time, PHRR, THR, LOI if available etc.). Performance of nanofillers has been evaluated based on the percentage reduction of PHRR. On the basis of PHRR reduction, different formulations of polymer nanocomposites have been sorted out systematically to see their range distribution. Other literatures reveal the recent developments literally, in this report we not only sorted out the best nanocomposite polymers but also showed the progress graphically.

CHAPTER III

THERMAL DECOMPOSITION OF POLYMERS

3.1 Self-Sustained Combustion Cycle

Organic polymeric materials undergo both chemical and physical changes when they are exposed to sufficient heat. Thermal decomposition of polymers occurs in two major phases. Initially when heat is applied through ignition source, chemical bonds begin to break when the temperature rises above decomposition temperature. Thus the polymeric material decomposes to produce volatile combustible vapor products. In second phase of the process which is called gas phase, the volatile gaseous products generated from condensed phase burn in presence of oxygen after they reach their lower flammability limit, and thus generating more heat. A portion of the heat generated by the combustion process is reradiated to the surface of condensed phase of polymer to create more volatile products and thus combust to create a self- sustained combustion cycle, which is depicted in figure 3 [19].

External heat causes polymeric materials to go through thermal decomposition, which is a combination of chemical and physical processes. In this study, both the processes are discussed briefly to understand the mechanism of thermal decomposition of polymers and how polymers' fire properties are improved when fire retardant materials are incorporated with polymers. Details of the mechanisms could be found elsewhere [6, 19, 30].

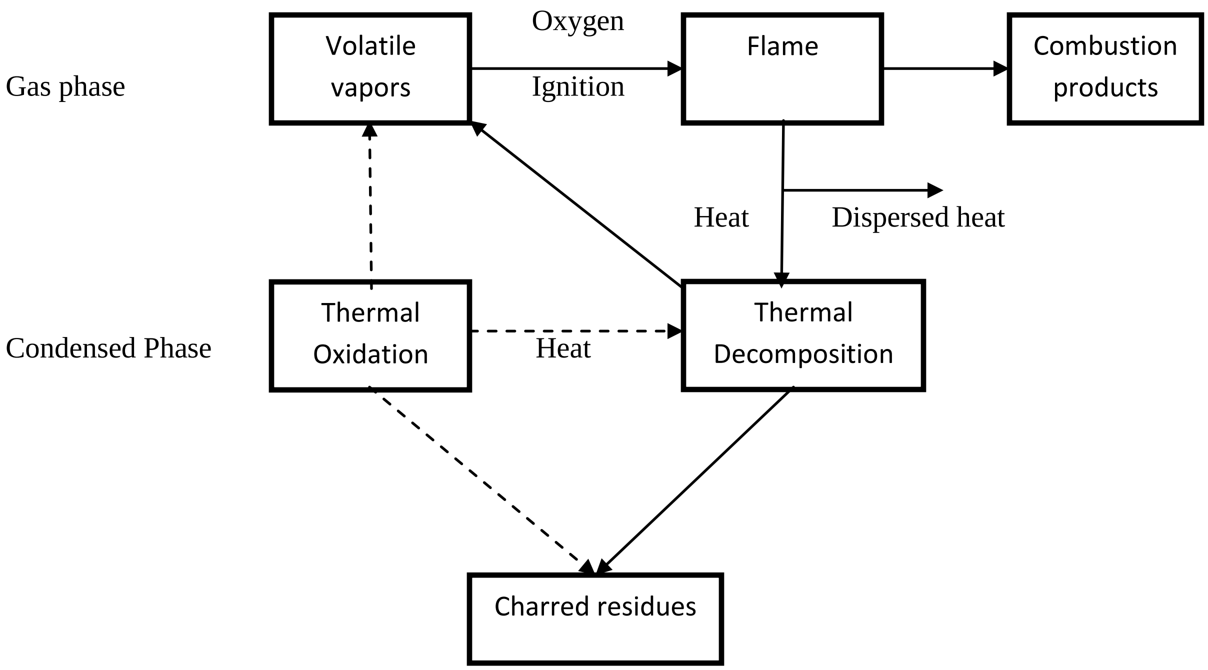

Figure 3. Self-sustained Combustion Cycle of Organic Polymers

3.2 General Chemical Breakdown Mechanisms

When sufficient heat is applied to a polymer, the chains of the polymers break down into pieces to create volatile flammable products. There are four major mechanisms in which the chemical bonds in a polymer chain is broken down. They are random-chain scission, end-chain scission, chain stripping and cross-linking. Not all the polymer decomposes in same way. Some polymers tend to follow a single chemical mechanism, but there are instances that some polymers chemical breakdown mechanism are combination of two or more mechanisms. Four major mechanisms mentioned above, is briefly explained below.

3.2.1 Chain-Scission

Chain-scission is the most common reaction mechanism observed in simple thermoplastics. In this mechanism the main polymer chain is broken down randomly (random chain-scission) or at the end (end-chain scisson), but either way they result into creating monomers or oligomers.

Oligomers are polymer units consisting of ten or fewer monomer units.This mechanism is also known as ‘unzipping’. Generally the polymers which undergo chain-scission have poor fire performance as they generate small flammable vapor products. As these small parts (monomers or oligomers) could easily ignite the solid polymer.

3.2.2 Chain Stripping

In chain stripping process atoms or side chains are stripped from the main chain of polymers by substiteuents (generally from the main chain) to form small molecules. The bond between side chain to the main polymer chain is broken, and the ripped off side groups often react with each other to form cyclic structure. This process may help to lead char formation, as the new groups formed are richer in carbon. But, if the stripped off groups are flammable then the fire performance of the polymer is likely to be poor.

3.2.3 Cross Linking

Cross linking occurs after atoms or side chains are striiped off, two adjacent main chain creates bond to form a longer polymer chain which is riicher in carbon. This mechanism is critical in char formation, hence improving fire performance of the polymeric material.

3.3 General Physical Changes During Decomposition Of Polymers

Heating of a polymeric material may have varied effects as the physical cange is dependent on the type of the polymer. Physical changes have great impact in chemical decomposition processes. Thermoplastics generally go through melting or glass transition whereas thermosetting materials involve charring and water desorption. Significant physical changes and their impact is explained below.

3.3.1 Melting and Glass Transition

In presence of external heat, thermoplastic materials generally transform from glass or solid state to the fluid state. In this transformation the material may drip and (or) flow. From the view point of fire safety this phenomena is complicate since it has its pros and cons. In some cases, flowing of material away from the heat source could hinder the fire growth. But if the polymer drips downwards, it may act as secondary fire source which could ignite surrounding materials. Materials which flows towards the heat source just worsens the fire scenerio. For example, polyethylene melts and flows easily when exposed to fire but PMMA hardly flows under fire conditions. Several techniques are applied to increase the melting temperature of the polymers. It has been observed that increase in crystallinity of the polymer increases the interactions between the polymer chains which provides extra forces to hinder the transformation to fluid state. Cross linking of polymer chains could also increase the melting temperature. Cross links are useful in a sense that they create carbon rich polymer chain instead of reducing into small volatile monomers (created by chain-scission). Thus fire retardant chemists prefer cross-linking to increase the fire performance of the polymers.

3.3.2 Charring

Chars are created by chemical processes, but its physical properties have great impact on fire performance. Char act as barriers as it hinders the transport of volatile compounds through it during the thermal decomposition of polymers. It also acts as a barrier between the flame and the virgin polymer beneath the char. Only disadvantage of the char is that it may act like a sustained source of soldering combustion.

CHAPTER IV

MECHANISMS OF FIRE RETARDANCE OF POLYMER CONTAINING FLAME RETARDANTS

Organic polymeric materials undergo thermal decomposition when external heat is applied. Applied heat initiates the breaking of bonds of polymer chains into smaller volatile flammable products. These products create flame in presence of oxygen and generate heat, a part of which is transferred back to the polymer to generate even more volatile products. This is known as self-sustained combustion cycle which has been discussed earlier. Fire retardants help to break this cycle by hindering chemical or physical processes of thermal decomposition. There are several ways both physical and chemical which can achieve this purpose. Troitzsch et al. have explained the general mechanism of chemical and physical action of fire retardants action [31].

Preheating, decomposition, ignition and combustion are the major four processes involved in polymer flammability. Firstly, the polymeric material has to be heated sufficiently by an external heat source so that the polymer degradation occurs. This weakens the chemical bonds of polymer resulting into breaking of bonds eventually and creating vapor combustion products. The gaseous vapor products create flame and start supplying heat back to the polymer when they reach lower flammability limit. The combustion process is controlled by many variables such as rate of heat generation, rate of heat transfer, decomposition rate and surface area of the polymer. Flame retardants interfere chemically or physically to eliminate these variables to hinder combustion, even extinguishing fire. The physical and chemical action of flame retardants are briefly described below.

4.1 Physical Action of Flame Retardants

There are three major ways identified by which flame retardants affects combustion process. They are as followings

a. **Cooling**

 In presence of heat, some flame retardants start to degrade and go through endothermic decomposition which cools down the substrate to a temperature lower than that required to sustain combustion process. For example, aluminum trihydroxide (ATH) follows this mode of action.

b. **Dilution:**

 Inert substances are added to the polymer which releases inert gases to dilute the flammable vapor products and keep the composition under required lower flammability limit.

c. **Formation of Protective Layer**

 The virgin polymer could be protected by a protective layer of chars or gaseous phase. This layer acts as a barrier which hinders diffusion of vapor products through it, thus reducing fuel supply. This layer also acts as insulator which decreases the reradiated heat supply. Thus virgin polymer beneath the protective layer is cooled, oxygen required for combustion process is reduced and reduction of heat supply leads to breaking down the fire triangle.

4.2 Chemical Action of the Flame Retardants

Reactions in condensed and gas phase are the two main chemical reactions by which combustion process is hampered. They are briefly discussed below.

a. **Reaction in Condensed Phase**

In this mechanism polymer is broken down in a way so that it melts like a liquid and flows away from the heat source (flame). Secondly, the flame retardant causes to generate char layers or intumescence. Intumescent fire retardants (IFR) have blowing agents which swells the contact surface which produces better insulating protective late. Details about IFRs are discussed later.

b. **Reaction in Gas Phase**

In gas phase mechanism, radical mechanism of the combustion process is intervened by the flame retardant or their degraded products to stop the exothermic combustion process. For example, mechanism of $Al(OH)_3$ or ATH's mechanism could be explained. When heated at 180-200◦ C, ATH decomposes to Al_2O_3 and generates vapor, which dilutes O2 and vapor helps to cool down the heat.

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O;\ \Delta H = +1.3\ KJg^{-1}$

H and OH radicals are the most reactive propagating species. H radical reacts with O_2 to create OH and O radicals. This way it dilutes the concentration of O_2.

$H\circ + O_2 \rightarrow OH\circ + O\circ$

CO then reacts with OH radical to create CO_2

$CO + OH\circ \rightarrow CO_2 + H\circ$

4.3 Different Types of Flame Retardants and their Mode of Action

4.3.1 Halogenated Flame Retardants

Halogenated flame retardants have been widely used since 1930s. Like their name suggests, these FR consists of F, Cl, Br and I based compounds. According to Grand et al. Organohalogenated compounds are most effective FR in this class [32]. Organochlorine and organobromine compounds are most popular FR of this class. C-Br bond is stable enough that it will not break in ambient conditions but unstable enough to break down under fire conditions releasing bromine radical to inhibit the combustion process in gas phase. These FR are often used with synergists e.g. Sb_2O_3 (antimony oxide), zinc borate or phosphorous based compounds etc. these synergists make halogens more effective in gas phase. Mechanism of bromine based FR is shown below.

H and OH radicals are highly reactive. They react to produce H2O, which is an exothermic reaction. Halogen based compounds breakdown into radicals and react with these H and OH radicals, substituting them by less reactive halogen radicals. Besides the halogen acid could be regenerated by hydrogen transfer reaction. Halogen acids then react with OH radical to generate water vapor and thus cooling down the heat.

- $H^\circ + O_2 \rightarrow OH^\circ + O^\circ$
  $H^\circ + OH^\circ \rightarrow H_2O$
  $CO + OH^\circ \rightarrow CO_2 + H^\circ$
- $R\text{-}Br \rightarrow R^\circ + Br^\circ$
  $Br^\circ + R\text{-}H \rightarrow HBr + R^\circ$
  $H^\circ + Br^\circ \rightarrow HBr$
- $OH^\circ + HBr \rightarrow H_2O + Br^\circ$
  $H^\circ + HBr \rightarrow H_2 + Br^\circ$
- $SbBr_3 + 3H^\circ \rightarrow Sb + 3HBr$
  $Sb + OH^\circ \rightarrow SbOH$
  $SbOH + OH^\circ \rightarrow SbO + H_2O$

There are advantages and disadvantages of using halogen based fire retardants. Major advantage of this technology that it is a proven cost effective technologies. There are many available halogen based fire retardants are available which are used widely. However, researchers are trying to replace this class of fire retardants since they release corrosive gases during burning process.

4.3.2 Phosphorous Based Flame Retardants

Phosphorous based FR contains phosphorous like its' name suggests. This is also an old and widely used technology like halogen based FR. Examples of this class of Fr are bisphenol diphosphate, resorcinol diphosphate, triphenyl phosphate, ammonium polyphosphate (APP), phosphate salts etc. Phosphorous cannot be directly incorporated with polymers. Since, creating direct carbon-phosphorus bonds could be expensive. Thus to limit the cost phosphorous based FR phosphorous is attached to oxygen which is generally attached to some organic compound. Red phosphorus is also used as FR materials in polystyrene [33], interestingly white phosphorous cannot be used since it is pyrophoric.

Phosphorous compounds could work as both gas phase and condensed phase flame retardants. Generally they are combined with other fire retardant additives to promote char formation. Mechanism reactions are shown below.

- $P_4 + 2O_2 \rightarrow 4PO^\circ$
- $H_3PO_4 \rightarrow HPO_2 + HPO + PO^\circ$
- $H^\circ + PO^\circ \rightarrow HPO$
- $H^\circ + HPO \rightarrow H_2 + PO^\circ$
- $2OH^\circ + PO^\circ \rightarrow HPO + H_2O$
- $OH^\circ + H_2 + PO^\circ \rightarrow HPO + H_2O$

This mechanism is similar to halogen based flame retardants. Hastie et al. had suggested that phosphorous is oxidized to PO to eliminate oxygen [34, 35]. Phosphorous based fire retardants are also widely used like halogenated FR. Less loading amount requirement and performance in higher heat flux makes them very effective, especially when they are combined with other fire retardants to form char layer. However, they have drawbacks also. As they also generate corrosive gas, they are under environmental scrutiny.

4.3.3 Mineral Filler Flame Retardant

Mineral fillers have been used as fire retardants since 1920s. The common mineral fillers are metal hydroxides or metal carbonate. For example, aluminum hydroxide, magnesium hydroxide, hydromagnesite etc. When exposed to fire conditions, mineral fillers undergo endothermic decomposition, which cools down the condensed phase. As a result, thermal decomposition of polymer is slowed down. Besides, when mineral filler decompose, they generate water vapor which dilutes the fuel available in gas phase. Moreover, the decomposition products of mineral filler (generally metal oxide) are non-flammable. Thus the residue left behind dilute the polymer fuel (solid phase) available for further burning. Aluminum hydroxide is also known as aluminum tri hydrate (ATH). Aluminum hydroxide decomposes at 180-200◦ C to produce alumina and water vapor.

$2Al(OH)_3 + \text{Heat} \rightarrow Al_2O_3 + 3\ H_2O\ (g) \uparrow$

$Al_2O_3.3H_2O\ (\text{ATH}) + \text{Heat} \rightarrow Al_2O_3 + 3\ H_2O\ (g) \uparrow$

Similarly, when heat is applied to a magnesium hydroxide incorporated polymer. Magnesium hydroxide decomposes at 300-320◦ C to produce magnesium oxide and water vapor.

$Mg(OH)_2 + \text{Heat} \rightarrow MgO + H_2O\ (g) \uparrow$

Hydromagnesite is mineral filler which contains magnesium carbonate. It also decomposes at lower temperature to produce water vapor and CO_2.

$3MgCO_3.Mg(OH)_2.3H_2O + \text{Heat}\ (220\text{-}240^\circ\ C) \rightarrow Mg_4(CO_3)_3(OH)_2 + 3H_2O\ (g) \uparrow$

$Mg_4(CO_3)_3(OH)_2$ + Heat (300-350◦ C) → $4MgO + 3CO_2$ (g)↑+H_2O (g)↑

Mineral fillers are environmentally friendly. They do not produce corrosive gas like halogen and phosphorous based fire retardants. They could be useful to reduce smoke when combined with other fire retardants. One of the major drawbacks of mineral filler is that they cannot fully extinguish the fire; they can only delay the process. Once all the miner fillers are consumed, they leave behind metal oxide. This layer does not work like protective char layer. Another drawback is requirement of high loading (50-70%) to achieve significant fire performance. This affects the mechanical properties of the polymer.

4.3.4 Inorganic Flame Retardant

Inorganic flame retardants cover wide range of chemical structures. Metal hydroxides are widely used commercially as inorganic flame retardant. Generally inorganic flame retardants cannot reduce the peak heat release rate significantly, but they are often used as synergists which help other fire retardants to work better. Antimony trioxide (Sb_2O_3) and lanthanum trioxide (La_2O_3) are used with halogen based fire retardants; incorporation of these metal oxides can reduce smoke production and suppress afterglow. Antimony oxides and antimonates are converted to volatile species by halogen acids at fire conditions. The halogen acid reacts with antimony to antimony trihalide (SbX_3). Where X is halogen, usually chlorine, bromine etc. antimony trihalide then reacts with H radical to form antimony, which later reacts with OH radical to antimony oxide and water vapor. This mechanism is shown below.

- $SbBr_3 + 3H^{\circ} \rightarrow Sb + 3HBr$

  $Sb + OH^{\circ} \rightarrow SbOH$

  $SbOH + OH^{\circ} \rightarrow SbO + H_2O$

Antimony trioxide is widely used as, this works in both condensed and gas phase. The substrate of antimony oxide promotes char formation in condensed phase and antimony halides and halide oxides create an inert gas barrier over the char to hinder oxygen transport, thus preventing flame spread. Zinc borates (2 $ZnO.3B_2O_3.3.5H_2O$) are capable of afterglow suppression. Zinc stannate and zinc hydroxyl stannates are used to reduce smoke generation. Among other inorganic fire retardants, molybdenum disulfide, titanium oxide, silica and zirconium based oxides have recently drawn attraction of researchers. As mentioned earlier that this class of FR helps other FR to work better by promoting char formation, smoke reduction, afterglow suppression. But, these FR additives are expensive.

4.3.5 Intumescent Fire Retardants

Intumescence is an old technology which's potential application in paint industries was first demonstrated by Vandersall during 1970s [36]. Since phosphorous and halogen based fire retardants are not environment friendly, concept of applying intumescence in polymers to improve their fire performance was first investigated by Camino et al. [19]. Intumescent fire retardant forms carbonaceous char at fire conditions and this char layer swells to provide better insulation. Intumescent flame retardant consists of three major chemical compounds. They are as followings

- Inorganic acid source: inorganic acid source forms acid when the polymer is heated to 100-250◦C. Inorganic acid initiates carbon source to cross-link between polymer chains or carbon source to form a protective carbonaceous char.
- Carbon source (Polyhydric compounds)
- Blowing agent: blowing agents release gases which make carbonaceous char to swell and form foam.

Bourbigot et al. summarized the sequences of events which take place when IFRs are exposed to heat [8]. They are as followings

- Release of inorganic acid between 150-215◦C.

- Esterification of carbon source compound at temperature slightly above acid release temperature.
- Melting of mixtures prior to or during the esterification.
- Formation of carbon-inorganic substrate due to decomposition of esters.
- Released gas from blowing agent cause the carbonaceous char to foam.
- Carbonaceous foam gels and solidifies near the end of the reactions.

Examples of components of IFR systems are listed in table 1.

Table 1: Examples of components of IFR systems [36]

(a) Inorganic acid source	**(b) Polyhydric compounds**
Phosphoric	Starch
Sulfuric	Dextrins
Boric	Sorbitol, mannitol
Ammonium salts	Pentaerythritol (PER), monomer, dimer, trimer
Phosphates, polyphosphates	Phenol-formaldehyde resins
Borates, polyborates	Char forming polymers (PA-6, PA-6/clay etc)
Sulfates	
Halides	
Phosphates of amine or amide	
Melamine phosphate	**(c) Blowing agents**
Products of reaction of ammonia with P_2O_5	Urea
Organophosphorous compounds	Urea formaldehyde resins
Tricresyl phosphate	Dicyandiamide
Alkyl phosphates	Melamine
Haloalkyl phosphates	Polyamides

4.3.6 Polymer Nanocomposites

Incorporation of nanofillers into polymer matrix to form polymer nanocomposite is the latest concept of reducing the flammability of polymers. Polymer nanocomposites are different than regular polymer matrix is that, nanofillers such as clays, LDHs, nanoparticles of TiO2, silica, carbon nanotube (CNT), multi walled carbon nanotube (MWNT) and polyhedral silsesquioxanes (POSS) are filled into polymer matrix. Nanoparticles have wide application and research area in this sector is very dynamic. Gilman et al. first reported the application of nanodispersed montmorillonite (MMT) with polymers significantly reduces the peak heat release rate [11, 37]. This observation drew other researchers' attention. Since then, nanocomposites had been incorporated with various polymers. Nanofillers basically work in condensed phase. Typically they can reduce the peak heat release rate by 40-70%, but in some cases the polymer fails to meet UL94 and LOI test. When polymer nanocomposite is exposed to external heat, the nanofillers tend to form a protective barrier on the surface of the polymer. This char layer acts like barrier between reradiated heat generated from the flame and hinders mass transfer of decomposed polymers to the flaming zone. This is shown in figure 5. Formation of carbon rich char layer slows down the mass loss rate caused by thermal decomposition, but does not stop the burning process. Char layer just helps to delay the burning process; this is why the amount of total heat release is constant. Another, noticeable observation was that time of ignition decreases when compared to virgin polymer. But, significant reduction in PHRR overwhelms this reduction in time of ignition, since HRR is the most significant parameter when considering fire performance of a material. Costache et al. investigated the fire properties of polystyrene nanocomposite filled with organically modified clay, Zn-Al layered double hydroxide and carbon nanotubes (CNT) [38]. Costache reported that for 5 wt% loading of clay, LDH and CNT the percentage reduction in PHRR was 60, 35 and 58% respectively. Time to ignition also decreased for all the nanofillers. This could be depicted from figure 4.

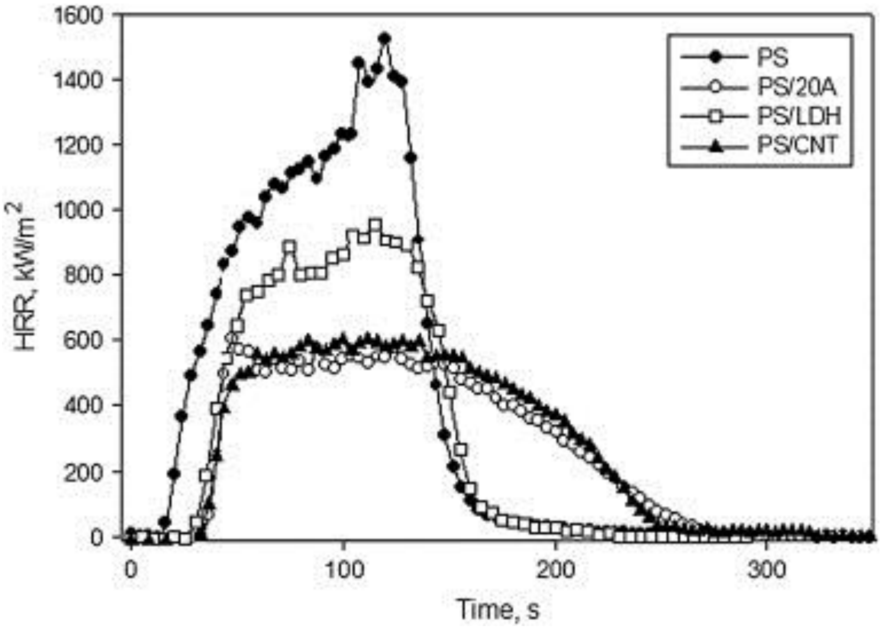

Figure 4. HRR curves for PS and its nanocomposites [38]

Even though, polymer nanocomposite is less flammable compared to its virgin state; the nanofillers often fail to meet other regulatory tests. Incorporating nanofillers with conventional fire retardants solve this issue. Not only, it improves the fire performance of the polymer, but also it helps to meet other regulatory tests' requirements. Besides, nanofillers reduce the required loading to achieve higher level of reduction in PHRR. Purpose of this study is to find the best formulations of nanofillers and conventional fire retardants which would reduce the PHRR to the maximum and discuss the possibilities of using these formulations for other polymers.

Nanofiller incorporation into polymer matrix could be done in various ways. Two of the most common processes are: (i) melt blending the nanofillers with the polymer chips to form polymer matrix and (ii) bulk polymerization of nanofillers with monomers. Generally, in melt blending process nanofillers are not well dispersed, thus they could be termed as microcomposite. Well dispersion is achieved via in situ bulk polymerization process. Now, one may ask if the degree of dispersion has any effect on flammability of polymers. Researchers had observed that, reduction in PHRR is significantly greater in a composite where nanofillers are well dispersed within the polymer matrix. Generally, polymer formed by melt blending is microcomposite whereas in bulk polymerization process nanofillers are nanodispersed. Higher the degree of dispersion, more effective is the polymer nanocomposite. This observation holds true for polymers e.g. PMMA, PS, PP and PE which are reported extensively in literature [39-42]. Thus, PHRR data obtained from cone calorimeter test could be used as the implication of the dispersion of nanofillers [43].

Now one could ask how carbonaceous char is formed during the burning process of polymer nanocomposite. Kashiwagi et al. first investigated the mechanism of char formation in polyamide-6 (PA-6) nanocomposite [44]. He suggested that accumulation of well dispersed nano clay particles accumulates to form a protective barrier. Two possible mechanisms were speculated. First, when polymer goes through thermal decomposition, polymer chain breaks up and undergoes pyrolysis; but, clay particles are left behind. Eventually, these left out clay particles stack up and form a protective layer. Another probable mechanism is that polymer chains break up to create bubbles of volatile products; these bubbles transport the nano clay particles to the surface of the polymer and when they burst, they create enough force to stack up the nano clay particles. CNT and POSS based polymer nanocomposites also follow the similar mechanism [45, 46].

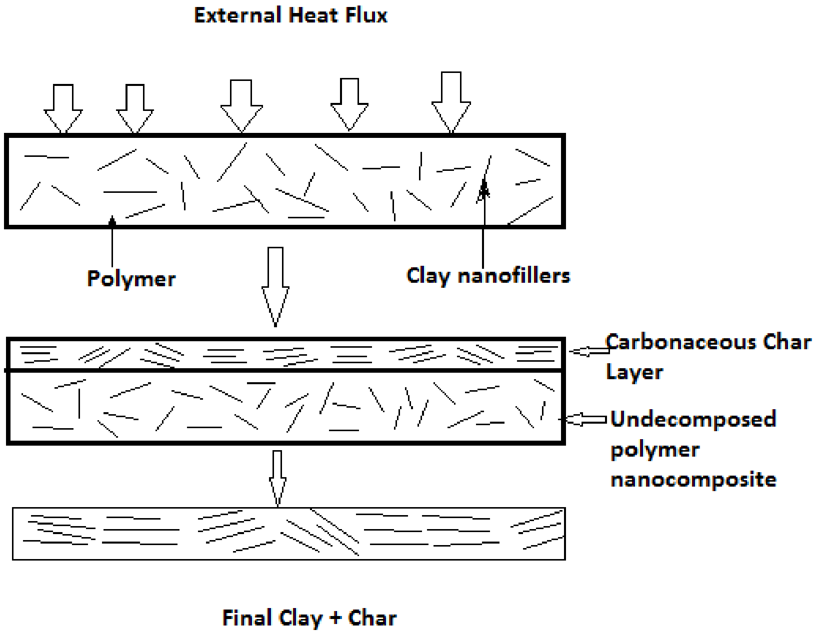

Figure 5. Char Formation in Nanocomposite Polymer [7]

CHAPTER V

BASICS OF CONE CALORIMETER

Cone calorimeter is the most widely accepted bench scale instrument in fire testing of materials. Basics of a cone calorimeter are briefly discussed in this section. Details of the working principle, parts description, performing experiments and calibration process could be found elsewhere [47-50]. Working principle of cone calorimeter, basic function of different parts of the cone calorimeter and important parameters measured by the device is discussed.

Almost all the research groups interested in fire safety carry out the bench scale fire testing (in order to measure the heat release rate) of the material of interest. Cone calorimeter tests are adopted by International Organization for Standardization (ISO 5660-1) for measuring heat release rate. Hugget et al. reported that almost all the fuels generate 13.1 MJ of heat per kilogram (Kg) of O_2 consumption [49]. He also reported that, HRR increases proportionally with increase in O_2 consumption by the fuel. Cone calorimeter utilizes this phenomenon by measuring the composition of exhaust gas during the burning of the material. An oxygen analyzer measures the oxygen concentration and correlates it to HRR. Other than measuring heat release rate by the fuel, it also measures important parameters utilized for fire modelling, prediction of fire behavior in reality. These parameters are time to ignition, mass loss of the sample, smoke amounts, total heat release, exhaust gas composition etc.

5.1 General Description of Cone Calorimeter

A typical cone calorimeter consists of different parts, sensors, gas analyzers to plot heat release, mass loss, gas flow and composition against time. Figure 6 shows the typical schematic diagram of a cone calorimeter.

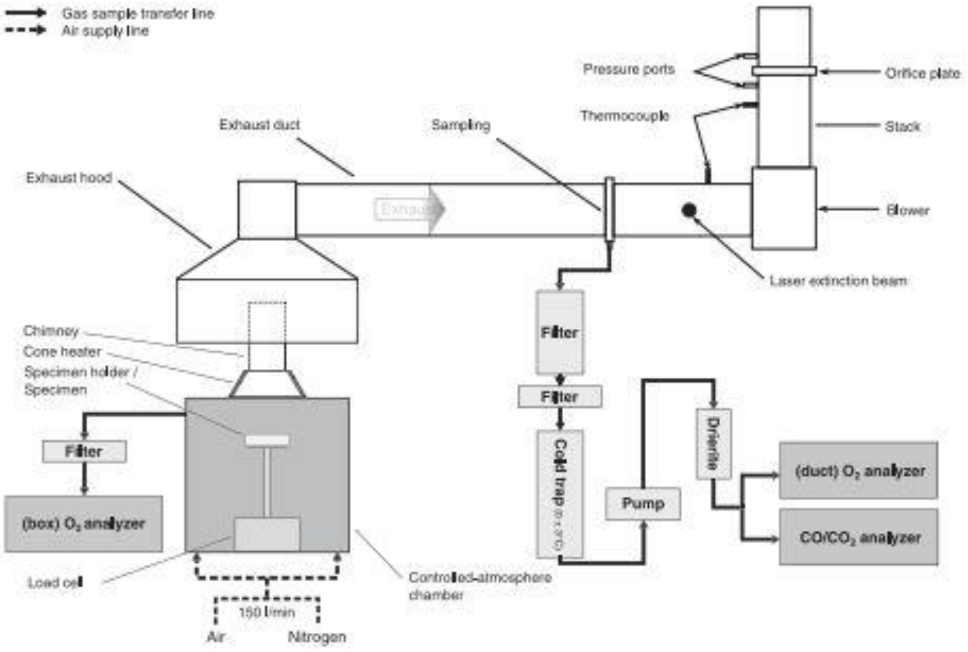

Figure 6. Schematic diagram of a cone calorimeter [51]

Generally a sample size of 100x100 mm^2 with maximum thickness of 50 mm is placed on a metal holder. Sample holder is placed on a load cell, which logs the weight of the sample during the testing period. Usually, the sample is covered by aluminum foil paper on all sides except the surface which is exposed to the heater. Major part of the cone calorimeter is the conical shape heater. A 3 m long heating wire packed in magnesium oxide refractory is winded within the cone. This cone heater radiates heat on the sample surface. Generally, the heat flux is set to 35, 50 or 90 KW/m^2 to reflect different fire scenarios. Sample is initially heated and ignited by a spark igniter, which is placed right above the sample surface. After the whole sample surface catches fire, the igniter is turned off and taken off from the sample surface. Flue gas generated by combustion process is collected by an exhaust hood. A blower is used to remove the exhaust gas. Speed of the blower is controlled to fix the exhaust gas flow rate. Stack of the exhaust duct contains orifice plate along with two differential pressure ports to measure the gas flow rate and a thermo couple to measure temperature. Flue gas is sampled by a sampling ring before it is sent to the blower. To ensure accuracy of the gas analyzers, solid particles are removed by filters and entrained water vapor is removed by a cold trap and drying agent. Then the particle free dried gas is sent to O_2 and CO/CO_2 gas analyzers.

Heat release rate is calculated by the following equation [51]:

$$\dot{q} = (13.1 * 10^3) * 1.10\ C\ \frac{(0.2095 - X_{O_2})}{(1.105 - 1.5 X_{O_2})} \qquad (1)$$

$$\dot{m}_e = C\sqrt{\frac{\Delta p}{T_e}} \qquad (2)$$

Where,

$\dot{q}$ = heat release rate (KW)

C = orifice plate coefficient ($kg^{0.5}m^{0.5}K^{0.5}$)

$\dot{m}_e$ = mass flow rate of exhaust gas (kg/s)

T_e = temperature at the orifice plate (K)

Δp = pressure drop across the orifice plate (Pa)

X_{O_2}= mole fraction of O_2 in the exhaust air

Total heat release could be calculated by integrating the heat release rate over the entire time period. This is shown in equation.

$$THR = \int_0^{\infty} Q(t)dt \tag{3}$$

Lindholm et al. reported that the results obtained from a cone calorimeter, can be used for several purposes. For example,

- Fire growth modelling
- Simulating real scale fire behavior
- Ranking of products on basis of their fire performance
- Pass/ fail test for newly developed materials or composites

Fire performance of polymers depends on various factors. Such as, ignitability, ease of extinction, heat release, smoke obscuration and smoke toxicity [30]. Among these factors, heat release rate is the most significant parameter which can answer how big the fire is. Fire spread depends on the heat release rate of the burning material. If the heat release rate is high enough then nearby materials could also catch fire. This is why researchers look into the reduction of peak heat release rate when they perform fire testing of a material using a cone calorimeter.

5.2 Methodology for Comparison of Fire Performance of Polymer Nanocomposites

Cone calorimeter is used worldwide to determine the fire performance of polymeric materials. Major cone calorimeter data are ignition time (T_{ig}), time to PHRR (T_{PHRR}), PHRR, and THR. Other than that, LOI are also determined. These data were collected for the four polymers of interest. In combined more than 110 peers reviewed journal articles were studied to collect these data. In this study, primary focus is paid on recording ignition time and PHRR for different compositions of polymer nanocomposites at different applied heat fluxes (mainly at 35 and 50 KW/m^2). Percentage increase in ignition time and percentage decrease of PHRR was calculated to see the performance of FR polymer nanocomposites. These parameters could be expresses by following equations 4 and 5.

$$\% \, Increase \, of \, Ignition \, Time = \frac{(Ignition \, time \, of \, composite - Ignition \, time \, of \, pure \, polymer) * 100\%}{Ignition \, time \, of \, pure \, polymer} \quad (4)$$

$$\% \, Reduction \, of \, PHRR = \frac{(PHRR \, of \, composite - PHRR \, of \, pure \, polymer) * 100\%}{PHRR \, of \, pure \, polymer} \quad (5)$$

Among all the parameters obtained from cone calorimeter test, PHRR is considered as the most significant parameter which controls the flame propagation of fire [52]. % reduction of PHRR is calculated for all the compositions of FR polymer nanocomposites. To systematically analyze these obtained data, following steps were taken:

- Formulations were arranged in different ranges of % reduction of PHRR. In this study only the formulations which reduce PHRR more than 80% are listed.
- Ignition time normally decreases when FR nanocomposites are used in polymer. To see this phenomena % increase of Ignition time is calculated. A negative value denotes the decrease in ignition time.
- Ranges of % reduction of PHRR of various groups of FRs and their combinations are determined for individual polymers.

CHAPTER VI

RESULTS AND DISCUSIONS

6.1 Systematic Analysis of Flammability Reduction of PMMA Nanocomposite

From literature review it is noted that clays, LDH (layered double hydroxides), phosphates, metal hydroxides, metal oxides are mainly used as fire retardants in PMMA. Impact of MMT (montmorillonite) clay as nanofiller FR is extensively studied for different polymers. Sahoo et al. directly incorporated MMT into PMMA to test its fire performance. Maximum 30% reduction in PHRR was reported for 15% clay loading at an applied flux of 35 KW/m^2 [15]. When the inorganic Na^+ or Ca^+ ions in MMT are exchanged by organic cations using quarter nary ammonium or phosphonium anions, the modified clay requires less loading to achieve the same level of % reduction of PHRR for PMMA [16, 53]. Organically modified MMT not only requires lesser loading, but they can reduce the PHRR as much as 55% [29, 54]. Effects of various LDHs (either normal or organically modified) are also investigated by many researchers [21, 41, 55-57]. These LDHs can reduce the PHRR from 10% to as high as 50%. Metal oxides such as alumina (Al_2O_3), titanium oxide (TiO_2) and bohemite (AlOOH) require similar loading as clays. For 5% loading, reduction of PHRR is not significant (only 5%). But, with the increased loading to 15%, mentioned metal oxides results into higher reduction of PHRR. Alumina and titanium oxide perform better than bohemite [27, 58].Metal hydroxide such as magnesium hydroxide (MDH) and alumina tri-hydrate are commonly used flame retardant materials [59]. Only 3% MDH can reduce 33% of PHRR. According to Nyambo et al. MDH has a higher edge over metal oxides, as MDH has higher % reduction of PHRR for the same loading [56, 57]. Effect of phosphate based fire retardants in PMMA has been investigated in [26, 27, 60]. Recently, researchers are mixing different types of FRs together to achieve higher reduction of PHRR. When clays are mixed with LDHs, better fire performance is achieved from the polymer nanocomposite. Several studies had been carried out by Wang et al. to support this observation [41, 54, 61]. Similarly, combination of MDH and phosphorous containing fire retardants can improve fire performance. The best combination is reported by Si et al. which can reduce the PHRR up to 75% [18]. Combination of decabromo diphenyl ether (DB), antimony trioxide and clay (Cloisite 20A) was studied and optimum composition was found out by the authors.

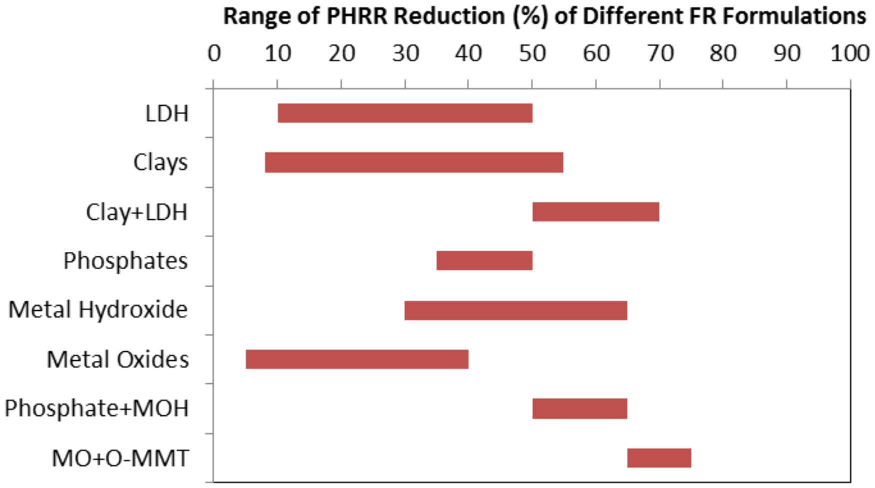

Figure 7. Range of PHRR Reduction (%) of Different FR Formulations Incorporated with PMMA

Range of PHRR reduction (%) of different fire retardants are shown in figure 7. Data for total 164 compositions of FRs have been recorded in this study. After building the database for PMMA, all the formulations were sorted out according to their range of % reduction of PHRR. In figure 8 the distribution of formulations and their range of PHRR reduction (%) is shown graphically. From figure 8, it could be depicted that highest number of formulations studied so far falls between % reductions of PHRR range of 20-30%. The trend in figure 8 follows normal distribution. There are only 6 formulations which have more than 60% PHRR reduction than virgin polymer. List of these formulations are shown in table 2.

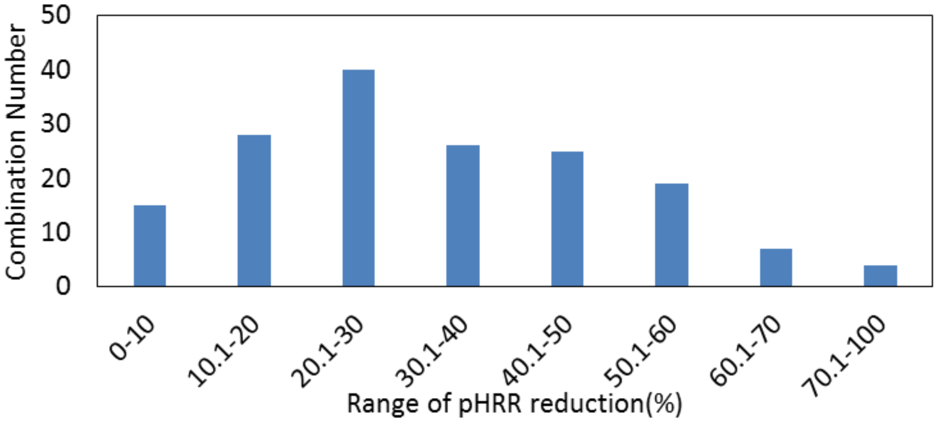

Figure 8. Distribution of Different Combinations of PMMA Nanocomposites

Table 2. List of FR Formulations Which Have % Reduction of PHRR Ranging Between 60-100%

Filler Name and Composition (wt%)	% Reduction of PHRR	% Increase in T_{ig}	Applied Heat Flux (KW/m^2)	Paper Reference
APP 10%+Sil-C8 5%	64	14	35	[26]
20% MgAl-C16 LDH	68	14	50	[57]
Sus CoPMMA+3% MMT	61	22	50	[61]
Sus CoPMMA+10% MMT	65	67	50	[61]
20% DB+5% AO	66	60	50	[18]
20% DB+5% AO+5% Cloisite 20A	75	110	50	[18]

From table 2, it is evident that combinations of different FR are effective in reducing PHRR. Cinausero has investigated the synergism on fire properties between nano-sized hydrophobic oxides (alumina and silica) and ammonium polyphosphate (APP) as flame retardant additive [26]. Applied heat flux was reported to be 35 KW/m^2. Magnesium and aluminum containing LDH was organically modified rehydration of hydrotalcite in a palmitate solution. Nyambo et al investigated fire properties of organically modified LDH (MgAl-C16) reported in [57]. Wang et al prepared copolymer of PMMA and bis [2-(methcryloyloxy) ethyl]phosphate by suspension copolymerization and investigated the fire properties of the copolymer after incorporation of LDH and MMT separately [61]. Most effective fire retardant polymer nanocomposite for PMMA is reported as 20% DB+ 5% AO +5% Cloisite 20A + 70% PMMA [17]. This polymer nanocomposite's PHRR is 75% less than that of virgin PMMA. From table 2 it could be observed that for all the listed formulations, ignition time increases from the original ignition time of pure polymer.

6.2 Systematic Analysis of Flammability Reduction of Polypropylene Nanocomposite

LDH, clays, IFR, vapor grown nano carbon fiber (VGNCF) and phosphate based fire retardants are used to limit the flammability of polypropylene. Oleate containing zinc aluminum and magnesium aluminum LDH could be useful to reduce the PHRR to 40% [62]. Most FR polypropylene nanocomposites are comprised of clays (including organically, polymerically modified) and IFRs. Different grade of clays such as cloisite, hectorite and MMT have been incorporated into PP and their fire performance test have been investigated [63-68]. According to these articles, clays have the widest range (10-68%) for % reduction of PHRR. Other than phosphate based FRs, IFRs are the most effective FR used in PP nanocomposite.

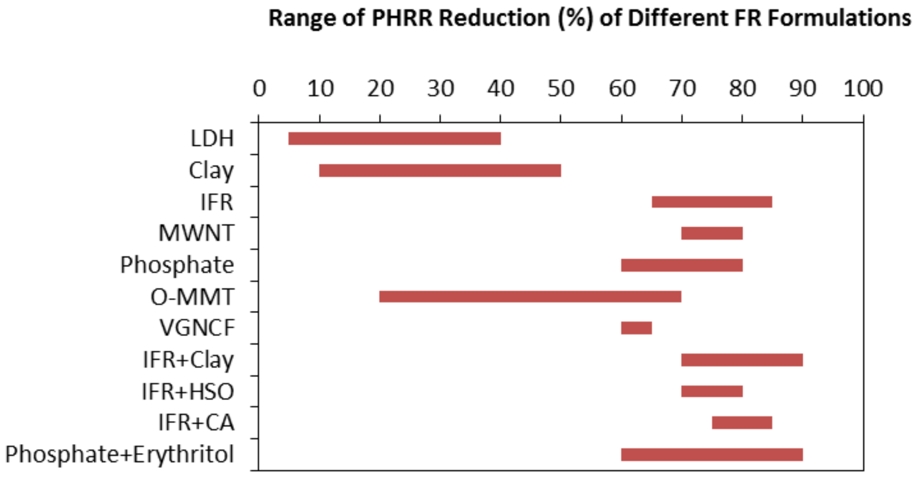

Figure 9. Range of PHRR Reduction (%) of Different FR Formulations

Comprehensive study on different kind of IFRs and combinations of IFR and clays, carbonizing agent, nanotubes, hydroxyl silicone oil (HSO), La_2O_3 (used as synergist) have been carried out by researchers. According to the available literature, IFR alone can reduce the PHRR up to 85% [65, 69-73]. All the combinations of IFRs and other additives such as clays, HSO, carbon nanotube and carbonizing agent can reduce PHRR starting from 70% to 92%. Phosphate and combination phosphates with erythritol are also effective FR for PP nanocomposite. figure 9 reflects the effective range distribution of % reduction of PHRR. In figure 10 combination number has been plotted against different range of % reduction of PHRR. Total 133 combinations fire performance data of PP nanocomposites have been recorded in this study. In figure 10, distribution of formulations of PP nanocomposites is shown according their range of % reduction of PHRR. Figures 9, reveals that all the formulations considered in this paper are evenly distributed. Maximum 45 formulations are currently available which could be utilized to reduce PHRR by more than 70%.

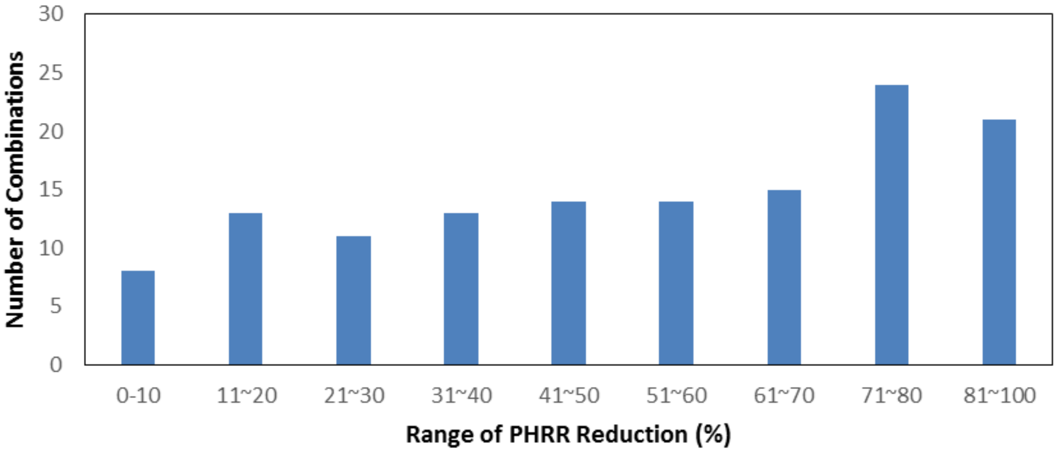

Figure 10. Distribution of Different Combinations of PP Nanocomposites

Total 21 formulations of FR PP nanocomposites were identified which could result into 90% reduction of PHRR; they are listed in Table 3. Combination of IFR with MMT clay and hexadecyl tri-methyl ammonium bromide (C16) used as reactive compatibilizer is a promising FR retardant formula which was added into PP. investigation of fire performance showed that this formulation could reduce the PHRR to 90%. Another promising formula consisting of penta erythritol (PER), di penta erythritol (DPER), tri penta erythritol (TPER) derivatives mixed with melamine phosphate showed that PHRR could be reduced significantly. Among these erythritol derivatives, PER is the most effective for PHRR reduction of PP nanocomposite. Recently multi walled carbon nanotubes has drawn attraction of academic and industrial sectors recently since they could be used in very limited loading to achieve more than 80% reduction of PHRR. Researchers have also reported that IFRs combined with either lanthanum oxide, zinc borate (BZn), maleic anhydrite grafted polypropylene or organo clay could also reduce PHRR significantly.

Table 3. List of FR formulations which Have % Reduction of PHRR Ranging Between 80-100%

Filler Name and Composition (wt%)	% Reduction of PHRR	% Increase in T_{ig}	Applied Heat Flux (KW/m^2)	Paper Reference
20%IFR+4%MMT+2%C16	90	-	50	[73]
40% MP	80	-24	35	[74]
30% MP+ 10% PER	91	-41	35	[74]
20% MP + 20% PER	92	-46	35	[74]
10% MP + 30% PER	85	-26	35	[74]
30% MP+ 10% DPER	87	-26	35	[74]
20% MP + 20% DPER	88	-34	35	[74]
30% MP+ 10% TPER	85	-41	35	[74]
20% MP + 20%TPER	86	-19	35	[74]
10% MP + 30% TPER	81	-56	35	[74]
25% IFR + 5% HSO	81	-	35	[69]
18% APP+ 6% MA + 6% BCPPO	83	-39	35	[75]
28% IFR+5% PP-g-MAH	85	-17	35	[70]
28% IFR+5% PP-g-MAH+1.5% Organo clay	85	-15	35	[70]
28% IFR+5% PP-g-MAH+1.5% SDS-LDH	83	-15	35	[70]
20% IFR	81	-13	35	[71]
20% IFR+ 1% La2O3	82	-16	35	[71]
28% NIFR+2% BZn	81	-50	50	[72]
1% MWNT	81	-56	50	[46]
26.25% APP+8.75% PA-6+5% EVA8	83	-6	50	[76]
26.25% APP+8.75% PA-6+5% EVA24	82	-13	50	[76]

Blend of PP/Ammonium poly phosphate (APP)/polyamide-6 (PA-6)/Ethylene vinyl acetate (EVA) also reduces the PHRR significantly. Almeras et al. incorporated APP, PA-6 and EVA with PP and reported that this blend can reduce PHRR up to 83%. For all the blends listed above in table 3, decrease of ignition time is observed. But, high reduction of PHRR makes these blends interesting to apply them for other commodity polymers.

6.3 Systematic Analysis of Flammability Reduction of Polystyrene Nanocomposites

Similar as PMMA and PP; clays, LDHs, IFRs, phosphates, carbon nano tubes (CNT) have been used as FR nanofillers. Blends consisting of two (or more) of these groups resulted into high reduction of PHRR. The range of PHRR reduction (%) of different FR formulations is reflected in figure 11. To understand the effect of dispersion, Matusinovic et al compared the cone calorimeter data of in situ bulk-polymerized calcium-aluminum LDH nanocomposite with melt blended CaAL-LDH microcomposite [77]. Results showed that, nanodispersed bulk polymerized CaAl-LDH has higher % reduction of PHRR than that of melt blended CaAl-LDH/PS blend. Variation of anions of LDHs by organic anions decreases the PHRR even more [41]. Incorporation of linear chain-alkyl carboxylates between the layers of magnesium-aluminum LDH organically modifies Mg-Al LDH system, and the blend of this organically modified LDH possesses better fire and thermal properties than normal LDHs [59]. From figure 11, it could be depicted that LDHs can reduce the PHRR within 5 to 40% range.

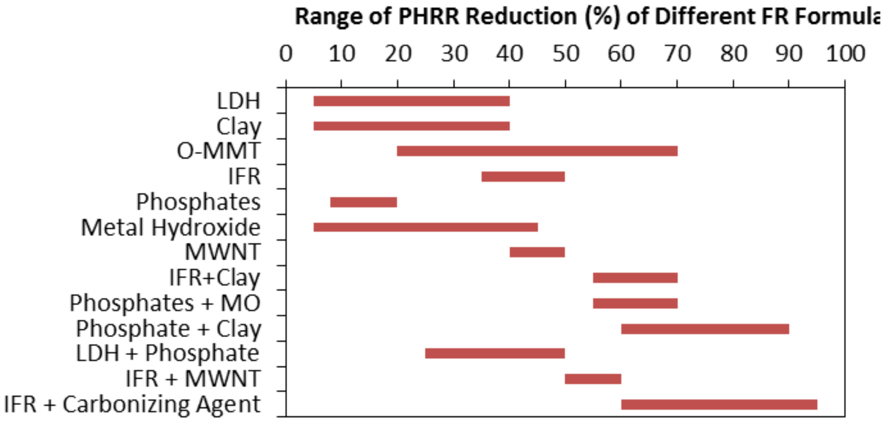

Figure 11. Range of PHRR Reduction (%) of Different Formulations

Fire and thermal properties of PS nanocomposites containing natural clays, synthetic inorganic clays, polymerically and organically modified clays have drawn attraction of researchers due to their well-balanced combination of thermal, mechanical and flammability properties [78].

Inorganic clays are slightly better than natural clays, but polymerically or organically modified clays reduce PHRR as much as 70% to reduce fire hazard caused by flammability of polymer [12, 79-82]. Organically modified clays can reduce the PHRR up to 50% of the original PHRR value. Different IFRs and phosphate based FR are also incorporated with PS.

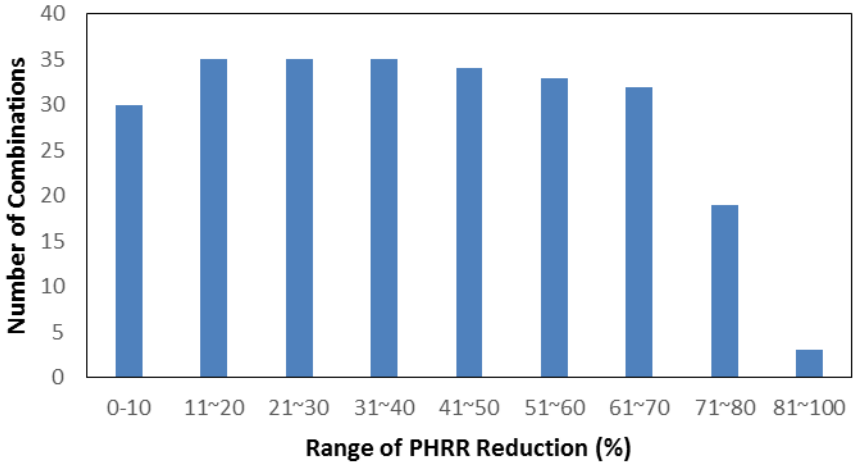

Figure 12. Distribution of Different Combinations of PS Nanocomposites

As shown in figure 11, IFRs can similarly reduce the PHRR by 50% but phosphates in this case are not effective enough. Their PHRR reduction range is limited (7-19%)[83-85]. Increase of phosphate loading eventually decreases the PHRR by more than 50%; but high loading of APP could be a drawback [86]. Combination of LDH and phosphate decreases PHRR even further as shown in figure 11. IFRs have been blended with clays, MWNT and carbonizing agent (CA) and their fire properties are available in literature [20, 24, 86, 87]. But the blend of IFR/APP/carbonization agent named poly (1, 3, 5-triazin-2-aminoethanol diethylenetriamine) is the most effective formula to reduce PHRR as high as 93% [86]. Total 256 formulations of FR Polystyrene nanocomposites have been considered in this paper to plot the distribution chart as shown in figure 6. From the trend it could be said that most of the combinations are distributed evenly, but there are only few combinations which are able to reduce the PHRR above 70%.

From literature review three blends of FR polystyrene nanocomposites were found which can reduce PHRR by more than 80%. Constituents of the blends and composition are listed in table 4.

Table 4. List of FR Formulations which have % Reduction of PHRR Ranging Between 80-100%

Filler Name and Composition (wt%)	% Reduction of PHRR	% Increase in T_{ig}	Applied Heat Flux (KW/m^2)	Paper Reference
30% RDP+ 5% clay	92	-11	50	[88]
10% of (75%) DPVPP clay (melt blended)	81	22	35	[40]
21 %APP+ 7%CA (IFR)	93	-40	35	[86]

Chigawada claimed that, organically modified commercial clay compound named as Cloisite-10A and mixture of phosphate based material resorcinol diphosphate (RDP) can reduce the PHRR significantly [88]. Author also investigated effects of tricresylphosphate (TCP) and trixylyl phosphate (TXP). According to him, addition of TXP and TCP can reduce PHRR by 78% but maximum reduction of PHRR is obtained by using RDP. Yan et al. developed an IFR by adding a novel carbonizing agent (which acted as both charring and blowing agent) with APP in 3:1 mass ratio [86]. Author claimed that, combination of PS/APP/CA can improve LOI and reduce PHRR significantly [86]. Poly (1, 3, 5-triazin-2-aminoethanol di-ethylene amine) was used as the carbonizing agent (CA). Third significant formulation is prepared by adding 10% of (75%) diphenyl 4-vinylphenyl phosphate (DPVPP) terpolymer modified clay into PS by melt blending process [40]. Ignition time decreased in RDP/Clay/PS and APP/CA/PS polymer nanocomposites; whereas increased ignition time was observed for DPVPP clay/PS polymer nanocomposite.

6.4 Systematic Analysis of Flammability Reduction of Polyethylene Nanocomposites

Polyethylene could be classified into low density polyethylene (LDPE) and high density polyethylene. Cone calorimeter data for both of these polymers have been recorded in this study. And like other polymers discussed; plotting distribution chart, estimating weighted average of % reduction of PHRR and listing of compositions have been carried out for both of these polymers.

6.4.1 Data Analysis of LDPE

Extensive studies based on natural clays, polymerically modified clays, organo clays and oligomerically modified clays' preparation procedure and their role in fire retardancy of polymer nanocomposites have been reported in different articles [43, 66, 67, 89, 90]. Figure 13 reveals that, clays including modified clays have a wide range (5-70%) of PHRR reduction. LDHs made of ZnAl, MgAl have effectively used for reduction of PHRR ranging between 5 to 39%. IFR/LDPE blends have been prepared by different methods and their fire properties have been evaluated in different articles [91-93]. IFRs have higher edge of performance when compared to clays, phosphates and LDHs [94]. IFRs alone can reduce the PHRR to 75%; this is shown in figure 13. Effective range of PHRR reduction increases when these groups are combined. This holds true for LDH/phosphate, ATH/Clay blends of LDPE nanocomposite. Calcium based mineral fillers have also been successfully used as FR additives [95].

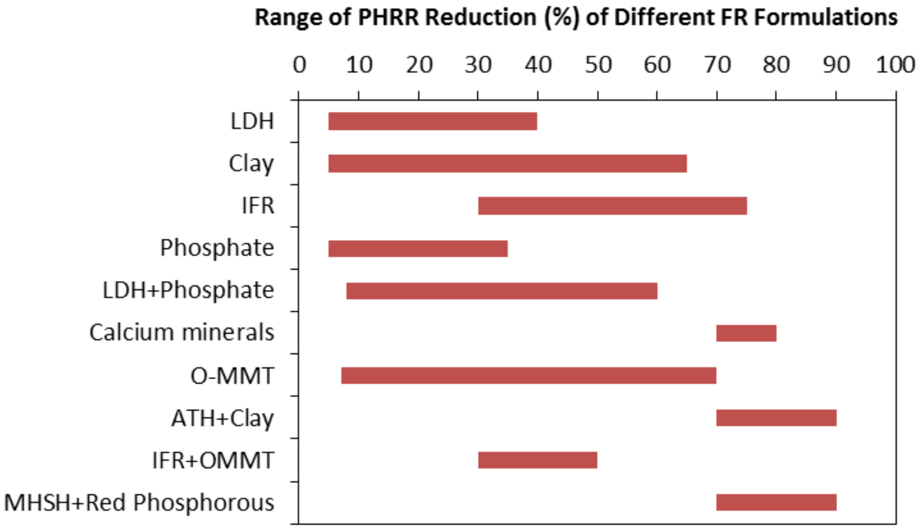

Figure 13. Range of PHRR Reduction (%) of Different FR Formulations of LDPE Nanocomposites

Combination of ATH/Clay and magnesium hydroxide sulfate hydrate (MHSH) whiskers along with red phosphorous (containing 85 wt% phosphorous) microencapsulated (MRP) with magnesium hydroxide and melamine formaldehyde are the most effective blends found which enhance the fire properties of LDPE [94, 96].

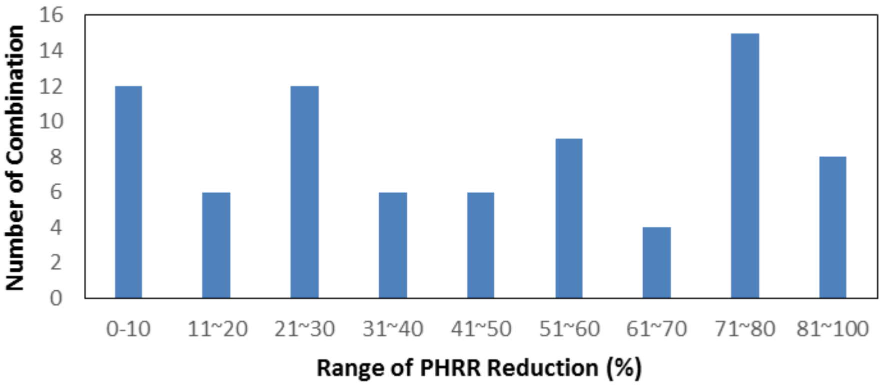

Figure 14. Distribution of Different Combinations of LDPE FR Nanocomposites

From figure 14, it could be observed that almost 33% of the combinations can reduce the PHRR above 70%. There are eight combinations available, which are able to reduce the PHRR above 80%. They are listed in table 5.

Table 5. List of FR Formulations which have % Reduction of PHRR ranging between 80-100%

Filler Name and Composition (wt%)	% Reduction	% increase in Tig	Applied Heat Flux	Reference Paper
40% ATH+10%Lauryl clay	84	-29	50	[90]
50% ATH+10%Lauryl clay	88	-17	50	[90]
60% ATH+10%Lauryl clay	92	-12	50	[90]
60% MHSH	87	-	35	[96]
38% MHSH+ 2% MRP	85	-	35	[96]
33% MHSH+ 7% MRP	91	-	35	[96]
30% MHSH+ 10% MRP	92	-	35	[96]
25% MHSH+ 15% MRP	84	-	35	[96]

Alumina trihydrate (ATH) normally requires higher loading. When, ATH is combined with oligomerically modified lauryl clay, the loading amount decreases. Although high loading of additives are required, but significant improve in PHRR reduction is observed [90]. Appropriate mixture of MHSH and MRP could reduce PHRR by 92% from its original value [96].

6.4.2 Data Analysis of HDPE

MMT nanoclays along with C16 as reactive compatibilizer is able to reduce the PHRR to 32% [97]. At applied heat flux of 50 KW/m^2, same amount of loading (5 wt%) of organically modified MMT (OMMT) significantly reduces the PHRR to 67%, whereas for 5% MMT reduction (%) of PHRR is only 37% [98]. Joanna et al. reported that 55 wt% MDH can reduce PHRR by 88%. Same level of reduction is also observed when MDH is blended with ethylene vinyl acetate (EVA) and MMT or OMMT. High loadings of MDH are required to achieve this significant reduction. 8 wt% VGCNF can reduce PHRR by 70% with much lesser loading [25]. MWNT could be also effective to achieve higher reduction with less loadings [99]. Szustakiewicz et al.

have investigated the effect of formulation like maleic grafted polyethylene (Plb)/clays modified by quaternary ammonium salt (ZR2) or by aluminum hydrogen sulfate (ZGI)/MPP or APP [100]. Authors reported that these combinations could reduce PHRR within 50-89%.

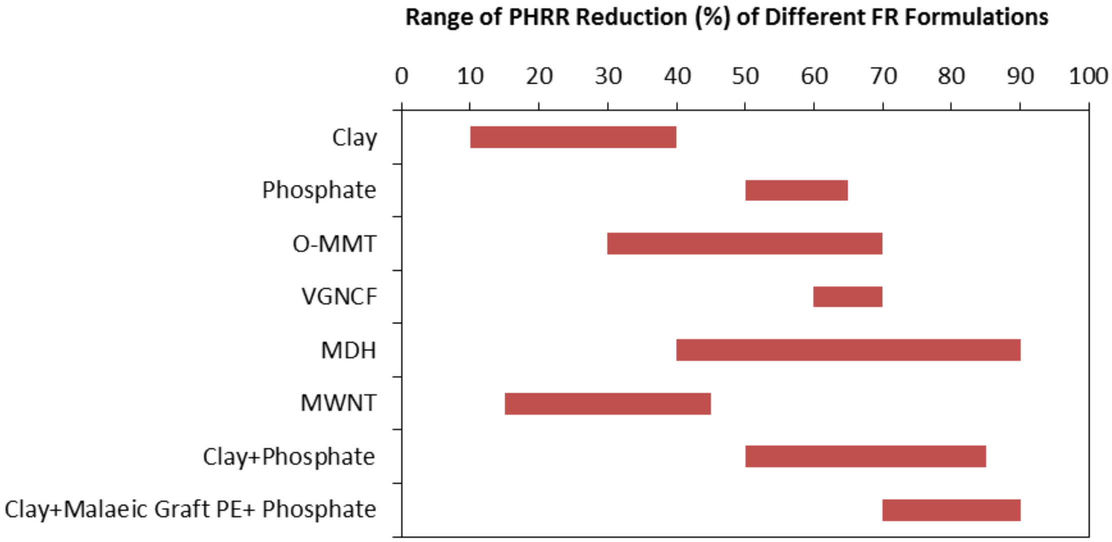

Figure 15. Range of PHRR Reduction (%) of Different FR Formulations of HDPE Nanocomposites

From figure 15, it is revealed that blend of MDH, clay/phosphate and clay/Plb/phosphate can greatly reduce the PHRR of FR polymer nanocomposites. Figure 16 shows the distribution of various combinations according to their % reduction of PHRR. As shown in figure 16, 29% of the compositions studied so far could reduce the PHRR by 80% from the virgin polymers PHRR value.

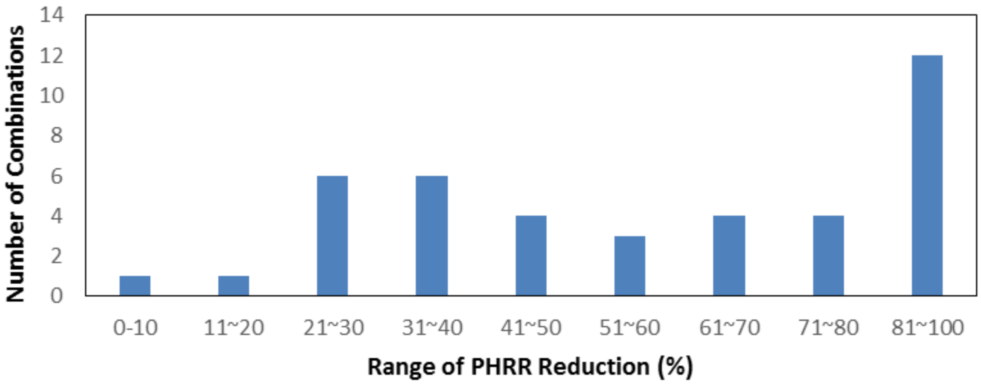

Figure 16. Distribution of Different Combinations of HDPE Nanocomposites

From literature, 6 formulations were identified which can reduce the PHRR by more than 80%. These formulations are listed in table 6. It could also be depicted that, formulations containing MDH has higher Ignition time, whereas rests of the combinations follow normal trends. Ignition time for them decreases.

Table 6. List of FR Formulations which have (%) Reduction of PHRR Ranging Between 80-100%

Filler Name	% Reduction	% Increase of T_{ig}	Applied Heat Flux (KW/m^2)	Reference Paper
40% MDH	81	15	50	[98]
45% MDH	86	29	50	[98]
50% MDH	88	50	50	[98]
55% MDH	89	53	50	[98]
45% MDH+5% EVA + 5% MMT	89	16	50	[98]
45% MDH+5% EVA + 5% OMMT	88	16	50	[98]
20% Plb +2% ZR2	82	-33	50	[100]
20% Plb +2% ZGI	86	-14	50	[100]
20% Plb +2% ZR2+20% MPP	86	-29	50	[100]
20% Plb +2% ZGI+ 20% MPP	89	-37	50	[100]
20% Plb +2% ZR2+ 20% APP	84	-33	50	[100]
20% Plb +2% ZGI+ 20% APP	83	-33	50	[100]

CHAPTER VII

CONCLUSIONS

Fire hazards associated with polymers are often responsible for fatalities and burn injury. Flame retardant polymer nanocomposites are exciting technology which limits the fire hazard of polymers. In this study, effect of various FR nanocomposites are recorded for four major commodity and engineering polymers. Effectivity of different types of FR was studied and the most effective formulations of the fire retardants were recorded. This study would be helpful for the future researcher in acquiring knowledge about different fire retardant materials and their uses in ensuring fire safety. To promote this idea, best formulations were identified and listed as shown in table 7.

Table 7. Best Formulations of Polymer Nanocomposites

Polymer	**Filler name and composition (wt%)**	**% Reduction of PHRR**
PMMA	20% DB+5% AO+5% Cloisite 20A	75
PP	20% MP + 20% PER	92
PS	21 % APP+ 7% CA (IFR)	93
LDPE	30% MHSH+ 10% MRP	92
HDPE	45% MDH+5% EVA + 5% MMT	89

With the help of effective range distribution curve one can easily pick the effective group of fire retardants. One novel FR could be utilized by others to investigate the effect of the new technologies on other commodity polymers. Major parameter controlling fire properties of polymers is peak heat release rate. Other than this, percentage increase in ignition time of polymers was calculated to see various FR blends effect on T_{ig}. Only for PMMA and HDPE, increased ignition time was observed for identified best formulations.

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APPENDICES

In this section cone calorimeter data of polymer nanocomposites have been recorded in tabular format for systematic analysis. Total 100 papers have been used as source of data recorded. Major cone calorimeter parameters such as ignition time, PHRR, THR have been recorded. Fire performance of polymer nanocomposites are determined based on percentage reduction of PHRR, percentage increase in ignition time. Effect of nanofillers on fire performance of polymer nanocomposites could be portrayed by % reduction of PHRR and % increase in ignition time; these mentioned parameters are also shown in table 12-16.

Table 8. Cone Calorimeter Data of PMMA Nanocomposites

Filler Composition (%wt)	Applied Heat Flux (kW/m^2)	Ignition Time (s)	Increase of T_{ig} (%)	pHRR, kW/m^2	%Reduction of pHRR	THR (MJ/m^2)	Paper Reference	Comment
Pure PMMA	35	57		639			[26]	Synergism on fire properties has been investigated between nano-sized hydrophobic oxides (alumina and silica) and ammonium polyphosphate (AP) flame-retardant additive
AP 15%		56	-2	419	34			
AP 10%/Alu 5%		58	2	266	58			
AP 10%/Alu-C8 5%		56	-2	262	59			
AP 10%/Sil 5%		69	21	313	51			
AP 10%/Sil-C8 5%		65	14	231	64			
Pure PMMA	35	62		533		117	[27]	APP : Ammonium polyphosphate MPP: Melamine Polyphosphate
15% TiO_2		88	42	347	35	100		
15% APP		63	2	345	35	100		
15% MPP		67	8	260	51	99		
7.5% APP/7.5% MPP		58	-6	255	52	103		
7.5% APP/7.5% TiO_2		75	21	257	52	93		
7.5% MPP/7.5% TiO_2		59	-5	278	48	99		
5% APP/5% MPP/5% TiO_2		65	5	271	49	99		
Pure PMMA	30	58		429		115	[28]	Sb_2O_3: Antimony Oxide ; for 5% Sb_2O_3 filler pHRR increases.
5% Sb_2O_3		78	3	481	-12	127		
10% Sb_2O_3		132	13	370	14	118		
20% Sb_2O_3		114	10	326	24	110		
Pure PMMA	50	14		1028		82	[56]	MgAl-LDH : Magnesium aluminium layered
3% MgAl-		10	-29	738	28	76		

BA LDH								double hydroxide BA: Benzyl Acetate BP: Benzyl Phosphate BS: Benzyl Sulfonate ABA: Amino Benzyl Acetate
10% MgAl-BA LDH		14	0	554	46	71		
3% MgAl-ABA LDH		9	-36	828	19	79		
10% MgAl-ABA LDH		12	-14	665	35	74		
3% MgAl-BS LDH		11	-21	795	23	77		
10% MgAl-BS LDH		12	-14	736	26	74		
3% MgAl-BP LDH		10	-29	819	20	78		
10% MgAl-BP LDH coprecipitation		11	-21	821	20	75		
10% MgAl-BP LDH rehydrated		11	-21	716	30	75		
10% MgAl-BP LDH exchanged		11	-21	718	30	77		
Pure PMMA	50	22		902		79	[101]	Ca_3Fe calcium iron undecenoate Ca_3Al calcium aluminium undecenoate
1% Ca_3Fe		20	-9	780	14	73		
5% Ca_3Fe		19	-14	655	27	73		
10% Ca_3Fe		15	-32	592	34	72		
5% Ca_3Al		17	-23	597	34	75		
10% Ca_3Al		17	-23	418	54	74		
Pure PMMA	50	14		1028		82	[57]	
3%MgAl-NO_3 LDH		11	-21	836	19	72		
10%MgAl-NO_3 LDH		8	-43	823	20	74		
3%MgAl-CO_3 LDH		12	-14	902	12	77		
10%MgAl-CO_3 LDH		14	0	721	30	77		
3% calcined		12	-14	900	12	77		

LDH								
10% calcined LDH		12	-14	704	32	71		
3%MgAl-C16 LDH		11	-21	782	24	80		
10%MgAl -C16 LDH		14	0	504	51	72		
20% MgAl-C16 LDH		16	14	329	68	67		
0%	50	9		1129		86	[54]	MMT: montmorillonite Kao: Kaolinite
3% LDH		10	11	915	19	77		
5% LDH		12	33	790	30	76		
10% LDH		9	0	615	46	72		
3% MMT		12	33	777	31	82		
5% MMT		13	44	625	45	80		
10% MMT		13	44	508	55	77		
3% Kao		10	11	1014	10	80		
5% Kao		10	11	970	14	76		
10% Kao		7	-22	875	23	78		
Pure PMMA	50	10		1092		79.9	[102]	ZHTMDBB: A boron-containing layered hydroxy salt (LHS)
3% ZHTMDBB		7	-30	849	22	77		
5% ZHTMDBB		8	-20	646	41	75.5		
10% ZHTMDBB		9	-10	568	48	72.4		
Pure PMMA	35	69		620		110	[29]	Nanocomposites of PMMA-oxide (oxide: nanoparticles of TiO_2 or Fe_2O_3), PMMA-organoclays (organomodified montmorillonite: OMMT) and PMMA-oxide-OMMT
10% OMMT		74	7	320	48	110		
5% OMMT/5 % Fe2O3		53	-23	350	44	100		
5% OMMT/5 % TiO2		86	25	360	42	100		
Pure PMMA	35	69		624		112	[103]	PMMA blended with phosphinate additives (Exolit OP930 and OP1311)
15% OP930		70	1	315	50	91		

15% OP1311		35	-49	270	57	73		
Pure PMMA	35	69		624		112	[104]	AlOOH : Bohemite Al$_2$O$_3$: Alumina
5% AlOOH		80	16	503	19	109		
10% AlOOH		74	7	489	22	109		
15% AlOOH		88	28	424	32	103		
20% AlOOH		82	19	348	44	99		
5% Al2O3		70	1	552	12	105		
10% Al2O3		70	1	414	34	106		
15% Al2O3		88	28	350	44	81		
Pure PMMA	50	9		1129		86	[61]	Copolymer nanocomposites were prepared by suspension copolymerization of bis[2-(methacryloyloxy) ethyl] phosphate and methyl methacrylate, together with bis(2-ethylhexyl) phosphate layered double hydroxide and a montmorillonite, Cloisite 93A
sus PMMA		7	-22	1081	4	81		
sus CoPMMA		8	-11	635	44	60		
Sus PMMA+3% LDH		8	-11	798	29	83		
Sus PMMA+5% LDH		6	-33	623	45	73		
Sus PMMA+10% LDH		7	-22	491	57	73		
Sus CoPMMA +3% LDH		10	11	720	36	61		
Sus CoPMMA +5% LDH		9	0	680	40	57		
Sus CoPMMA +10% LDH		11	22	542	52	63		
Sus PMMA+3% MMT		5	-44	539	52	69		
Sus PMMA+5% MMT		6	-33	538	52	66		
Sus CoPMMA		11	22	439	61	57		

+3% MMT								
Sus CoPMMA +5% MMT		14	56	482	57	61		
Sus CoPMMA +10% MMT		15	67	392	65	51		
Pure PMMA	35	69		625		114	[58]	
5% Ti02		94	36	598	4	112		
10% TiO_2		87	-10	440	30	105		
15% TiO_2		89	3	350	44	100		
5% Al_2O_3		70	-28	550	12	105		
10% Al_2O_3		70	0	410	34	105		
15% Al_2O_3		89	28	350	44	80		
5% AlOOH		80	-13	500	20	108		
10% AlOOH		73	-10	490	22	108		
15% AlOOH		89	23	425	32	104		
Pure PMMA	50	10		1456.8			[18]	decabromodiphenyl ether (DB) and antimony trioxide (AO)
20% DB/5% AO		16	60	490.4	66			
20% DB/5% AO/%5 Cloisite 20A		21	110	359.4	75			
Pure PMMA	35	50		641			[60]	DEEP : Di ethyl ethyl-phosphonate
3.5% DEEP		63	26	583	9			
Pure PMMA	50	13		1109		80	[41]	HDEHP: Bis(2-ethylhexyl) phosphate SEHS: Sodium 2-
3% SDBS-LDH		10	-23	915	18	77		
5% SDBS-		12	-8	790	29	76		

LDH								ethylhexyl sulfate SDBS: Sodium dodecyl benzene sulfonate
10% SDBS-LDH		9	-31	615	44	72		
3% HDEHP-LDH		14	8	784	29	76		
5% HDEHP-LDH		12	-8	739	33	75		
10% HDEHP-LDH		8	-38	703	37	73		
3% SEHS-LDH		11	-15	974	12	79		
5% SEHS-LDH		12	-8	901	19	78		
10% SEHS-LDH		9	-31	811	27	74		
Pure PMMA	50	13		883		80		
3% HDEHP-LDH		10	-23	806	9	78		
5% HDEHP-LDH		11	-15	755	14	77		
10% HDEHP-LDH		9	-31	611	31	74		
Pure PMMA	35	32		789		100	[21]	
Ca-Al-LDH-B 1%		25	-22	699	11	101		
Ca-Al-LDH-B 3%		26	-19	590	25	83		
Ca-Al-LDH-B 5%		24	-25	552	30	83		
Ca-Al-LDH-B 7%		26	-19	502	36	79		
Ca-Al-LDH-B 10%		23	-28	436	45	80		
Zn-Al-LDH-B		26	-19	642	19	83		

3%								
Zn-Al-LDH-B 5%		22	-31	573	27	89		
Zn-Al-LDH-B 10%		21	-34	530	33	76		
Mg-Al-LDH-B 3%		32	0	612	22	81		
Mg-Al-LDH-B 5%		32	0	550	30	80		
Mg-Al-LDH-B 10%		30	-6	363	54	70		
Pure PMMA	35	69		640		23.2	[15]	
2.5% MMT		65	-6	560	12	22.9		
5% MMT		60	-13	485	24	22.7		
7.5% MMT		55	-20	464	27	22.5		
10% MMT		52	-25	458	28	22.1		
15% MMT		51	-26	450	30	21.7		
Pure PMMA	50	9		1024		78	[55]	The thermal and fire properties of PMMA modified with various loadings of melamine or zinc aluminum undecenoate LDH were evaluated
5% Mel		17	89	761	26	76		
7.5% Mel		16	78	834	19	74		
10% Mel		17	89	762	26	74		
15% Mel		17	89	703	31	74		
30% Mel		22	144	541	47	69		
5% ZnAl		21	133	689	33	74		
10% ZnAl		21	133	558	45	71		
2.5% Mel/2.5% ZnAl		16	78	704	31	77		
2.5% Mel/7.25% ZnAl		18	100	533	48	72		
5% mel/5% ZnAl		17	89	559	45	72		
7.5% Mel/2.5% ZnAl		18	100	633	38	74		
12.5% Mel/ 2.5%		15	67	599	41	71		

ZnAl								
10% Mel/ 5% ZnAl		19	111	536	48	69		
27.5% Mel/2.5% ZnAl		15	67	491	52	67		
25% Mel/5% ZnAl		18	100	512	50	66		
Pure PMMA	50	15		817		95	[105]	Transition metal sulfides, molybdenum sulfide (MoS2) MMT, Hectorite and POSS are clays
10% MoS_2		18	20	619	24	88		
pure PMMA	35	21		790		76	[16]	
Montmorillonite (MMT)								POSS: polyhedral oligo silsesquioxanes.The organically-modified clays include dimethyl,dihydrogenatedtallow ammonium, 6A and 15A (they differ in the amount of surfactant that has been added); dimethyl,hydrogenatedtallow,2-ethylhexyl ammonium, 25A; methyl,tallow,bis-2-hydroxyethyl ammonium,30B; and methyl,dihydrogenatedtallow ammonium,93A. The POSS material that has been studied,trisylanol phenyl POSS, was kindly provided by Hybrid Plastics, Inc. Cloisite is better
0.1% 6A		23	10	853	-8	75		
2% 6A		24	14	725	8	71		
4% 6A		20	-5	634	20	72		
6% 6A		20	-5	579	27	68		
0.1% 15A		25	19	865	-10	76		
2% 15A		21	0	771	2	72		
4% 15A		21	0	635	20	67		
6% 15A		18	-14	548	31	68		
0.1% 25A		15	-29	862	-9	76		
2% 25A		19	-10	748	5	73		
4% 25A		19	-10	623	21	67		
6% 25A		20	-5	548	31	68		
0.1% 30B		16	-24	929	-18	77		
2% 30B		16	-24	730	8	71		
4% 30B		21	0	627	21	71		
6% 30B		34	62	536	32	66		
0.1% 93A		26	24	911	-15	80		
2% 93A		20	-5	793	-0.4	67		
4% 93A		25	19	626	21	71		
6% 93A		21	0	600	24	69		
4% Phos1		24	14	592	25	69		
4% Phos2		23	10	794	-0.5	71		
Hectorite	35							

								than Hectorite and POSS
4% 6A		19	-10	747	5	72		
6% 6A		22	5	656	17	75		
4% 15A		20	-5	771	2	75		
6% 15A		25	19	657	17	80		
4% 25A		18	-14	717	9	73		
6% 25A		23	10	693	12	77		
4% 30B		23	10	707	10	74		
6% 30B		21	0	724	8	74		
POSS	35							
0.10%		19	-10	758	4	72		
1%		17	-19	789	0.1	74		
3%		17	-19	825	-4	68		
6%		20	-5	765	3	71		
70% PMMA+30% PS	50	25		1570.8			[17]	Copolymer of PMMA and PS was tested for fire performance using decabromodiphenyl ether (DB)
10% Cloisite 20A		21	-16	563	64			
10% DB+3% AO		15	-40	721	54			
10% DB+3% AO+5%Cloisite 20A		18	-28	320.2	80			
15% DB+4% AO		12	-52	570	64			
15% DB+4% AO+3%Cloisite 20A		15	-40	375	76			
15% DB+4% AO+10%Cloisite 20A		18	-28	219	86			
Pure PMMA	50	13		935			[53]	Three ammonium salts, hexa decyl allyl dimethyl ammonium chloride (Allyl16), hexa decyl vinyl benzyl
3%MMT-Bz16		14	8	676	28			
3% MMT-VB16		14	8	706	25			

3% MMT-Allyl16		29	123	744	20			dimethyl ammonium chloride (VB16) and hexa decyl vinyl benzyl dimethyl ammonium chloride (Bz16) were synthesized and ion exchanged onto montmorillonite.
Pure PMMA	35	30		1078		94	[83]	In situ emulsion polymerization was employed
2.3% CeO_2		17	-43	636	41	91		
4.6% CeO_3		20	-33	614	43	93		
100% PS	50	13		933		78	[59]	MDH : magnesium hydroxide ATH: alumina trihydrate Mg-Al LDH
3% MDH		13	0	625	33	72		
5% MDH		12	-8	544	42	70		
10% MDH		13	0	395	58	64		
20% MDH		11	-15	316	66	50		
3% ATH		9	-31	861	8	73		
5% ATH		10	-23	853	9	75		
10% ATH		10	-23	655	30	70		
20% ATH		10	-23	341	63	60		
2% MDH+1% ATH		14	8	684	27	74		
3.3% MDH+1.7 % ATH		10	-23	599	36	73		
6.7% MDH+3.3 %ATH		9	-31	445	52	65		

Table 9. Cone Calorimeter Data of Polystyrene Nanocomposites

Composition	Applied Heat Flux (kW/m^2)	Ignition Time (s)	Increase in T_{ig} (%)	pHRR, kW/m^2	%Reduction of pHRR	THR (MJ/m^2)	Paper Reference	Comments
PurePS	35	83		752			[84]	Synergism on fire properties has been investigated between nano-sized hydrophobic oxides (alumina and silica) and ammonium polyphosphate (AP) flame-retardant additive
AP 15%		62	-25	690	8			
AP 10%/Alu 5%		50	-40	342	55			
AP 10%/Alu-C8 5%		53	-36	329	56			
AP 10%/Sil 5%		61	-27	360	52			
AP 10%/Sil-C8 5%		66	-20	233	69			
Pure PS (685DW)	35	43		1212			[106]	SINK: NASA formulated FR. 685DW grade for PS used for this study nanosilica & attapulgite (601p) used as nanoclay filler
3% 601p		36	-16	1052	13			
20% SINK		22	-49	838	31			
3% 601p+20% SINK		23	-47	675	44			
10% Silica		26	-40	1060	13			
10% Silica+ 20% SINK		25	-42	532	56			
Pure PS	35	62		1419		109.7	[88]	samples were prepared by bulk polymerization. Clay: An organically-modified montmorillonite, dimethylbenzyl hydrogenated tallow ammonium (hydrogenated tallow is a mixture of 65% C18, 30% C16, 5% C14) substituted clay, Cloisite-10A
3% Clay		57	-8	610	57	85.5		
15% TCP		59	-5	1122	21	63.4		
15% TCP+3% clay		59	-5	495	65	59.1		
30% TCP+3% clay		43	-31	378	73	49.5		
30% TCP+5% clay		53	-15	342	76	45.8		
30%		55	-11	324	77	47.3		

TCP+10% clay								TCP: tricresylphosphate TXP: trixylylphosphate RDP: resorcinoldiphosphate
5% TCP+3% Clay		60	-3	704	50	75.3		
10% TCP+3% Clay		49	-21	485	66	62.4		
10% TCP+5% Clay		48	-23	508	64	70.7		
5% RDP+ 3% clay		67	8	502	65	69.8		
5% RDP+ 5% clay		59	-5	458	68	79.1		
15% RDP+ 3% clay		68	10	474	67	58.3		
30% RDP+ 3% clay		75	21	358	75	42.3		
15% RDP		63	2	710	50	56.8		
15% RDP+ 3% clay		68	10	474	67	58.3		
15% RDP+ 5% clay		74	19	433	69	57.5		
15% RDP+ 10% clay		73	18	424	70	60.1		
30% RDP		77	24	499	65	41		
30% RDP+ 3% clay		75	21	358	75	42.3		
30% RDP+ 5% clay		55	-11	110	92	43.1		
30% RDP+ 10% clay		63	2	307	78	44.7		
15% TXP		64	3	890	37	58.5		
15% TXP+ 3% clay		69	11	390	73	62.4		
15% TXP+ 5% clay		58	-6	449	68	59.4		
15% TXP+ 10% clay		61	-2	475	67	63.2		
30% TXP		57	-8	864	39	53.9		
30% TXP+ 5% clay		38	-39	313	78	45.5		
30% TXP+ 10% clay		59	-5	372	74	49.4		
Pure PS	35	31		1587		98	[77]	CaAl-LDH prepared by in situ bulk

1% CaAl-LDH		23	-26	1393	12	107		polymerization
3% CaAl-LDH		23	-26	1282	19	91		
5% CaAl-LDH		26	-16	1198	25	101		
7% CaAl-LDH		27	-13	1053	34	94		
10% CaAl-LDH		30	-3	926	42	101		
Pure PS	35	31		1587		98		CaAl-LDH was prepared by melt blending
1% CaAl-LDH		23	-26	1387	13	106		
3% CaAl-LDH		20	-35	1232	22	108		
5% CaAl-LDH		19	-39	1297	18	111		
7% CaAl-LDH		17	-45	1319	17	109		
10% CaAl-LDH		23	-26	1213	24	110		
Pure PS	50	30		1158		91	[105]	PS/Molybodenum di sulfide nano composite
1% MoS2		20	-33	1041	10	92		
5% MoS2		16	-47	950	18	82		
10% MoS2		12	-60	736	36	73		
Pure PS	50	46		1599		115	[41]	HDEHP: Bis(2-ethylhexyl) phosphate SEHS: Sodium 2-ethylhexyl sulfate SDBS: Sodium dodecyl benzenesulfonate
3% SDBS-LDH		26	-43	954	40	106		
5% SDBS-LDH		27	-41	893	44	105		
10% SDBS-LDH		20	-57	817	49	89		
3% HDEHP-LDH		32	-30	1125	30	96		
5% HDEHP-LDH		25	-46	1094	32	98		
10% HDEHP-LDH		22	-52	1076	33	85		
3% SEHS-LDH		28	-39	1381	14	114		
5% SEHS-		21	-54	1402	12	114		

LDH								
10% SEHS-LDH		19	-59	1088	32	110		
Pure PS	50	50		1260		99		
3% HDEHP-LDH		22	-56	1201	5	103		
5% HDEHP-LDH		13	-74	1181	6	105		
10% HDEHP-LDH		14	-72	1002	20	101		
Pure PS	35	53		1425		89	[43]	polycaprolactone—PCL-modified clay
30% 30BCL		47	-11	735	48	79		
30% 15APCL		50	-6	832	42	84		
30%30BPCL		46	-13	483	66	78		
Pure PS	35	36		1411		102	[40]	
5% of (55%) DPVPP clay (melt blended)		40	11	837	41	58		
10% of (55%) DPVPP clay (solution blended)		39	8	374	73	47		
5% of (75%) DPVPP clay (solution blended)		42	17	389	72	57		
10% of (75%) DPVPP clay (solution blended)		35	-3	331	77	55		
3% of (75%) DPVPP clay (melt blended)		54	50	638	55	76		

5% of (75%) DPVPP clay (melt blended)		43	19	416	71	58		
10% of (75%) DPVPP clay (melt blended)		44	22	268	81	54		
Pure PS	35	63		1111		98	[85]	MgAl LDH : MAU APP: Ammonium Polyphosphate
5% APP		39	-38	986	11	104		
2.5% MAU+2.5% APP		25	-60	808	27	107		
5% MAU		35	-44	924	17	96		
10% APP		34	-46	862	22	98		
5% MAU+ 5% APP		25	-60	642	42	101		
10% MAU		35	-44	815	27	95		
Pure PS	35	31		1587		98	[21]	
1% ZnAl-LDH		31	0	1533	3	108		
3% ZnAl-LDH		19	-39	1377	13	106		
5% ZnAl-LDH		16	-48	1019	36	88		
7% ZnAl-LDH		9	-71	951	40	89		
10% ZnAl-LDH		14	-55	942	41	87		
100% PS	35	39		1198		90		
1% MgAl-LDH		28	-28	1157	3	97		
3% MgAl-LDH		25	-36	1164	3	95		
5% MgAl-LDH		28	-28	1178	2	95		
7% MgAl-LDH		24	-38	1068	11	98		
10% MgAl-LDH		10	-74	1023	15	87		
Pure PS	35	59		1242		100	[39]	ACPB: acrylic acid pentabromobenzyl ester MEPB: methacrylate acid pentabromo
3% BUPB+3% 30B		43	-27	1065	14	77		

3% BUPB+3% 30B+ 3% Sb2O3		41	-31	590	52	50		pentabromobenzyl benzyl ester BUPB: butyric acid pentabromobenzyl ester PBPA: pentabromobenzyl ester polyacrylate F5C16-clay: fluorine-containing clay DBS: Di bromo styrene St-30B-Sb2O3-PTFE system contains 3% 30B clay, 3% Sb2o3, 0.2%PTFE and the copolymer makes up the balance. ACPB-St: styrene bulk polymerized in the presence of 3% of the pentabromo benzyl ester of acrylic acid
3% PBPA+3% 30B		33	-44	707	43	62		
3% PBPA+3% 30B+ 3% Sb2O3		42	-29	541	56	45		
3% MEPB+3% 30B		34	-42	967	22	71		
3% MEPB+3% 30B+ 3% Sb2O3		43	-27	813	35	51		
3% ACPB+3% 30B		34	-42	813	35	75		
3% ACPB+3% 30B+ 3% Sb2O3		44	-25	875	30	61		
5%DBS+95 % St-30B-Sb2O3-PTFE		37	-37	445	64	42		
10%DBS+90% St-30B-Sb2O3-PTFE		42	-29	344	72	41		
F5C16-St (bulk polymerized)		53	-10	929	25	93		
F5C16-St+ Sb2O3(bulk polymerized)		30	-49	813	35	75		
ACPB-St		43	-27	342	72	34		
Pure PS	35	63		1351		100	[42]	PyC16 salt was prepared by a combination of pyridine and hexadecyl bromide (C16Br)
3% QC16 clay, bulk		42	-33	1100	19	95		
5% QC16 clay, bulk		20	-68	806	40	88		
3% QC16		63	0	998	26	94		

clay, melt blend								QC16 salt was prepared by the combination of quinoline and hexadecyl bromide (C16Br) Both bulk polymerisation and melt blending processes were utilized for the preparation of PS nanocomposites
5% QC16 clay, melt blend		60	-5	848	37	94		
3%PyC16 clay, bulk		51	-19	782	42	90		
5% PyC16 clay, bulk		44	-30	762	44	82		
7% PyC16 clay, bulk		25	-60	683	49	88		
3% PyC16 clay, melt blend		58	-8	1265	6	102		
5% PyC16 clay, melt blend		49	-22	1319	2	97		
7% PyC16 clay, melt blend		47	-25	1021	24	95		
100% PS	35	56		1480		102	[107]	ferrocenium clay : FERIC14
0.5% FERIC14		56	0	1354	9	99		
1% FERIC14		43	-23	1313	11	99		
3% FERIC14		35	-38	1089	26	97		
5% FERIC14		37	-34	1045	29	96		
100% PS	35	52		1334		98	[108]	The montmorillonite clay (MMT) modified with 1,3-dihexadecyl-3H-benzimidazol-1-ium (BZ32) was named MB32 and the montmorillonite modified with 2-methyl-1,3-dihexadecyl-3H-benzimidazol-1-ium (BZ33) was named MB33
1% MB32		54	4	1219	9	97		
3% MB32		56	8	844	37	96		
100% PS		55	6	1449		93		
1% MB33		54	4	1409	3	97		
3% MB33		53	2	934	36	96		
100% PS	35	44		1166		101	[23]	BFR is brominated FR. Which contains 5 parts of decabromophenyl oxide and 1 part of antimony oxide.
1.2% BFR		42	-5	1123	4	94		
3.6% BFR		46	5	958	18	74		
6% BFR		51	16	808	31	58		
9.6% BFR		54	23	784	33	51		

12% BFR		55	25	591	49	46		cloisite15A was used as clay (OMT) MWNT: multi walled carbon nanotube
18% BFR		53	20	509	56	40		
24% BFR		52	18	590	49	39		
11.5% BFR + 0.5% MWNT		29	-34	455	61	40		
10% BFR+ 2% MWNT		34	-23	340	71	43		
9%BFR + 3% MWNT		38	-14	339	71	45		
10% BFR+2% OMT		35	-20	442	62	43		
10% BFR+1% MWNT+1 %OMT		30	-32	381	67	43		
100% PS	35	44		1166		101	[20]	IFR : ammonium polyphosphate/tripentaerythritol (APP/TPE) montmorillonite clay and zirconium phosphate were used as organically modified layered materials Hexadecyl trimethyl ammonium bromide (CTBA) Benzyl di methyl hexa decyl ammonium chloride (HDBAC) [3-(3,4-Dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-2-hydroxy-propyl] trimethylammonium chloride (DOHAC)
15% IFR		33	-25	617	47	78		
20% IFR		34	-23	601	48	73		
30% IFR		36	-18	515	56	68		
19% IFR+ 1% clay		34	-23	333	71	72		
18% IFR+ 2% clay		34	-23	320	73	77		
19% IFR+1% MWNT		26	-41	519	55	71		
18% IFR+2% MWNT		32	-27	457	61	69		
19% IFR+ 1%Fe2O3		28	-36	456	61	74		
18% IFR+2% Fe2O3		32	-27	467	60	75		
19% IFR+ 1% Ni-Cat		28	-36	398	66	73		
18% IFR+ 2% Ni-Cat		23	-48	324	72	63		CTBA, HDBAC and DOHAC were used to improve ZrP as intercalating agent
100% PS	35	53		1105		90		
20% IFR		34	-36	629	43	72		
19% IFR+ 1% clay		44	-17	382	65	73		
18% IFR+		42	-21	332	70	77		

2% clay								
19% IFR+ 1% ZrP-CTBA		38	-28	495	55	72		
18% IFR+ 2% ZrP-CTBA		37	-30	421	62	72		
19% IFR+ 1% ZrP-HDBAC		37	-30	537	51	71		
18% IFR+ 2% ZrP-HDBAC		36	-32	488	56	74		
19% IFR+ 1% ZrP-DOHAC		43	-19	688	38	73		
18% IFR+ 2% ZrP-DOHAC		41	-23	703	36	80		
100% PS	35	54		1475		94	[38]	Zn-Al LDH was used
5% MMT		46	-15	592	60	90		
5% CNT		43	-20	620	58	96		
5% LDH		41	-24	956	35	94		
100% PS	35	42		980		89	[80]	
3% Fluoro Hectorite (melt)		32	-24	472	52	81		
3% Fluoro Hectorite (solution)		26	-38	425	57	91		
3% MMT (melt)		52	24	614	37	80		
3% MMT(solution)		54	29	604	38	84		
100% PS	35	61		1376		95	[79]	The bromo-alkyl carbazoles, containing a 5-carbon chain, 5AC, and a 10-carbon chain, 10AC di-alkyl carbazole salt (10ACDD)
1% 5AC (bulk)		39	-36	1254	9	89		
3% 5AC (bulk)		43	-30	827	40	88		
5% 5AC (bulk)		52	-15	693	50	86		
3% 5AC (melt)		49	-20	1233	10	100		
5% 5AC		47	-23	1023	26	99		

(melt)								
10% 5AC (melt)		38	-38	889	35	92		
1% 10AC (bulk)		43	-30	1297	6	91		
3% 10AC (bulk)		46	-25	923	33	85		
5% 10AC (bulk)		40	-34	828	40	86		
3% 10AC (melt)		37	-39	1062	23	99		
5% 10AC (melt)		42	-31	1159	16	100		
10% 10AC (melt)		36	-41	945	31	99		
3% 10ACDD (bulk)		15	-75	864	37	99		
5% 10ACDD (bulk)		19	-69	695	49	98		
7% 10ACDD (bulk)		23	-62	626	55	90		
3% 10ACDD (melt)		42	-31	1227	11	96		
5% 10ACDD (melt)		44	-28	1193	13	106		
100% PS	35	29		1353		100	[83]	In situ emulsion polymerization was employed
2.3% CeO2		12	-59	1236	9	99		
4.6% CeO2		11	-62	1040	23	98		
100% PS	35	68		1399		108	[12]	ter-1-clay : (dibromostyrene : styrene : vinyl benzyl cholride)=(10:85:5) ter-2-clay : (dibromostyrene : styrene : vinyl benzyl cholride)=(20:75:5) ter-3-clay : (dibromostyrene :
3% Br(DBDPO)		66	-3	1352	3	78		
7% Br(DBDPO)		69	1	1404	-0.4	80		

1% ter-1-clay		45	-34	1530	-9	110		styrene : vinyl benzyl cholride)=(50:45:5) ter-4-clay : (dibromostyrene : styrene : vinyl benzyl cholride)=(70:25:5) Di-clay: (dibromostyrene : styrene : vinyl benzyl cholride)= (95:0:5) these are the clay identification
3% ter-1-clay		40	-41	1586	-13	119		
5% ter-1-clay		51	-25	1472	-5	111		
10% ter-1-clay		41	-40	1051	25	101		
3% ter-2-clay		23	-66	970	31	86		
5% ter-2-clay		42	-38	968	31	94		
10% ter-2-clay		39	-43	820	41	85		
1% ter-3-clay		35	-49	1341	4	109		
3% ter-3-clay		39	-43	1197	14	111		
10% ter-3-clay		27	-60	713	49	87		
3% ter-4-clay		28	-59	1325	5	101		
5% ter-4-clay		25	-63	1072	23	95		
10% ter-4-clay		24	-65	896	36	83		
1% di-clay		50	-26	1200	14	100		
3% di-clay		46	-32	1436	-3	95		
10% di-clay		20	-71	737	47	73		
100% PS	35	62		1289		82	[82]	sodium montmorillonite was modified. See reference for details
2% tri-clay		53	-15	1035	20	81		
6% tri-clay		54	-13	999	23	77		
10% tri-clay		45	-27	871	32	79		
100% PS	35	52		1006		255	[86]	IFR consisting APP and carbonizing agent (CA) Nitrogen-containing carbonization agent named poly(1,3,5-triazin-2-aminoethanol diethylenetriamine) was used.
30% CA		50	-4	384	62	204		
30% APP		38	-27	376	63	162		
21 %APP+ 7%CA		31	-40	68	93	40		

100% PS	35	28		930		34	[24]	a novel phosphorous-nitrogen containing intumescent flame retardant, poly (diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB) was grafted on MWNT
0.2% MWNT		27	-4	523	44	28.8		
0.5% MWNT		28	0	517	44	29.1		
1% MWNT		34	21	425	54	28.2		
0.2% MWNT-PDPSB		32	14	462	50	27.4		
0.5% MWNT-PDPSB		33	18	453	51	26.6		
1% MWNT-PDPSB		34	21	444	52	26.1		
100% PS	35	59		1291		103	[81]	dimethylhexadecyl(2-methacryloyloxyethyl) ammonium chloride (MMA) di(2-methacryolyoxyethyl) methyloctadecylammonium chloride (DMA)
3% 30B cloisite		59	0	1017	21	99		
3% MMA		57	-3	954	26	94		
3% DMA		62	5	928	28	102		
100% PS	35	65		1293.6		110.2	[78]	In this study, two clays were compared: a natural clay, montmorillonite (MMT), and a synthetic clay, fluorinated synthetic mica (FSM). Organo FSM [dimethyl, di(hydrogenated tallow) ammonium treated FSM, or O-FSM: Source DOW chemicals Triphenyl, n-hexadecyl phosphonium treated FSM [P-FSM]: DOW Chemi. Cloisite 15A: O-MMT a compatabilizer (polystyrene-co-
1% NaFSM		52	-20	1201.3	7	117		
5% NaFSM		43	-34	1146.2	11	117		
10% NaFSM		41	-37	995.1	23	112		
1.9% O-FSM		63	-3	910.6	30	110		
9.3% O-FSM		49	-25	428.4	67	97		
18.6% O-FSM		51	-22	513.3	60	94		
1% NaMMT		57	-12	1110.75	14	110		
5% NaMMT		41	-37	993	23	111		
10% NaMMT		40	-38	791.9	39	106		
1.9% O-MMT		66	2	1079.5	16	111		
9.3% O-		58	-11	554.	57	98		

MMT				9				maleic anhydride, or SMA)
18.6% O-MMT		52	-20	445.8	65	97		
8.3% P-FSM		64	-2	586.2	55	100		
9.2% SMA + 8.3% P-FSM		65	0	557.3	57	100		
100% PS	35	65		806			[33]	In this study, polystyrene (PS)-encapsulated magnesium hydroxide-microencapsulated red phosphorus (MHRP) was prepared by in situ polymerization of styreneon the surface of MHRP in a high speed mixer PS-encapsulated MHRP is termed MHRP-T
10% MHRP		49	-25	382	53			
15% MHRP		43	-34	370	54			
20% MHRP		49	-25	309	62			
25% MHRP		53	-18	264	67			
10% MHRP-T		47	-28	390	52			
15% MHRP-T		44	-32	319	60			
20% MHRP-T		55	-15	242	70			
25% MHRP-T		49	-25	304	62			
100% PS	35	49		736		51	[87]	sample size : 10x10x1.5 mm^3 organically modified clay (DK4) poly(4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) is known as PDSPB
4% DK4		36	-27	579	21	49		
7.5% DK4		37	-24	505	31	49		
20% PDSPB		25	-49	502	32	47		
19.2 % PDSPB + 4% DK4		35	-29	527	28	48		
18 .5% PDSPB + 7.5% DK4		36	-27	488	34	48		
100% PS	35	72		922			[109]	Fe-MMT was modified by cetyl trimethyl ammonium bromide (CTAB)
1% Fe-OMT		50	-31	497	46			
3% Fe-OMT		49	-32	422	54			
5% Fe-OMT		45	-38	416	55			
100% PS	35	54		1196		100	[59]	MDH : magnesium

3% MDH		46	-15	1110	7	95		hydroxide ATH: alumina trihydrate Mg-Al LDH
5% MDH		50	-7	1043	13	95		
10% MDH		48	-11	919	23	94		
3% ATH		47	-13	630	47	84		
5% ATH		35	-35	1152	4	99		
10% ATH		35	-35	1048	12	101		
20% ATH		31	-43	863	28	96		
2% MDH+1% ATH		33	-39	621	48	80		
3.3% MDH+1.7% ATH		42	-22	1154	4	101		
6.7% MDH+3.3% ATH		37	-31	1095	8	101		
100% PS	35	50		1703			[110]	10x10x2 mm3 (sample size) FGO: functionalized grapheme oxide. FGO–PS composites were prepared by in situ polymerization.
0.5% FGO		30	-40	1127	34			
1% FGO		25	-50	1058	38			
2% FGO		20	-60	908	47			
3% FGO		20	-60	805	53			
100%	35	52		1120			[111]	
3% silicate mix		44	-15	1080	4			
3% silicate nanocomposite (intercalated and delaminated)		35	-33	567	48			
100% PS	35	53		1274		110	[112]	organically (HDBAC) modified zirconium phosphate OZrP SMA: poly(styrene-co-maleic anhydride)
SMA+ 1% OZrP		41	-23	1079	15	100		
SMA+ 3% OZrP		37	-30	1238	3	112		
SMA+ 5% OZrP		36	-32	1195	6	116		
SMA+ 20% IFR		39	-26	668	48	88		
SMA+2% OZrP+ 18% IFR		53	0	656	49	104		

100% PS	35	49		1250		97	[113]	ZrP was silyated by chlorotrimethylsilane (TMSCI) R stands for reflux
1% R-ZrP		32	-35	1075	14	93		
3% R-ZrP		36	-27	1170	8	93		
1% S-R-ZrP		30	-39	937	25	90		
3% S-R-ZrP		28	-43	1054	16	90		
5% S-R-ZrP		28	-43	1042	17	90		
8% S-R-ZrP		25	-49	985	21	83		

Table 10. Cone Calorimeter Data of Polypropylene Nanocomposites

Composition	Applied Heat Flux (kW/m^2)	Ignition Time (s)	Increase in Tig (%)	pHRR, kW/m^2	Reduction (%) of pHRR	THR, (MJ/m^2)	Paper Reference	Comments
100% PP	25	38		2207			[114]	
5% silica ash		35	-8	1337	39			
2.5% silica ash+2.5% silicone powder		30	-21	1398	37			
5% FR additive		30	-21	1059	52			
100% PP	35	48		1518			[25]	VGNCF: Vapor grown carbon nanofiber
4% VGCNF		35	-27	610	60			
8% VGNCF		47	-2	525	65			
12% VGNCF		49	2	547	64			

100%	50	20		1849		121	[62]	
1% Zn-Al LDH (2:1)		16	-20	1977	-7	136		
2% Zn-Al LDH (2:1)		17	-15	1543	17	113		
4% Zn-Al LDH (2:1)		14	-30	1382	25	126		
1% ZnMgAl LDH (1.5:.5:1)		18	-10	1938	-5	135		
2% ZnMgAl LDH (1.5:.5:1)		15	-25	1656	10	130		
4% ZnMgAl LDH (1.5:.5:1)		13	-35	1294	30	123		
1% ZnMgAl LDH (1:1:1)		18	-10	2004	-8	135		
2% ZnMgAl LDH (1:1:1)		14	-30	1546	16	132		
4% ZnMgAl LDH (1:1:1)		12	-40	1225	34	125		
1% ZnMgAl LDH (0.5:1.5:1)		14	-30	1997	-8	136		
2% ZnMgAl LDH (0.5:1.5:1)		14	-30	1512	18	133		
4% ZnMgAl LDH (0.5:1.5:1)		13	-35	1153	38	128		
1% MgAl LDH (2:1)		15	-25	1981	-7	141		
2% MgAl LDH (2:1)		16	-20	1764	5	139		
100% PP	35	8.8		1083			[115]	Halloysite nanotuves (HNT) with hollow nanotubular structure. Halloysite nanotubes(HNTs) are a kind of aluminosilicate clays
10% HNT		11.6	32	871	20			
30% HNT		5	-43	567	48			
10% modified HNT		15.3	74	763	30			
30% Modified HNT		19.5	122	519	52			
100%	50			1750.8			[73]	MMT: mont morillonite reactive compatibilizer hexadecyltrimethylammonium bromide (C16)
4% MMT				1092.3	37.0			
4% MMT + 2% C16				1282.5	27.0			
20% IFR				554.4	68.0			

20% IFR + 4% MMT				390.2	78.0			
20%IFR+4%MMT +2%C16				168.1	90.0			
100%	35	60		1136		296	[64]	organophilic montmorillonite (organo-clay, OMMT)
2% OMMT		58	-3	870	23	297		
5% OMMT		55	-8	459	60	295		
10% OMMT		56	-7	357	69	293		
5% MMT		51	-15	633	44	295		
100%	35	53		1792		219	[64]	Organic clay (termed OMMT) protonic clay(termed H-MMT) purchased from The maleic anhydride-grafted-polypropylene copolymer Octadecyltrimethyl ammonium chloride [C18H37NC(CH3)3ClK, denoted with C18]
1.2% C18		53	0	1463	18	215		
5%Na-MMT		45	-15	1196	33	216		
5% H-MMT		42	-21	1000	44	211		
5% OMMT		43	-19	996	44	210		
15% PP-g-MA		55	4	1740	3	219		
15%PP-g-MA+ 5%OMMT		50	-6	982	45	208		
100%	50	43		1845		118	[116]	
2.5% COPS		47	9	1953		118		
5% COPS		45	5	1889		114		
15% COPS		37	-14	1448	22	111		
25% COPS		38	-12	1191	35	108		
2.5%MAPS		44	2	2025		123		
5%MAPS		42	-2	1738	6	120		
15% MAPS		39	-9	1651	11	115		
25% MAPS		41	-5	1139	38	105		
100%	35	68		1141			[74]	MP: melamine phosphate PER: penta erythritol DPER: di penta erythritol TPER: tri penta erythritol
20% MP		51	-25	442	61			
30% MP		54	-21	323	72			
40% MP		52	-24	232	80			
30% MP+ 10% PER		40	-41	101	91			
20% MP + 20%		37	-46	92	92			

PER								
10% MP + 30% PER		50	-26	174	85			
40% PER		30	-56	382	67			
30% MP+ 10% DPER		50	-26	148	87			
20% MP + 20% DPER		45	-34	131	89			
10% MP + 30% DPER		36	-47	253	78			
40% DPER		45	-34	427	63			
30% MP+ 10% TPER		40	-41	167	85			
20% MP + 20%TPER		55	-19	160	86			
10% MP + 30% TPER		30	-56	218	81			
40%TPER		45	-34	263	77			
100% PP	25	96		1400			[117]	LIG :hydrolytic lignin
20% LIG		69	-28	410	71			melamine phosphate (MeP), aluminium hydroxide (Al(OH)3) monoammonium phosphate (AHP) poly vinyl alcohol (PVA) Ammonium poly phosphate (APP)
14% LIG + 6% Al(OH)3		55	-43	310	78			
14% LIG + 6% PVA		72	-25	500	64			
14% LIG + 6% MeP		57	-41	370	74			
14% LIG + 6% AHP		47	-51	325	77			
14% LIG + 6% APP		70	-27	395	72			
100% PP	35	52		1659			[66]	see reference for material preparation
4% Lauryl clay		54	4	1498	10			
12% lauryl clay		50	-4	1467	12			
20% lauryl clay		49	-6	989	40			
100%	35			1520			[69]	hydroxy silicone oil : HSO and the IFR system mainly consisted of the
30% IFR				402	74			
29% IFR+1% HSO				420	72			
28% IFR+2% HSO				370	76			
27% IFR+3% HSO				300	80			

25% IFR + 5% HSO				287	81			ammonium polyphosphate(APP) and pentaerythritol(PER)
100% PP	35	44		729.6			[75]	A novel charring agent, bis(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-1-oxo-4-hydroxymethyl) phenylphosphonate (BCPPO) APP: Ammonium polyphosphate and MA: Melamine as IFR
18% APP+ 6% MA + 6% BCPPO		27	-39	122.7	83			
100% PP	35	53		1896		102	[68]	new polymeric surfactant, containing 4-nonylstyrene, was used to modify sodium montmorillonite
3% clay		50	-6	1502	21	99		
10% clay		50	-6	1200	37	94		
16% clay		51	-4	882	53	95		
100% PP	35	41		426			[70]	sodium dodecyl sulfonate intercalated NiAl-LDHs (SDS-LDH) maleic anhydride-graft-polypropylene copolymer (PP-g-MAH) Flame retardantwas a commercial product of nitrogen–phosphorus containing intumescent
28% IFR+5% PP-g-MAH		34	-17	66	85			
28% IFR+5% PP-g-MAH+1.5% Organo clay		35	-15	63	85			
28% IFR+5% PP-g-MAH+1.5% SDS-LDH		37	-10	71	83			

								flame retardant (N–P IFR, JLS Flame Retardants Chemical Co., Ltd, Hangzhou, China,
100% PP	35	39					[118]	Nanoflaky manganese phosphate (NMP)
20% IFR		34	-13	483				
19% IFR+ 1% NMP		33	-15	333				
17% IFR+ 3% NMP		34	-13	275				
15% IFR+ 5% NMP		37	-5	325				
100% PP	35	55		1733		109	[43]	polycaprolactone—PCL-modified clay
30% 30BCL		40	-27	850	51	91		
30% 15APCL		52	-5	1565	11	122		
30%30BPCL		49	-11	704	59	94		
100% PP	35	53		1723		97	[67]	triclay contains styrene, lauryl acrylate and vinylbenzyl chloride
4% triclay		54	2	1530	11	98		
12% triclay		53	0	950	45	91		
20% triclay		48	-9	747	57	90		
32% triclay		40	-25	610	65	87		
100% PP	35	56		1103			[63]	POSS : polyhedral oligomeric silsesquioxane nanocomposites PSS: polysilsesquioxane composites
10% T8-POSS		50	-11	1325	-20			
10% Al-POSS		37	-34	624	43			
10% Zn-POSS		54	-4	1069	3			
100%	35	60		968		100		
5% me-PSS		60	0	786	19	96		
5% vi-PSS		72	20	616	36	94		
5% ph-PSS		53	20	872	10	96		
100%	35	50.2		789		156.6	[119]	Nf : nanofill SE3000 ZW3: organically
5%Nf		48	-4	739	6	173.4		

5% Nf+5%Pb+5%ZW3		45.6	-9	774	2	166.6		modified clay bentonite NanoBent APP: Ammonium polyphosphate Pb: Polybond 3150
5%Nf+15%APP		40.8	-19	399	49	167.9		
5%Pb+5%ZW3+15 %APP		42.6	-15	386	51	155.1		
100%	50	33		847		159.8		
5%Nf		37	12	1047	-24	174		
5% Nf+5%Pb+5%ZW3		36	9	1093	-29	164		
5%Nf+15%APP		39	18	426	50	168.2		
5%Pb+5%ZW3+15 %APP		24	-27	445	47	150		
100% PP	35	31		817		157	[71]	In this work, a novel char-forming agent (CNCA-DA) was used, which is an oligomeric triazine derivative containing aniline, triazine rings and ethylenediamino groups , and the APP and CNCA-DA is combined together to be a novel IFR system
20% IFR		25	-19	154	81	59		
20% IFR+ 1% La2O3		26	-16	144	82	53		
100% PP	50	20		1849		121	[62]	AA, AE, AC, AB and AD are code of LDH used in this study. Mole ratios of metals used (Zn,Mg,Al) could be found at the paper. AA (Zn:Mg:Al) = (O:2:1)
1% AE		16	-20	1977	-7	136		
2% AE		17	-15	1543	17	113		
4% AE		14	-30	1382	25	126		
1% AD		18	-10	1938	-5	135		
2% AD		15	-25	1656	10	130		
4% AD		13	-35	1294	30	123		
1% AC		18	-10	2004	-8	135		
2% AC		14	-30	1546	16	132		

4% AC		12	-40	1225	34	125		AB (Zn:Mg:Al) = (0.5:1.5:1) AC (Zn:Mg:Al) = (1:1:1) AD (Zn:Mg:Al) = (1.5:0.5:1) AE (Zn:Mg:Al) = (2:0:1)
1% AB		14	-30	1997	-8	136		
2% AB		14	-30	1512	18	133		
4%Ab		13	-35	1153	38	128		
1% AA		15	-25	1981	-7	141		
2% AA		16	-20	1764	5	139		
100% PP	50	24		800			[72]	see reference for material preparation BZn : Zinc Borate
30% NIFR		12	-50	160	80			
29% NIFR+1% BZn		12	-50	160	80			
28% NIFR+2% BZn		12	-50	150	81			
100% PP	50	25		3180			[46]	
0.5% MWNT		12	-52	690	78			
1% MWNT		11	-56	600	81			
2% MWNT		12	-52	780	75			
4% MWNT		14	-44	900	72			
100% PP	50	32		1025			[120]	IFR-PP matrix composites were perapred by blending 79% PP powder, 20% IFR,0.7% lubricant EBS and 0.3 % wt antioxidant 1010 using high speed mixer
20% IFR		20	-37.5	261	75			
20% IFR +5% La2O3		16	-50	247	76			
100%	50	37		1718			[65]	PP1 : 93% (PP+MAPP)+3% C16+4% MMT PP+MAPP = 4:1
93% (PP+MAPP)+3% C16+4% MMT		35	-6	959.4	44			
95% PP1+ 5% nanosized CaCO3		35	-6	751.3	56			
88% (PP+MAPP)+ 3% C16+4%		34	-9	799.5	54			

MMT+5%CaCO3								
95% (PP+MAPP)+ 5% nanosized CaCO3		33	-11	1029.5	40			
100% PP	50	31		1400			[76]	APP+PA6 blend = 3:1 interfacial agent: EBuAMA and EVA EBuAMA : ethylene-butyl acrylate-maleic anhydride EVA : ethylene vinyl acetate
26.25% APP+8.75% PA-6+2.5% EBuAMa		29	-6	290	79			
26.25% APP+8.75% PA-6+5% EBuAMa		28	-10	320	77			
26.25% APP+8.75% PA-6+7.5% EBuAMa		28	-10	440	69			
26.25% APP+8.75% PA-6+5% EVA8		29	-6	240	83			
26.25% APP+8.75% PA-6+5% EVA19		27	-13	310	78			
26.25% APP+8.75% PA-6+5% EVA24		27	-13	250	82			
100% PP	50	24		1620		110	[99]	MWNT : multi walled C nanotube
97% PP+ 3% MWNT		17	-29	931	42	102		
100% PP	50	39		998			[121]	basic formulation: PP/APP/DPER (80:15:5) mass ratio APP: ammonium poly phosphate DPER: di penta erythritol; Zn salts were used to improve LOI
80%PP+15%APP+ 5%DPER		35	-10	533	47			
79%PP+15%APP+ 5%DPER+1%ZnO		32	-18	457	54			
79%PP+15%APP+ 5%DPER+1%ZnSO4.7H2O		34	-13	409	59			
72% PP+28% PPgMA	35	62		1435.4		122.9	[122]	PPgMA: polypropylene graft malaeic anhydride Organoclays were used. See referance paper for details. clay#1 : 0 day
65.9%PP+25.6%PPgMA+8.5%Clay#1		59	-5	498.4	65	115.8		
66.3%PP+25.6%PPgMA+7.9%Clay#2		65	5	518.6	64	113.7		
66.3%PP+25.6%PPgMA+7.9%Clay#3		66	6	510.1	64	112.3		

66.3%PP+25.6%PPgMA+7.9%Clay#4		68	10	494.1	66	112.9		extraction clay#2: 1 day extraction clay#3 : 2 day extraction clay#4:3 day extraction clay#5 : 4 day extraction
66.3%PP+25.6%PPgMA+7.9%Clay#5		70	13	491	66	113.4		
100% PP	35	50		1642		60	[39]	acrylic acid pentabromobenzyl ester (ACPB) methacrylate acid pentabromo pentabromobenzyl benzyl ester (MEPB) butyric acid pentabromobenzyl ester (BUPB) pentabromobenzyl ester polyacrylate (PBPA) Cloisite 30B clay
3% ACPB+3% 30B		44	-14	1656	-1	72		
3% BUPB+3% 30B		48	-5	1281	22	73		
3% MEPB+3% 30B		46	-9	957	42	74		
3%PBPA+3% 30B		47	-7	762	54	61		

Table 11. Cone Calorimeter Data of Low Density Polyethylene Nanocomposites

Composition	Applied Heat Flux (kW/m^2)	Ignition Time (s)	Increase in Tig (%)	pHRR, kW/m^2	%Reduction of pHRR	THR, (MJ/m^2)	Paper Reference	Comments
100% LDPE	35	71		1835			[66]	
4% Lauryl clay		72	1	1699	7			
12% lauryl clay		70	-1	1657	10			
20% lauryl clay		56	-21	1031	44			
100% LDPE	35	72		2067			[68]	new polymeric surfactant, containing
3% clay		87	21	1626	21			

10% clay		76	6	1216	41			4-nonylstyrene, was used to modify sodium montmorillonite
16% clay		75	4	942	54			
100% LDPE	35	69		1794		95	[67]	triclay contains three components, styrene, lauryl acrylate and vinylbenzyl chloride
4% triclay		65	-6	1790	0.2	91		
12% triclay		71	3	1162	35	93		
20% triclay		56	-19	727	59	90		
32% triclay		51	-26	542	70	77		
100% LDPE	35	76		1740		114	[43]	polycaprolactone—PCL-modified clay
30% 30BCL		75	-1	1156	34	107		
30% 15APCL		79	4	1484	15	98		
30%30BPCL		71	-7	861	51	92		
100% LDPE	35	74		2128		113	[116]	
2.5% COPS		73	-1	1869	12	118		
5% COPS		73	-1	2048	4	118		
15% COPS		66	-11	1643	23	112		
25% COPS		59	-20	1482	30	101		
100% LDPE	35	74		2128		113		
2.5% MAPS		68	-8	2088	2	112		
5% MAPS		63	-15	1780	16	110		
15% MAPS		56	-24	1678	21	104		
25% MAPS		45	-39	1227	42	99		
100% LDPE	35	92		806			[94]	IFR is based upon based on the esterification of melamine phosphate and pentaerythritol plus APP. Where wt ratio is (MP+PER):APP=2:1 chelated copper(II)salicylaldehyde (CuSA) salicylaldoxime, (CuSAO)
30% IFR		78	-15	197	76			
29.8% IFR + 0.2% CuSA		124	35	206	74			
29.8% IFR + 0.2% CuSAO		151	64	209	74			
100% LDPE	50	34		2089			[93]	oleate containing LDH : ZnAl and MgAl
1% ZnAl		33	-3	2038	2			
3%ZnAl		32	-6	1822	13			
7% ZnAl		23	-32	1452	30			
10% ZnAl		20	-41	868	58			

10% MgAl		22	-35	1831	12			
100% LDPE	30	125		800			[91]	
2.43% MgAl LDH		124	-1	590	26			
4.72% MgAl LDH		102	-18	510	36			
6.89% MgAl LDH		107	-14	410	49			
8.95% MgAl LDH		108	-14	350	56			
12.75% MgAl LDH		112	-10	295	63			
16.20% MgAl LDH		114	-9	280	65			
100% LDPE	50	38		1888		148	[92]	Antimony oxide (AO) Decabromophenyloxide (DECA) Melamine polyphosphate (MPP) PHOS-CHEK (APP) Fyrolflex RDP (RDP) Triphenyl phosphate (TPP) These are all commercial grade FR
10% ZnAl LDH		19	-50	796	58	118		
20% ZnAl LDH		18	-53	520	72	116		
10% APP		28	-26	1965	-4	123		
20% APP		31	-18	1226	35	110		
10% Melapur		23	-39	1425	25	125		
20% Melapur		26	-32	1400	26	135		
10% ZnAl+10%APP		17	-55	1077	43	128		
10% ZnAl+10%Melapur		14	-63	835	56	127		
10% RDP		41	8	1391	26	122		
20%RDP		23	-39	1249	34	108		
10% TPP		41	8	1795	5	135		
20% TPP		35	-8	1434	24	122		
10% ZnAl+10% RDP		22	-42	1626	14	124		
10% ZnAl+10% TPP		26	-32	1736	8	138		
20% DECA		47	24	1724	9	109		
16% DECA + 4% AO		54	42	1946	-3	89		
10% ZnAL+8% DECA+2% AO		20	-47	1431	24	122		
100% LDPE	50	41		1624		65	[90]	alumina trihydrate

20% ATH		29	-29	893	45	60		(ATH)
40% ATH		33	-20	437	73	51		
20% ATH + 10% Lauryl clay		23	-44	436	73	55		
20% ATH+20%Lauryl clay		23	-44	400	75	53		
40% ATH+10%Lauryl clay		29	-29	263	84	47		
50% ATH+10%Lauryl clay		34	-17	202	88	41		
60% ATH+10%Lauryl clay		36	-12	127	92	35		
100% LDPE	35	73		1949		100	[39]	acrylic acid pentabromobenzyl ester (ACPB) methacrylate acid pentabromo pentabromobenzyl benzyl ester (MEPB) butyric acid pentabromobenzyl ester (BUPB) pentabromobenzyl ester polyacrylate (PBPA) Cloisite 30B clay
3% ACPB + 3% 30B clay		75	3	1577	19	92		
3% PBPA + 3% 30B clay		64	-12	1817	7	95		
3% BUPB + 3% 30B clay		75	3	1190	39	88		
3%MEPB + 3% 30B clay		67	-8	1762	10	97		
100% LDPE	35			1268			[96]	Magnesium hydroxide sulfate hydrate (MHSH) whiskers. Red phosphorous (containing 85 wt.-% phosphorous) microencapsulated with magnesium hydroxide and melamine-formaldehyde resins (MRP) was prepared in laboratory. Ignition times were not recorded in the paper
20% MHSH				605	52			
40% MHSH				403	68			
60% MHSH				167	87			
38% MHSH+ 2% MRP				194	85			
33% MHSH+ 7% MRP				115	91			
30% MHSH+ 10% MRP				100	92			
25% MHSH+ 15% MRP				205	84			
6% EVA+40% MHSH				277	78			
12% EVA+40%MHSH				283	78			

18% EVA+40%MHSH				300	76			
24% EVA+40%MHSH				329	74			
100% LDPE	35	44		523		105	[89]	diphenylmethanamine spirocyclic pentaerythritol bisphosphonate (PSPD) which is a novel IFR
5 %OMMT		41	-7	493	6	103		
10% PSPD		54	23	485	7	83		
20% PSPD		59	34	383	27	76		
15% PSPD+ 5%OMMT		56	27	253	52	80		
100% LDPE	50	50		972			[95]	Magnesium di-hydroxide (MDH) Completely hydrated Dolime $Ca(OH)_2$. $Mg(OH)_2$ Semi-hydrated Dolime $Ca(OH)_2$. $yMg(OH)_2$. (1- y)MgO Hydrated lime $Ca(OH)_2$
50% $Mg(OH)_2$		90	80	220	77			
50% $Ca(OH)_2$		77	54	252	74			
50% $Ca(OH)_2.Mg(OH)_2.MgO$		78	56	211	78			
50% $Ca(OH)_2.Mg(OH)_2$		74	48	231	76			

Table 12. Cone Calorimeter Data of High Density Polyethylene Nanocomposites

Composition	Applied Heat Flux (kW/m^2)	Ignition Time (s)	Increase in Tig (%)	pHRR, kW/m^2	%Reduction of pHRR	THR, (MJ/m^2)	Paper Reference	Comments
100% HDPE	35	91		1902		128.2	[25]	
8% vgncf		100	10	554	71	118.3		
100% HDPE	35	85		896		133	[123]	US : Single screw ultra sound intusion process ATH : aluminium trihyroxide ZB: zink borate OBEN: sodium bentonite clay
50% ATH		65	-24	477	47	119		
30%ATH+3% ZB3		61	-28	581	35	121		
30% ATH+3%ZB3(US)		72	-15	545	39	123		
30% ATH+ 3%ZB3+2%OBEN2		65	-24	526	41	119		
30%ATH+ 3%ZB3+2% OBEN2 (US)		69	-19	503	44	119		
100% HDPE	50	75		1640			[97]	Na$^+$ montmorillonite (MMT) was used as FR. Hexadecyl trimethyl ammonium bromide (C16) as reactive compatibilizer
5% MMT		65	-13	1500	9			
5% MMT+4% C16		50	-33	1120	32			
100% HDPE	35	113		1470		310	[124]	reactive (N-g-trimethoxylsilanepropyl) octadecyldimethylammonium chloride was used as intercalating agent to modify MMT
2% JS		184	63	670	54	320		
5% JS		157.5	39	620	58	320		
10% JS		114	1	540	63	310		
15% JS		103	-9	390	73	300		
100% HDPE	50	68		1146		272	[98]	Ethylene Vinyl Acetate copolymer was used as compatibilizer MDH: Magnesium hydroxide, Vertex 60 HST was chosen as a FR
1% MMT		50	-26	989	14	360		
2% MMT		46	-32	896	22	259		
3% MMT		42	-38	845	26	257		
4% MMT		36	-47	815	29	331		
5% MMT		34	-50	720	37	324		
1% OMMT		64	-6	819	29	386		

2% OMMT		58	-15	746	35	304		OMMT: MMT modified with quarternary ammonium salt.
3% OMMT		52	-24	510	55	261		
5% OMMT		50	-26	382	67	275		
5% OMMT + 5% EVA		82	21	425	63	257		
10% MDH		68	0	688	40	312		
20% MDH		70	3	439	62	304		
30% MDH		72	6	292	75	295		
35% MDH		76	12	244	79	275		
40% MDH		78	15	214	81	270		
45% MDH		88	29	157	86	213		
50% MDH		102	50	134	88	200		
55% MDH		104	53	124	89	184		
45% MDH+5% EVA + 5% MMT		86	26	131	89	205		
45% MDH+5% EVA + 5% OMMT		86	26	137	88	187		
100% HDPE	35	56		660		84.8	[125]	Maleic HDPE-g-MA(CMG 9804); ND: nano diamond powder HDPE/ND nanocomposites were fabricated via melt blending
1% HP-m-ND		62	11	465	30	79.5		
1% HPgND		65	16	420	36	77.1		
2% HPgND		65	16	480	27	78.6		
100% HDPE	50	39		1700		125	[99]	
3% MWNT		37	-5	920	46	111		
100% HDPE	50			1226			[126]	CeHPP: cerium phenyl phosphonate BFR: bromin containing FR which contains DBDPEand Sb2O3 in 4:1 wt ratio Deca bromo diphenyl ethane (DBDPE)
13% BFR				1123	8			
10% BFR+3%CeHPP				1030	16			
10% BFR+2.25 CeHPP+ 0.75% MWNT				1049	14			
10% BFR+3%Ce-MWNT				920	25			
10% BFR+3%MWNT				1038	15			
20% Plb	50	51		2476			[100]	ZR2: MMT modified

20% Plb+ 20% MPP		75	47	1213	51			with qurternary ammonium salt ZGl: MMT modified with aluminium hydrogen sulfate Plb: malaeic grafted polyethylene MPP: melamine poly phosphate APP: aluminium polyphosphate
20% Plb+ 20% APP		43	-16	902	64			
20% Plb+2% ZR2		34	-33	446	82			
20% Plb+2%ZGl		44	-14	346	86			
20%Plb+2%ZR2 +20%MPP		36	-29	349	86			
20%Plb+2%ZGl +20%MPP		32	-37	262	89			
20%Plb+2%ZR2 +20%APP		34	-33	404	84			
20%Plb+2%ZGl +20%APP		33	-35	428	83			

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