THERMAL, MECHANICAL AND FLAMMABILITY STUDIES OF FLAME-RETARDANT POLYMER NANOCOMPOSITES

A Dissertation

by

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ABSTRACT

Polymers are widely used in our day-to-day lives and we are often oblivious to the fire hazard imposed by these hydrocarbon-based materials. The current study introduces the application of fire retardant nanofillers for enhanced flame retardancy as a potential remedy against flame spread. With the objective of understanding how the flame retardant nanofillers work; the thermal, mechanical and fire reaction properties have been investigated. For this purpose, neat polystyrene (PS), PS-silica and PS-montmorillonite (MMT) have been prepared via *in-situ* polymerization method. The thermal degradation mechanism of the neat polymer and polymer nanocomposites and the effect of nanoparticle loading on thermal properties have been investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) equipment. TGA and corresponding derivative TG (DTG) results show that there has been improvement in thermal stability for the nanocomposites in terms of higher onset temperature of degradation and 72-87% more char yield with respect to neat PS. The mechanical test revealed that increased loading reduces hardness for the nanocomposites compared to the neat polystyrene.

To obtain the full scenario of the performance of the flame-retardant polymer nanocomposite system, it is important to explore the aspect of a real fire scenario in cone calorimeter. According to the fire reaction properties as measured in the cone calorimeter,

both neat polystyrene and polystyrene nanocomposites have shown the trend of a thermally thick charring polymer in the heat release rate over time data. The nanocomposites had an overall better flame retardancy than the neat polystyrene in terms of lower peak heat release rate, lower average mass loss rate and enhanced char formation. The nanocomposites had also reduced smoke emission with lower CO and CO_2 yield compared to the neat polystyrene.

It was concluded that the addition of nanosilica and nanoclay in small loading can significantly improve thermal stability, fire reaction properties and mechanical properties; however, higher loading may result in agglomeration and reduction in hardness.

DEDICATION

I dedicate my dissertation to my husband Md. Abu Obaida and my son Aryan Ahmed who have been my inspiration throughout my journey of achieving the doctoral degree.

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This work was supervised by a dissertation committee consisting of Professor Dr. M. Sam Mannan [advisor] and Professors Dr. Zhengdong Cheng and Dr. Charles Glover of the Artie McFerrin Department of Chemical Engineering [Home department] and Professor Dr. Debjyoti Banerjee of the department of Mechanical Engineering in Texas A&M University.

Part of the analysis as presented in chapter 5 was conducted using the cone calorimeter situated in Fire Protection and Safety Engineering Technology department in Oklahoma State University in collaboration with Dr. Qingsheng Wang and his team. The resulting work was sent for publication to Journal of Thermal Analysis and Calorimetry which is currently under review.

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NOMENCLATURE

DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
FIGRA	Fire growth rate index
FPI	Fire performance index
HRR	Heat release rate
MARHE	Maximum average rate of heat emission
MLR	Mass loss rate
MMT	Montmorillonite
NFPA	National Fire Protection Association
PHRR	Peak heat release rate
PMLR	Peak mass loss rate
PMMA	Poly (methyl methacrylate)
PS	Polystyrene
TGA	Thermogravimetric analysis
THE	Total heat evolved
THR	Total heat release
TSP	Total smoke production
TSR	Total smoke release

SEA	Specific extinction area
SP	Smoke parameter
SPR	Smoke production rate

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1. INTRODUCTION AND LITERATURE REVIEW*

1.1 Background

Advancements in polymer science has led to the application of polymers in a wide variety of products including electronics, vehicles, computers, furniture, clothing. Usually, polymers are produced as commercialized products in the form of bulk product, such as films, coatings, fibers. Polymers are hydrocarbon-based products which make them combustible and/or flammable [1]; the thin parts are more combustible in comparison to molded parts [2]. Polymeric materials, therefore, pose a fire hazard in general. In fact, according to statistics provided by National Fire Protection Association (NFPA), the first item(s) that typically catch fire in a home structure fire are polymeric materials. Table 1 involve products that have polymer as an active ingredient.

In fact, polymers have played role in rapid spread of fire in many of the incidents in industry, home and public venues. The tragic loss of 48 lives and 200 injuries sustained in Dublin Startdust disco fire in 1981 is one such incident where the combined effect of

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* "Study of thermal and mechanical behaviors of flame retardant polystyrene-based nanocomposites prepared via *in-situ* polymerization method." by L. Ahmed, B. Zhang, S. Hawkins, M. S. Mannan and Z. Cheng, 2017. Journal of Loss Prevention in the Process Industries, Volume 49, Part B, September 2017, pp.228-239, Copyright [2017] by Elsevier. Part of this section is reprinted with permission from Elsevier Ltd.

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burning seating and wall linings made of polyvinylchloride (PVC) over polyurethane foam and polyester played a major role in the augmented fire growth and release of toxic gases and smoke [4, 5].

Table 1 Partial list of the first item ignited on a home structure fire during 2010-14 annual average data (adapted from [3])

Items first caught on fire	Fires	Fatalities	Injuries	Property damage (in million USD)
Clothing	7400	140	490	189
Interior wall covering without drapes	6600	100	250	280
Upholstered furniture	5600	440	700	269
Cabinetry	5600	40	310	165
Structural member of framing	20500	130	410	1088
Electrical wire and cable insulation	17000	110	430	401
Exterior wall covering or finish	13900	30	230	494
Appliance housing or casing	13100	20	310	133
Mattress or bedding	9300	340	1270	317

The PVC used in the judo mats in the Mayfield Leisure Center in Belfast incident in 1984 was responsible for aiding in rapid fire growth that claimed 6 lives including that of 2 children [5]. Plastic components of the intermediate bulk containers (IBC) played a role in the spread of fire in the incident of Distillex fire in North Shield in 2002 [6]. The plant fire originated in the waste skit from the sparks of an angle grinder and later spread to the storage area. The fire aggravated as a result of mix of chemicals and melt plastics from the IBC that eventually flowed offsite [6]. In a more recent fire incident at Grenfell Tower in London, UK, it is alleged that the exterior cladding made of composites encasing polyethylene insulation could be responsible for the rapid fire growth [7].

Despite the fact that polymers pose a fire hazard, it is neither pragmatic nor possible to eliminate the use of polymers. Rather, it is more practical to look for alternatives that will ensure protection against fire. Fire safety of the polymeric materials can be enhanced by increasing ignition resistance, reducing heat release, decreasing amount of toxic and smoke products, *etc.* [8].

Using inherently flame retardant or thermally stable polymers is one potential way to reduce the possibility of a fire spread and consequent damage associated with the fire. However, due to the high cost, this alternative is often not a viable option. Considering the expenses involved and ease of processing, applying flame retardant additives to polymers is an efficient way to mitigate the fire hazard. Flame retardants reduce fire hazard by interfering with the polymer combustion process [9].

Polymer nanocomposites comprise a new area of development for fire retardancy with no potential harmful effect on the environment. This new class of materials offers an opportunity for exploring new behavior and functionality beyond what conventional materials offer. Polymer nanocomposites have the potential to bring remarkable improvement in terms of mechanical, thermal, optical, magnetic and electrical properties [10]. As a result, polymer nanocomposites have been investigated for potential applications for flame retardancy, electronic and optical applications [11]. For the current study, the flame retardancy effect and subsequent thermal and mechanical behaviors of polymer nanocomposites will be investigated.

However, to obtain the full scenario of the performance of the flame-retardant polymer nanocomposite system, it is important to explore the aspect of a real fire scenario. Small-scale tests using thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) can give insight into the thermal degradation pattern of the nanocomposites and the neat polymer; but these methods cannot comprehend the impact of heat release rate, time to ignition, smoke release and other parameters that affect the flame spread and the corresponding human reaction to the fire. Therefore, the aim of the present study is to extend the scope to understand the impact of different types and loadings of nanofiller additives on the fire reaction properties of the neat polystyrene. Cone calorimeter is a bench scale test method predominantly used to give insight to fire reaction properties during a well-developed fire scenario. It is a well-recognized instrument for testing of fire properties and has been accepted as a standard by International Standards Organization (ISO-5660) and American Society for Testing and Materials (ASTM E-1354). It functions upon the principal that oxygen consumption is in proportional relationship with the heat release rate [12]. Cone calorimeter illustrates the fire behavior of a material using a relatively smaller size specimen which makes it a more economic test method. The limiting factors are that it does not cover flame spread and generates data for one-dimensional burning. Despite the limitations, cone calorimeter can provide reasonable insight into the material's fire performance in a developing fire [13] and therefore, has been used as a standard test method to measure fire reaction properties of flame retardant polymeric materials. Overall, by tying the analysis of fire reaction properties of flame retardant nanocomposite system in cone calorimeter with the investigation on thermal and mechanical attributes; this study can contribute to developing our understanding of how the flame-retardant additives can be effectively used in fire control and therefore, saving lives and properties.

1.2 Overview of modern flame retardants

Halogen-based flame retardants are one of the most diversified kind of additives. They function in the gas phase by scavenging free radicals and thus reduces the heat release rate [2, 14, 15]. The reduction of heat release can be enhanced by increased char formation and often times phosphorus-based flame retardants or antimony oxides are used synergistically with halogen-based flame retardants as a means of improving fire retardance performance [16]. Examples of halogen-based flame retardants include decabromodiphenyl oxide with antimony trioxide, decabromodiphenyl ether, organomontmorillonite with antimony oxide [17]. The effectiveness of this type of flame retardants is often dictated by the type of halogen being used. Fluorine containing flame retardants are steady and they do not emit radicals of halogens if the polymer decomposition temperature becomes near the temperature of the additive. Iodinated organics have the low thermal stability that prevents their use in commercial polymeric products. Bromine and chlorine can easily get released since they have a low bonding energy requirement for bonding with carbon. As a result, they take part in combustion procedure if released. Due to environmental and toxicological concerns, halogenated flame retardants have been limited in use.

Among the non-halogenated flame retardants, phosphorus-based flame retardants are popular and are mainly used with thermoplastics and thermosets. These type of flame retardants includes a variety of products such as elemental red phosphorus, inorganic phosphates, phosphinates, phosphonates, phosphine oxides and chloro-organophosphates. These flame retardants are incorporated into the polymer during synthesis procedure and they can be active in the condensed and/or gas phase [2, 15, 18].

Among the nitrogen-based flame retardants, melamine is a thermally stable product containing 67% nitrogen. It has high thermal stability. It is commonly used in polyurethane foams and in intumescent coatings [2, 15].

The addition of small amounts of silicon-based compound such as silica, silicones, organosilanes, silicates and silsesquioxanes are known to enhance fire retardancy of polymeric materials [15] and this falls under the category of silicon-based retardants. Borates are another type of inorganic type of additives which display properties of flame retardancy. Water soluble borates such as boric acid, borax (sodium borate) have very commonly been used as flame retardants in textiles, paper boards, wood *etc.* These function in a way different then insoluble in water but thermally more stable borates as zinc borates. Among the zinc borates, one of the frequently used is $2ZnO.3B_2O_3.3.5\ H_2O$ [2, 15].

Another popular class of flame retardants is the intumescent flame-retardant systems that function by creating a swollen char which acts as an insulating barrier. This barrier reduces heat transfer between polymer and heat source. An intumescent system is generally composed of three components, namely: a char former or carbonizing agent, an acid source and a blowing agent. The acid (*e.g.,* ammonium polyphosphate, APP) catalyzes the dehydration reaction leading the carbonizing agent (*e.g.,* polyol) to form char. The blowing agent (*e.g.,* melamine, urea, guanidine) decomposes and releases gas that foams the carbon char [18].

Nanometric particles are relatively new class of flame retardants and these additives enhance mechanical, fire and thermal properties when dispersed in polymer metrics. Depending upon the geometry and chemical structure of the nanometric particles, the fire retardancy varies. Some common nanoparticles are: layered materials (*e.g.,* nanoclay), particulate materials (*e.g.,* POSS (polyhedral oligosilsesquioxane)) and fibrous material (*e.g.,* carbon nanotubes) [15]. Table 2 summarizes some of the common categories of flame retardants and their relative advantages and disadvantages.

As evident from Table 2, many of the flame retardants have shown good thermal stability. However, some of them have limited application due to environmental scrutiny or due to inefficient thermal stability performance. Some flame retardants generate toxic gas and smoke upon heating which compromises the purpose of fire safety. From that perspective, research interest has been diverted toward developing an effective, yet environment friendly, flame retardant polymer composite system.

Table 2 Different flame retardants and relative advantages and disadvantages [14, 15, 19]

Type of flame retardant	Advantage	Disadvantage
Mineral Filler (1920's) Endothermal cooling (*e.g.,* metal hydroxides, metal carbonates)	▪ Environment friendly ▪ Low smoke ▪ Inexpensive	▪ Limited fire performance window ▪ High loading needed that often compromises the mechanical property of polymer
Halogenated (1930's) Works in vapor phase	▪ Cost Effective ▪ Optimal Properties	▪ Increase in smoke release ▪ Releases corrosive gas upon heating ▪ Under environmental scrutiny
Phosphorus (1940-50's) Works in vapor or condensed phase (*e.g.,* ammonium polyphosphate and triphenyl phosphate)	▪ Used for synergistic application ▪ Low loading level required ▪ Functions well in high heat flux fire conditions	▪ More CO and smoke generation ▪ Under environmental scrutiny
Intumescent Condensed (*e.g.,* ammonium phosphate-acid source, graphite)	▪ Versatility in application mode ▪ Robust fire protection	▪ Issues with water absorption ▪ Low thermal stability
Inorganic (*e.g.,* borates, silicates, stannates)	▪ Minimal environmental impact	▪ Expensive
Polymer Nanocomposites (Newest technology) Works strictly in condensed phase	▪ Light-weight application ▪ Ease of preparation ▪ Lower peak heat release rate ▪ Inhibition of polymer dripping	▪ Less information is available since it is a new technology

1.3 Mechanism of flame retardant

Most of the flame-retardant additives commercially used achieve fire protection for a polymer through one or more of the following mechanisms:

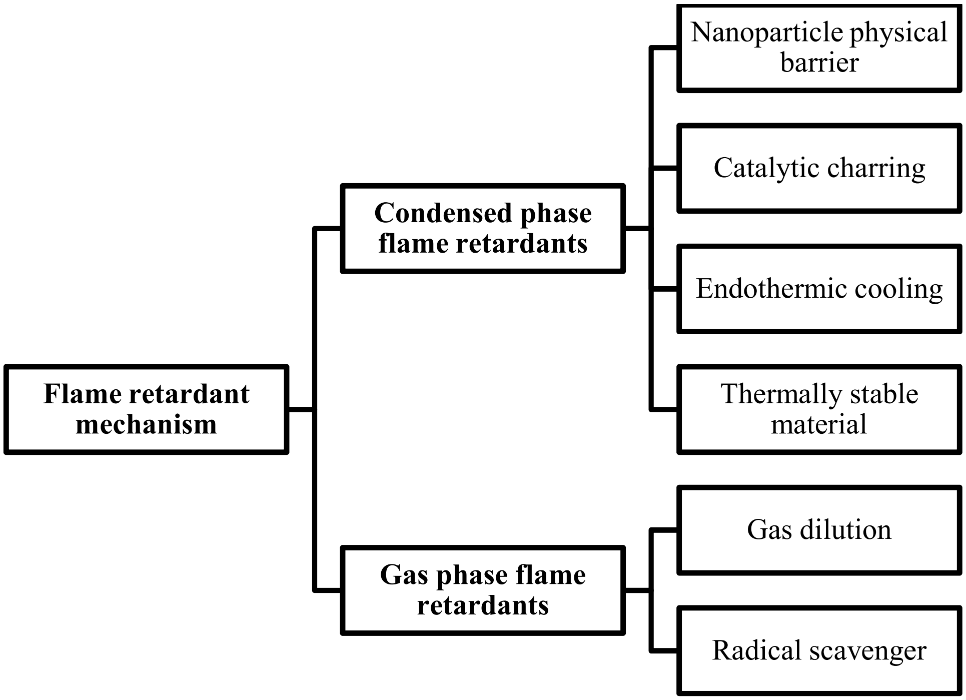

Figure 1 Classification of flame retardant additives based on the flame-retardant mechanism

1.3.1 Nanoparticle physical barrier

Polymeric nanocomposites have demonstrated great potential as flame retardant materials and possess high thermal stability. The cutback of heat release rate (HRR) and an increase in thermal stability are induced by the presence of nanoparticles in polymers [20]. The combustion behavior of polymer nanocomposites due to the addition of nanofillers is because of the twofold mechanism; namely: physical barrier effect and catalytic charring effect [21].

Physical barrier effect, also known as surface ceramization process, occurs during the combustion when nanoparticles form a network of floccules. These floccules combine with an apparently small portion of carbonaceous char. This char or ceramic layer is thermally stable and acts as a barrier to heat transfer between the material and flame and flame and degradation products. It provides thermal shield by acting as surface re-irradiant [21].

1.3.2 Catalytic charring

Extensive charring of the polymer material is the eventual target in fire retardancy. It would allow the formation of char in presence of a heat source and limit potential production of combustible products thereby ensuring safety [21]. These types of flame retardants react with the thermally decomposing polymer by creating new, more stable bonds while breaking the old bonds by heat. Examples of this kind include phosphorus flame retardants, intumescent *etc.* These materials mainly operate in the condensed phase by binding up the polymer into highly cross-linked char. Some flame-retardant additives, *e.g.,* phosphorus-based additives can have some vapor phase activity [14, 22].

Polymer degradation mechanism can be of two types, namely: non-charring and charring mechanism.

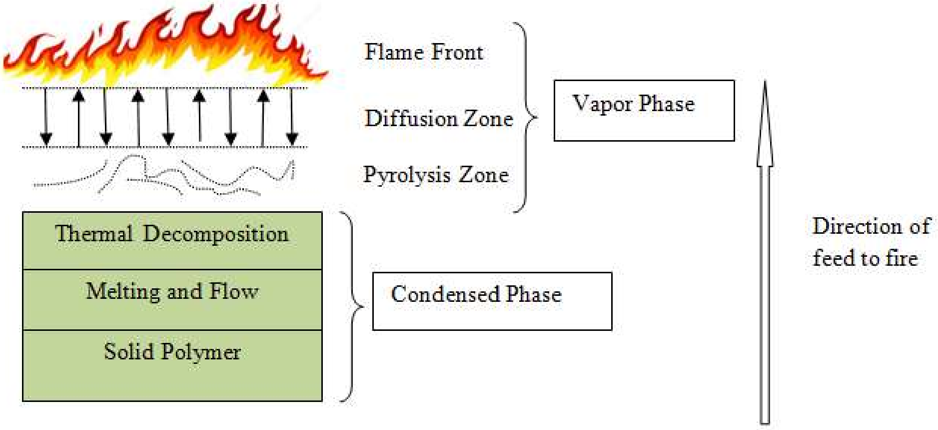

Figure 2 Physical heat-induced decomposition behaviors for non- charring polymers

Polymers degrade when heated beyond glass transition temperature (T_g) in a process known as pyrolysis. It is the temperature beyond which the polymer chains slip past one another to form a semi-liquid or rubbery phase from their initial solid phase. A polymer can lose its mechanical integrity, *i.e.*, stiffness and modulus above this temperature. The general burning pattern of a polymer is depicted in Figure 2. As material is heated in a typical fire; it begins to become liquid from solid and can flow. As further heat is induced, thermal decomposition occurs [22]. The thermal decomposition of polymers involves interacting chemical and physical processes. The physical changes such as melting, and charring can change the burning and decomposition polymer. After pyrolysis, the material will go to the gas-phase, mix with oxygen and will combust. This combustion process releases further heat, which continues to engage into more pyrolysis and combustion through convection and other fire-induced thermal flows until a dearth of heat, oxygen and/or fuel causes the fire to cease [14].This is essentially the non-charring mechanism, shown graphically in Figure 2.

Generally, a solid polymer upon heating to a certain temperature will decompose and produce a varying quantity of volatile products and solid residue. The residue can be carbonaceous char, inorganic or a combination of both [23].

In the charring mechanism (Figure 3) pyrolysis forms lighter compounds from the original polymer as it does in the non-charring mechanism. These lighter compounds, rather than diffusing away from the surface and then burning, form cross-linking within the polymer. The highly cross-linked material then turns into char that covers the unburned cross-linked material with an unreacted polymer melt and solid below it. The char layer slows down the rate of fuel release or pyrolysis products into the gas phase for combustion. This char formation lowers the heat release rate.

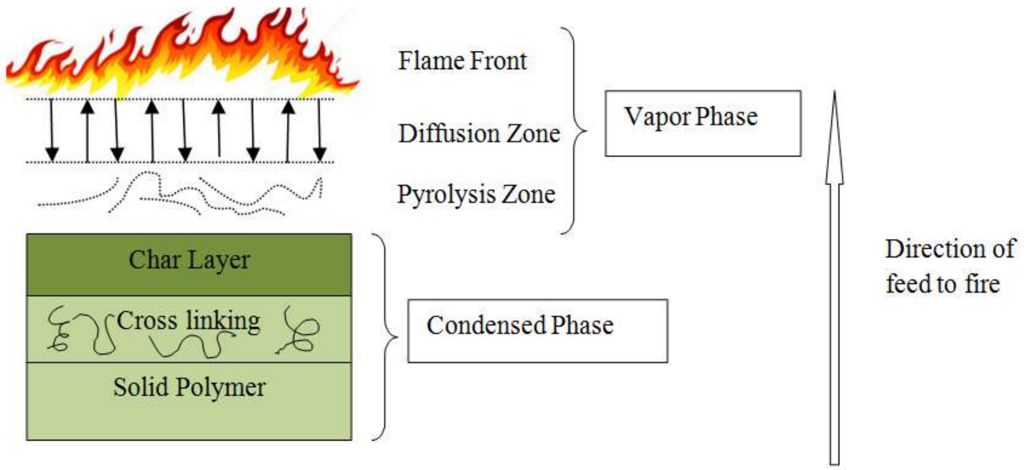

Figure 3 Physical heat-induced decomposition behaviors for charring polymers

Nanofillers exhibiting physical barrier effect during polymer burning slow down the rate of heat release. The total rate of heat release remains the same; however, since the entire polymer is eventually burned. In contrast, the total heat release rate is reduced with catalytic char forming nanofillers. It is because of the formation of char that reduces the carbon supply to the flame keeping it in the condensed phase. The concept of synergism comes from the viewpoint that in most cases, the nanofillers causing the physical barrier or the catalytic charring effect is not very effective itself to reduce the overall heat release rate. Hence it is important to conduct more research about the synergism of these two effects in order to achieve higher fire retardancy performance levels.

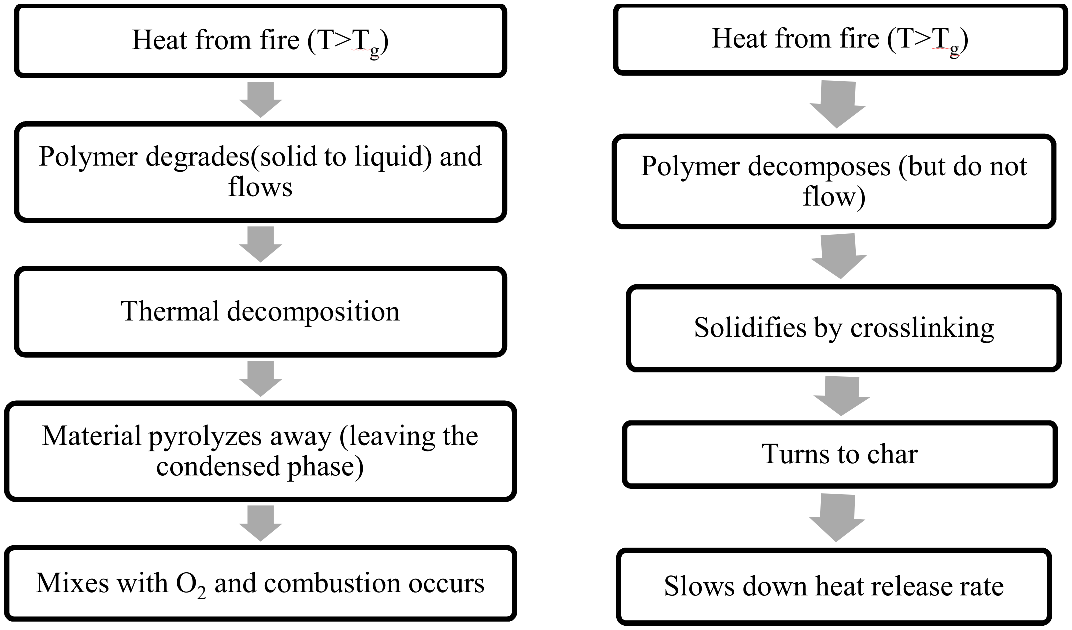

Figure 4 Flowchart showing steps of non-charring (left) and charring mechanism (right)

1.3.3 Endothermic cooling

Endothermic cooling type flame retardants may function in both condensed and gas phase. When the polymer composite is introduced to heat, this type of filler decomposes endothermically which cools off the polymer. Simultaneously, the additive gives off non-flammable gases like carbon dioxide and water vapor that dilutes the fuel source that is the polymer. The additive is also known to leave a residue that essentially protects the underlying polymer. Examples of this type of additives include mineral fillers, including hydroxides(aluminum hydroxides, magnesium hydroxides) and carbonates (hydromagnesites) [14, 22].

1.3.4 Radical scavengers

Vapor phase radical inhibitor flame retardants fragment into stable radicals after being pyrolyzed with polymer fuel. This helps in prevention of free radical propagation reaction in flame front. These flame retardants reduce the heat release rate by scavenging free radicals. Once enough radicals and heat has been removed, combustion ceases. Examples of this kind of flame retardants include organochlorine, organobromine compounds and phosphorus compounds. [14, 22]

1.4 Literature review in thermal, mechanical and fire reaction studies

While polymer nanocomposites have a good potential application for flame retardancy, they are limited by the fact that it is a relatively new technology; hence not much information is available. There exists no universal flame retardant approach, which means approaches that work for one polymer may not work for another system [14]. However, considerable research is being conducted to identify the thermal degradation behavior of polymer nanocomposites and factors influencing this behavior. Bera *et al.* (2011) studied the thermal stability of polystyrene/silica nanocomposite. The study identified that properties of polymer composites are reliant on the nanofiller dispersion and their thermal behavior depends on the type and size of nanofiller. The study investigated the optimum silica content for attaining maximum thermal stability and developed a correlation to define the influence of filler loading on glass transition temperatures of PS [11]. Vaziri *et al.* (2011) investigated the thermo-physical properties of polystyrene-silica nanocomposites and postulated that the thermo-physical properties of the composites can be connected to the nanoparticles loading or concentration [10]. In fact, this study showed that the storage modulus and glass transition temperature rose with temperature as the nanoparticle loading increased; however, both values reduced after a nanoparticle loading of 10 wt%. More research is required to investigate this changing trend in thermo-physical properties with nanoparticle concentration. Hatanaka *et al.*

(2017) investigated the thermal and morphological changes as a result of alpha-zirconium phosphate (ZrP) loading on poly (methyl methacrylate) (PMMA) and found that there was increase in onset temperature and temperature at peak mass loss rate at 30% loading of ZrP while the transparency remained almost same. There was also increase in activation energy as the loading increased which stabilized the degradation kinetics [24]. In another study by Hatanaka *et al.* (2016), the impact of cross-linkage of silica nanoparticles on PMMA was investigated. The study revealed that due to cross-linkage to silica, the composite had 30% reduction in peak mass loss rate in thermal analysis and an increase in degradation activation energy by 100 $kJmol^{-1}$. High char yield and thermal stability were observed due to the reduced peak heat release rate of both the cross-linked and linear PMMA-silica nanocomposites compared to neat PMMA [16]. The impact of cross-linkage on char yield and thermal stability was also studied for the linear and cross-linked varieties of PMMA embedded with silica, aluminum oxide and montmorillonite [25]. While the silica cross-linked samples showed increased char yield in comparison to the neat polymer, the 3 and 5 wt% aluminum oxide cross-linked samples had shown a reduction in char yield. The study recommended further research on medium and large-scale samples in cone calorimeter [25]. Based on the literature review on the thermal studies of polymer nanocomposites, it is apparent that more research is needed for understanding the impact of nanofiller loading on the thermal properties and char yield.

The thermal degradation behavior and char analysis study can provide insight into the flame retardancy aspect of the polymer nanocomposites. It is simultaneously important to study the mechanical properties of the nanocomposites since it dictates the applicability and marketability of the products. If the addition of nanofillers compromises the mechanical properties of the polymer to a great extent, then the application of flame retardant nanofillers would hinder the usefulness of the polymer as a product. A recent study [26] conducted on carbon nanotube and nanofiber reinforced polymer identified a gap in research that the mechanical behavior of material has not been studied under changing strain and frequency. The results showed that the compatibility of nanofillers can be dictated by changing frequency and strain in the dynamic mechanical analysis (DMA). Kalajahi *et al.* (2012) investigated the impact of silica nanoparticle loading on the kinetics of polymerization and obtained the optimum loading for attaining improved thermal and mechanical properties [27]. While the study demonstrates that the nanofillers loading has an impact on the storage modulus value of the nanocomposites, further research is required to explain the loading effect on the mechanical properties of polymer nanocomposites.

To obtain the full scenario of the performance of the flame-retardant polymer nanocomposite system, it is important to explore the aspect of a real fire scenario along with the small-scale thermal and mechanical analyses. Small-scale tests such as TGA and DSC give insight into the thermal degradation pattern of nanocomposites and polymers but fail to reproduce the impact of heat release rate, time to ignition and other parameters that affect the flame spread and predict the corresponding human reaction to the fire. To extend the study on the flame retardancy of polymer nanocomposites; it is, therefore, necessary to use cone calorimeter analysis. Various studies have been conducted utilizing cone calorimeter as an analyzing tool. Gilman *et al.* (1999) studied the effect of particle size, filler concentration, and pore volume on the flammability of polypropylene. The study found that the physical structure of the char residue formed after ignition is of importance. Brittle and thin char is apparently less fire resistant that thick and foamy char [28]. Shen *et al.* (2017) explored the flammability properties of the poly (methyl methacrylate)-silica crosslinked and non-crosslinked samples and primarily found that at higher loading, the nanocomposites show negative performance in terms of soot production and ignitability; however, simultaneously demonstrates reduction in heat release rate, total heat release and mass loss rate. The study explained that the effectiveness of polymer nanocomposites in flame retardancy even at a lower loading such as 5 mass% and below can be attributed to the high interfacial area [29]. Mouritz *et al.* (2006) investigated the relationship between heat release rate (HRR) and other fire reaction properties over various levels of heat flux. Thermoset matrix composites reinforced with both combustible and noncombustible fibers were used for the purpose of the study. A linear relationship was observed between HRR and other fire reaction properties, such as specific extinction area, mass loss rate, total mass loss and CO yield; however, no correlation was obtained for HRR and time to ignition [30]. Li (2000) investigated the smoke suppressant method of metal oxides on poly (vinyl chloride), which is a good flame retardant but generates black smoke and therefore poses fire hazard. In this study, it was found by cone calorimeter analysis that the metal oxides (CuO, MoO_3 and Fe_2O_3) in PVC enhance specific extinction area (SEA) in smoldering mode whereas reduces SEA in flaming mode. The role of the metal oxides in reducing SEA was attributed to the fact that these metal oxides reduce the amount of aromatic compounds which are generally responsible for the smoke production [31].

Overall, there has been noteworthy effort going on in investigating the thermal, mechanical stability and fire reaction properties of polymer composites and other systems; however, a few efforts have been undertaken that have tried to relate the impact of nanofiller loading on the thermal, mechanical and fire reaction properties simultaneously with the intention of portraying a holistic view. The literature review section aims at identifying the existing gaps in flame retardancy studies and thereafter help in defining the problem statement and corresponding objectives of the study.

2. PROBLEM STATEMENT AND OBJECTIVES

It is obvious that there is a gap in the literature in identifying the impact of nanofillers on the thermal properties of the polymer nanocomposites while accounting for the mechanical properties. The primary objective was, therefore, to identify potential flame-retardant additives suitable for flame retardant application as well as understanding the thermal properties of these novel nanocomposites in comparison to neat polymer. The thermal degradation behavior and char analysis study can provide insight into the flame retardancy aspect of the polymer nanocomposites. It is simultaneously important to study the mechanical properties of the nanocomposites since it dictates the applicability and marketability of the products. If the addition of nanofillers compromises the mechanical properties of the polymer to a greater extent, then the application of flame retardant nanofillers would hinder the usefulness of the polymer as a product.

To explore the full-scale fire performance and corresponding human reactions to parameters, such as exposure to smoke and carbon dioxide; it is important to analyze fire reaction properties in a well-developed fire scenario. It is apparent from literature review that though there have been studies in literature to investigate the fire reaction properties of individual nanocomposite systems; there is lack of systematic studies to compare the performance of different nanofillers on fire reaction properties while making a connection to the thermal and mechanical properties to provide a holistic view of the system.

Based on the gaps identified in the literature; the problem statement, therefore, has been defined as follows:

“To identify and synthesize non-toxic, potentially thermally stable flame-retardant polymer nanocomposite system and identify the role of nanofiller loading on the thermal, mechanical and fire reaction properties with the intent to understand the effect of loading on thermal degradation behavior, char yield, heat release rate and flame retardancy in general while accounting for the impact on the mechanical stability of the product.”

With the intent to address the problem statement, the current study will be looking into how different types, as well as loading concentration of nanofillers, affect the thermal stability, flammability properties, and the mechanical properties. The objectives of this study are as follows:

2.1 Identifying potentially thermally stable polymer nanocomposite

To identify potential additives or nanofillers in polymeric nanocomposites that have the ability to induce thermal and mechanical stability; a literature review was conducted. Polystyrene has been selected as base polymer which has wide-spread application owing to its ease of processing and excellent properties such as low density, mechanical stability and thermal stability. However, PS is highly flammable and drips severely during combustion [32] which makes it an ideal candidate for studying the impact of flame retardant nanofillers.

As potential fire retardant nanofiller candidates for the PS in this study; nanosilica and montmorillonite have been chosen. Montmorillonite (MMT) is a smectite type of layer of lattice silica-alumina clay that is composed of stacks of negatively charged nanolayers separated by a balance of positive cations. The clay layer is made up of tetrahedral-octahedral-tetrahedral structure [33, 34]. According to literature, polymer-nanoclay composites have demonstrated improved thermal, mechanical properties along with flame retardancy and gas permeability [35]. Nanosilica is another noteworthy inorganic additive that has shown improved thermal, mechanical and water-resistance properties [27]. Large interfacial area is obtained for nanosilica when the particle diameter is at the nanoscale in the least and is well dispersed in the polymer matrix [36]. Overall, owing to the potentially improved thermal properties introduced by the nanofillers, both nanosilica and MMT have been chosen as ideal flame-retardant filler candidates for preparing the polystyrene-nanocomposites.

2.2 Synthesize nanocomposites

In-situ polymerization method has been used for producing the polymer nanocomposite systems. Although the methodology is similar for all the samples, some of the process variables and concentration have been modified to accommodate the sample size requirement of different characterization methods. For example, small, medium and large-scale samples have been prepared for thermal, mechanical and flammability analysis respectively and for that purpose; modifications have been made in initiator concentration, curing time, oil bath size, mold size. For curing the samples for small-scale tests, such as TGA or DSC; small polypropylene vials have been used. For medium and larger scale tests, such as cone calorimeter or DMA; a specialized mold prepared by two pairs of parallel glass plates separated by a silicon tubing and held together by clips is used.

2.3 Characterization and data analysis

Nanocomposites are characterized to understand thermal degradation behavior, enhancements to the char yield, flammability properties (*e.g.*, heat release rate, peak heat release rate, smoke generation) and corresponding mechanical strength giving additional insight into how other nanocomposites can be improved. Following is a brief description of the characterization techniques that has been followed:

2.3.1 Thermal analysis

The thermal stability of a material can be understood well by studying the mass loss behavior with temperature or time. TGA or derivative thermogravimetric analysis (DTG) is the typical method employed to explore the thermal stability and study the thermal properties of nanocomposites [11]. For the thermal analysis, the samples were heated up to a certain temperature while maintaining a constant ramp rate. The thermal degradation behavior, the onset of degradation and retention of mass after degradation are monitored for the thermal analysis and char yield study. The phase shift in the plot of heat flow versus temperature plot in differential scanning calorimetry (DSC) is used as a measure of the temperature for phase change.

2.3.2 Mechanical analysis

Due to the viscoelastic properties of polymers, their behavior can be dictated by the relationship between stress and strain [37]. In dynamic mechanical analysis (DMA), a sinusoidal stress or strain is applied to the sample and the stress is measured or vice versa. The storage and loss modulus and dampening factor with respect to temperature can give information regarding glass transition temperature and level of agglomeration due to the addition of nanofiller. Furthermore, the nanoindentation analysis can provide a comparative value for hardness for the nanocomposites and the neat polymer which in turn can predict the applicability of nanocomposites as products.

2.3.3 Cone calorimeter analysis

To study the flammability and fire reaction properties, cone calorimeter analysis was conducted. It is important to understand how the nanofiller loading can impact fire reaction properties including smoke generation, CO and CO_2 yield since these gases obscure vision and make it difficult for a human to evacuate during a fire scenario. The samples were tested by using the cone calorimeter under the standard of ASTM E 1354 by the cone calorimeter manufactured by Fire Testing Technology (FTT) Limited. During the testing, these samples were evaluated in the horizontal orientation and were exposed to a heater with the heat flux of 50 kWm^{-2}. The unexposed surfaces of these samples were wrapped in aluminum foil prior to testing. Data analysis was based on output readings of heat release rate, peak heat release rate, the total heat evolved, mass loss, smoke generation and CO or CO_2 generation.

3. THERMAL AND MECHANICAL STUDIES[*]

3.1 Synopsis

Polymers are widely used in our day-to-day lives and we are often oblivious to the fire hazard imposed by these hydrocarbon-based materials. This paper introduces the application of fire retardant nanofillers for enhanced flame retardancy as a potential remedy for flame spread. The paper also investigates changes in mechanical properties as a result of nanofiller addition. For this purpose, neat polystyrene (PS), PS-silica and PS-montmorillonite (MMT) have been prepared via *in-situ* polymerization method. The thermal degradation mechanism of the neat polymer and polymer nanocomposites and the effect of nanoparticle loading on thermal properties have been investigated using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) equipment. TGA and corresponding Derivative TG (DTG) results show that there has been improvement in thermal stability for the nanocomposites. PS-1 wt% silica and PS-3 wt% silica nanocomposites have shown approximately 23% and 15% reduction of Peak Mass

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[*] "Study of thermal and mechanical behaviors of flame retardant polystyrene-based nanocomposites prepared via *in-situ* polymerization method." by L. Ahmed, B. Zhang, S. Hawkins, M. S. Mannan and Z. Cheng, 2017. Journal of Loss Prevention in the Process Industries, Volume 49, Part B, September 2017, pp.228-239, Copyright [2017] by Elsevier. Part of this section is reprinted with permission from Elsevier Ltd.

Loss Rate (PMLR) respectively. The polymer nanocomposites also showed 72e87% more char yield with respect to neat PS. The glass transition temperature (Tg) as measured by the DSC was comparable to those obtained by the Dynamic Mechanical Analysis (DMA) and the greatest agglomeration was observed for PS-3 wt% MMT. According to the nanoindentation results, there was reduction in hardness of the nanocomposites compared to the neat polystyrene. It was concluded that the addition of nanosilica and nanoclay in small loading can significantly improve thermal stability and mechanical properties; however, higher loading may result in agglomeration and reduction in hardness.

3.2 Introduction

Using inherently flame retardant or thermally stable polymers is one potential way to reduce the possibility of a fire spread and consequent damage associated with the fire. However, due to the high cost, this alternative is often not a viable option. Considering the expenses involved and ease of processing, applying flame retardant additives to polymers is an efficient way to mitigate the fire hazard. Flame retardants reduce fire hazard by interfering with the polymer combustion process [9].

Polymer nanocomposites comprise a new area of development for fire retardancy with no potential harmful effects on the environment. This new class of materials offers an opportunity for exploring new behavior and functionality beyond what conventional materials offer. Polymer nanocomposites have the potential to bring remarkable improvement in terms of mechanical, thermal, optical, magnetic and electrical properties [10]. As a result, polymer nanocomposites have been investigated for potential applications for flame retardancy, electronic and optical applications [11]. For the current study, the flame retardancy effect and subsequent thermal and mechanical behaviors of polymer nanocomposites is investigated.

3.3 Experimental

3.3.1 Materials

The monomer styrene and the nanofiller montmorillonite (MMT) nanoclay were purchased from Sigma Aldrich. MMT is modified nanoclay sheets. The nanosilica surface treated with KH570, has a diameter of 20-30 nm and was purchased from US Nano. The initiator 1, 1'-azobis (cyclohexanecarbonitrile) (ABCN) was purchased from PolySciences.

3.3.2 Synthesis

An *in-situ* polymerization technique was followed for preparing the polymer nanocomposites. This method involves dispersion of nanofiller in the monomer and then polymerizing the solution thereby interlocking the filler within the matrix of the polymer. A glass vial with polytetrafluorethylene (PTFE)/silicone septum was used as the reaction vessel. In the vessel, styrene monomer and massed amount of nanofiller (silica with KH 570 or MMT) were taken into account for the final concentration of the filler as 1 or 3 weight percent of the total composite. The different varieties of nanocomposites prepared for the experiments have been listed in Table 3.

Table 3 Summary of polystyrene nanocomposites samples

Sample code	**Sample name**	**Composition (wt.%)**		
		Polystyrene (PS)	Surface modified silica	Montmorillonite (MMT)
P1	Neat polystyrene	100	0	0
P2	Polystyrene-1wt% Silica	99	1	0
P3	Polystyrene-3wt% Silica	97	3	0
P4	Polystyrene-1wt% MMT	99	0	1
P5	Polystyrene-3wt% MMT	97	0	3

After adding the filler, the reaction vessel is subjected to vortex mixing for 1-2 minutes, regular mixing for half an hour and sonication for 20 minutes. These steps ensure complete mixing and particle wetting of the nanofiller. Then the initiator was added in 1 weight percent of the monomer solution and carbon dioxide was bubbled through the solution for 10 minutes to inert as shown in Figure 5.

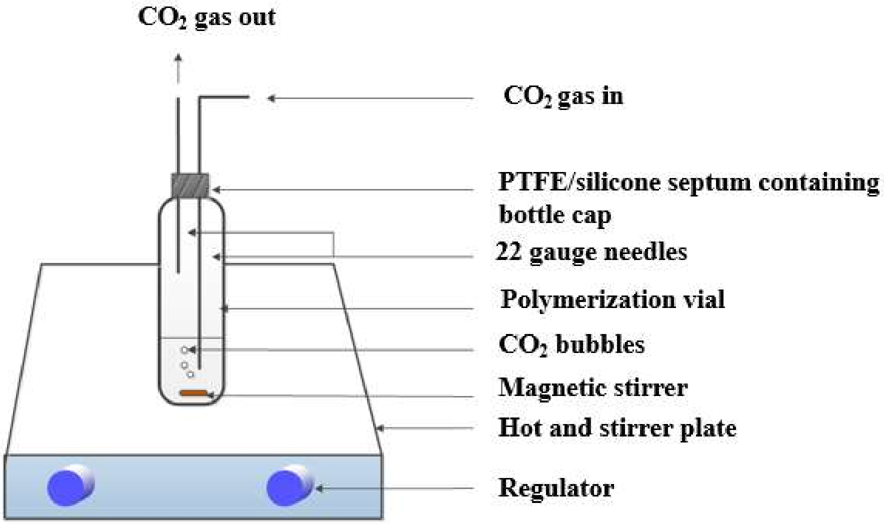

Figure 5 Schematic setup for inerting monomer solution

The reaction vessel was then transferred to an oil bath maintained at 70±1°C while the stirring continued via a magnetic stirrer in the reaction vessel as shown in Figure 6. It took about 2 hours before the solution gelling began and when the solution became viscous.

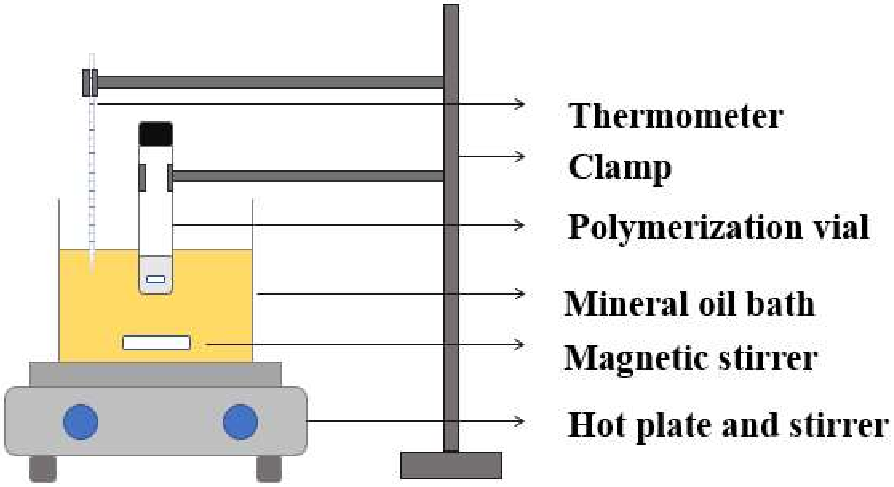

Figure 6 Schematic experimental setup for *in-situ* polymerization

3.3.3 Casting into mold

After solution gelling began, the sample was transferred into mold for casting and solidifying. Characterization in dynamic mechanical analyzer (DMA) and nanoindentation require the samples to have certain dimension. Therefore, a specialized mold was prepared to develop the composites to have a rectangular shape. Two pair of parallel glass plates separated by silicone tubing were clamped tight to develop the mold. The solution, when ready for gelling, was poured into the cavity formed in between the plates and the opening was closed by another piece of silicone tubing. The thickness of the silicone tubing was the determining factor for the thickness of the sample. After 24 hours of curing in oil bath, the polymer composite was produced. The slab of material produced was later cut and polished to give the desired length and width as shown in Figure 7 (a and b).

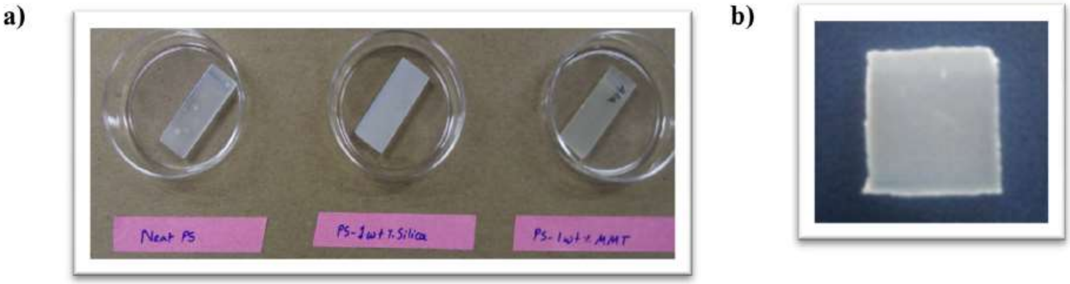

Figure 7 Polystyrene nanocomposites: a) 36 mm × 10 mm × 3.25 mm sample prepared for dynamic mechanical analysis and b) square 1 mm × 1mm sample made for nanoindentation

For thermal analysis in thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC), about 3-5 mg of sample is needed. Therefore, after the rectangular samples were prepared, cut and polished for the tests in DMA and nanoindentation, a small blade was used to chip out small portion of the remaining part to produce small flakes.

3.3.4 Characterization

Thermogravimetric analysis

Thermal analysis was conducted using TA instruments thermogravimetric analyzer. The sample size varied between 3 to 6 mg. The samples were heated from 25 °C to 500 °C at a constant ramp rate of 20 °C/min in an aluminum pan under argon environment.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed under argon environment in TA Instruments DSC - Q2000. The sample size varied between 3-6 mg and the samples were heated from 40°C to 150 °C at a constant ramp rate of 10°C/min, cooled back and another heating and cooling cycle followed. The glass transition temperature was taken from the second heating cycle.

Dynamic mechanical analysis (DMA)

Rheological performance of the composites was measured using TA instruments G2 RSA rheometer. The neat polystyrene and the nanocomposites were prepared with approximate dimension of 36 mm × 10 mm × 3.25 mm for testing. Torsion method was employed for the sample mounting and the measuring frequency was 1 Hz. The strain amplitude of 0.05% was used after the strain amplitude sweep run. Then a temperature sweep run was conducted within the temperature range of 25°C to 130 °C.

Nanoindentation

For determining the hardness and reduced modulus of the polymer and nanocomposites, Hystiron TI 950 triboindenter was used. Quasi-static nanoindentation technique was employed and nanoindentation trapezoid (5s loading - 2 s holding - 5 s unloading cycle) was used as the standard load function.

3.4 Results and discussion

3.4.1 Thermal analysis and char yield study

The thermal stability of a material can be understood well by studying the mass loss behavior as a function of temperature or time. TGA or derivative thermogravimetric analysis (DTG) is the typical method employed to explore the thermal stability and study the thermal properties of nanocomposites [11]. The dynamic mode of the TGA equipment allows for increasing temperature while maintaining a constant ramp rate. For the current study, a constant ramp rate of 20 °C/min was applied while the temperature was raised from 25°C to 500 °C.

According to Vyazovkin and Wight *et al.* (2011), the polystyrene degradation has been explained to have initially occurred at the weak link sites and after the mass loss at the initiation part is over, the maximum mass loss due to polymer degradation is subjected to random scission [38]. The TGA (Figure 8) and the DTG plot (Figure 9) for neat polystyrene and polystyrene nanocomposites revealed that there was one main degradation pathway. The weight loss steps at specific temperature revealed information about polymer degradation and dependence on temperature. The mass loss at lowest $T \approx 174$ °C to 228°C (as evident by a phase shift in Figure 8 and from the first peak in DTG plot in Figure 9), which corresponds to around 3-9% weight loss, is due to residual solvent content. The second mass loss at T ≈ 425°C to 451 °C (as evident by the second phase shift in Figure 8 and second peak in DTG plot in Figure 9) is due to random depolymerization along the polymer backbone.

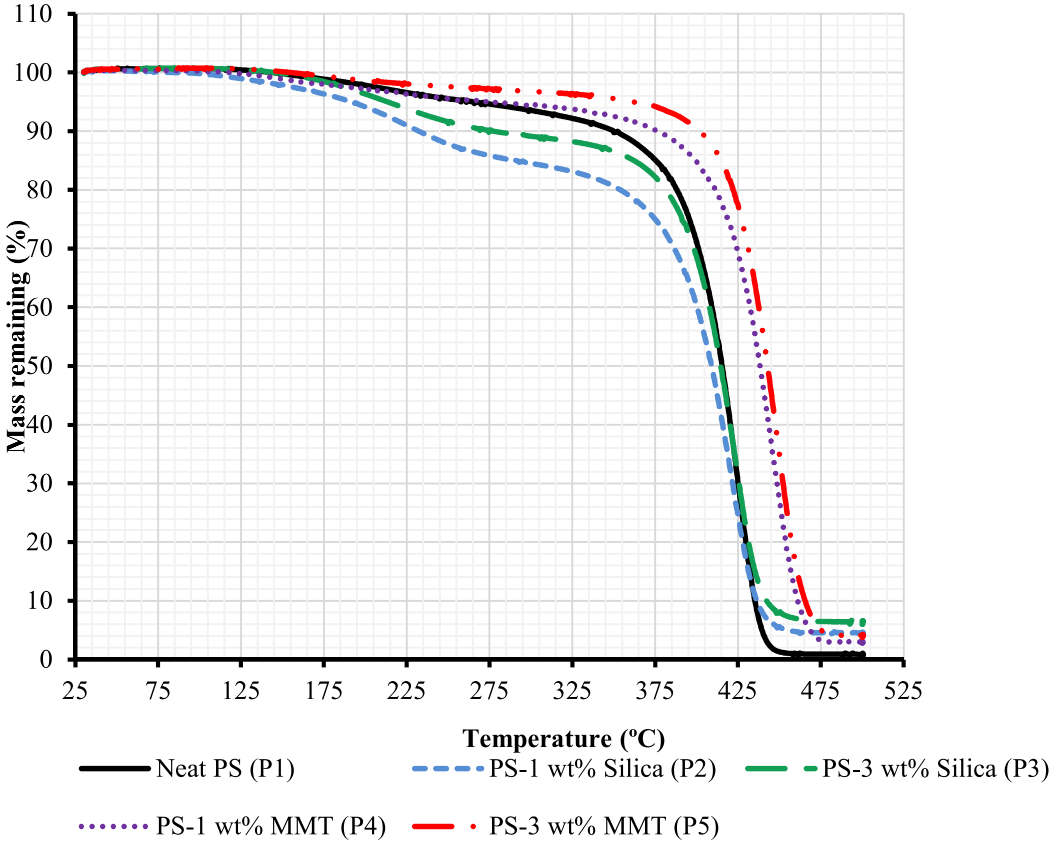

Figure 8 Thermogravimetric analysis curves for neat polystyrene and polystyrene nanocomposites

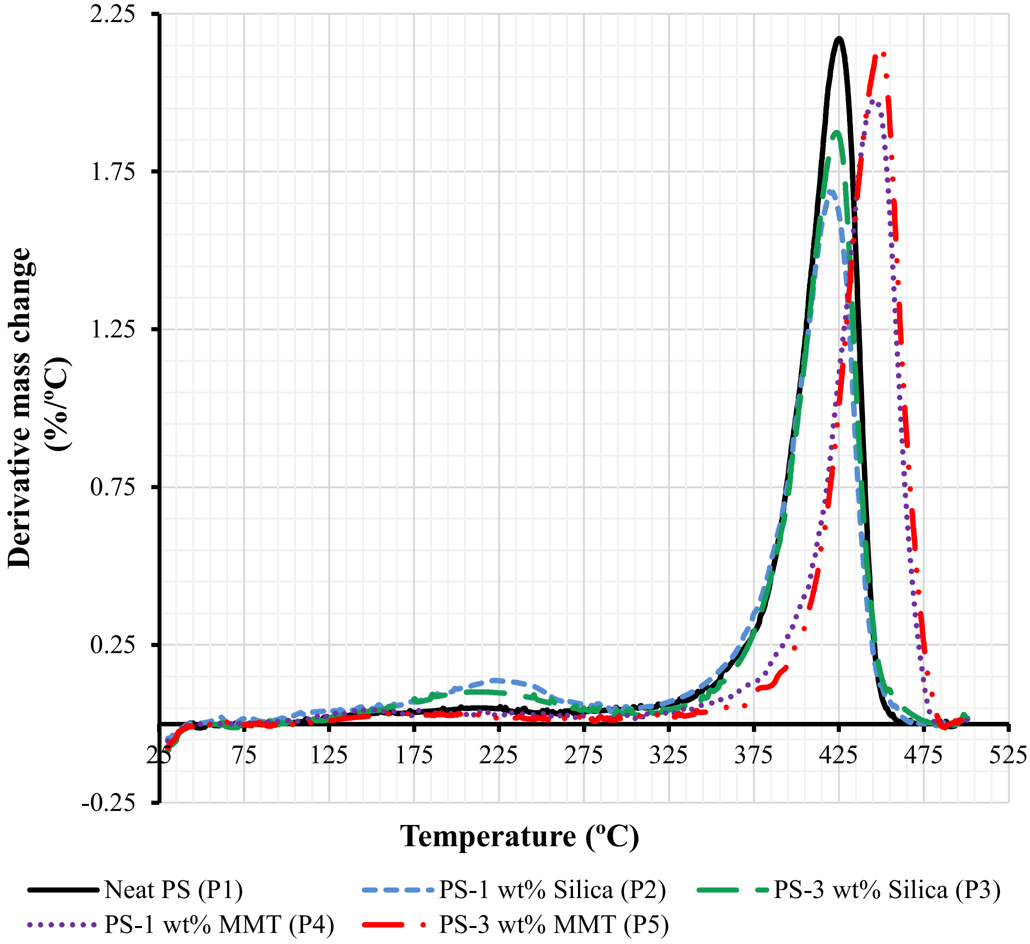

Figure 9 Derivative thermogravimetric analysis curves of neat polystyrene and polystyrene nanocomposites

Table 4 summarizes the onset of thermal degradation (defined as the temperature where the polymer starts to degrade or disintegrate), the temperature at 5% mass loss, the temperature at 25% mass loss and the temperature at 50% mass loss. The mass loss corresponding to onset of thermal degradation temperature corresponds to 10 to 25 wt% mass losses as indicated by column 3 in Table 4. For the neat polystyrene, the onset temperature of degradation is 370 °C and it varies between 376.8 °C to 405 °C for polystyrene nanocomposites. The higher onset temperature of degradation for the nanocomposites compared to the neat polystyrene can be attributed to the fact that addition of nanofillers reduce polymer mobility and hence delays the degradation reaction.

Table 4 TGA data for onset degradation temperature, weight percent and temperature at 5, 25 and 50% degradation

Sample name	Onset of degradation T_{onset} (°C)	Weight loss at T_{onset} (%)	T at 5% degradation (°C)	T at 25% degradation (°C)	T at 50% degradation (°C)
PS	370	13.5	265	395.6	415
PS-1wt% Silica	376.8	25.6	191.6	374.8	408.8
PS-3wt% Silica	374.7	17.7	213.4	391	414.5
PS-1wt% MMT	389.7	12	276.5	418.8	430
PS-3wt% MMT	405	10.9	361.8	427	442.7

Table 5 summarizes the temperature and weight percentage at the peak mass loss rate (PMLR) from DTG plot. DTG at PMLR indicates the temperature at which the maximum rate of the polymer or nanocomposite degrades.

Table 5 Derivative thermogravimetric (DTG) analysis data for polystyrene and polystyrene nanocomposites

Sample name	DTG peak temperature or temperature at PMLR (°C)	DTG at peak temperature (%/°C)	Reduction in DTG (%)
Neat PS	425.5	2.2	-
PS-1wt% Silica	422	1.7	22.7%
PS-3wt% Silica	425.9	1.8	15%
PS-1wt% MMT	447.8	1.9	9%
PS-3wt% MMT	451.4	2.1	2.4%

For polystyrene and polystyrene nanocomposites, the temperature for DTG peak mass loss rate varies between 425 °C and 451°C (Table 5). The DTG plots in

Figure 9 shows that the temperature at peak mass loss rate (DTG Peak temperature or temperature at PMLR) increased by almost 22 °C for the PS-1wt% MMT and 25.85 °C for PS-3wt% MMT nanocomposites respectively; but the peak shifted slightly to the right indicating that the peak mass loss occurred at an elevated temperature. To get a better understanding of the thermal behavior, it is important to look at the percentage change in derivative mass change. PS-1wt% silica and PS-3wt% silica nanocomposites showed a promising ~23% and 15% reduction of derivative mass loss rate with respect to neat polystyrene. On the other hand, PS-1wt% MMT and PS-3wt% MMT showed a 9% and 2.4% reduction of peak mass loss rate when compared to neat polystyrene respectively.

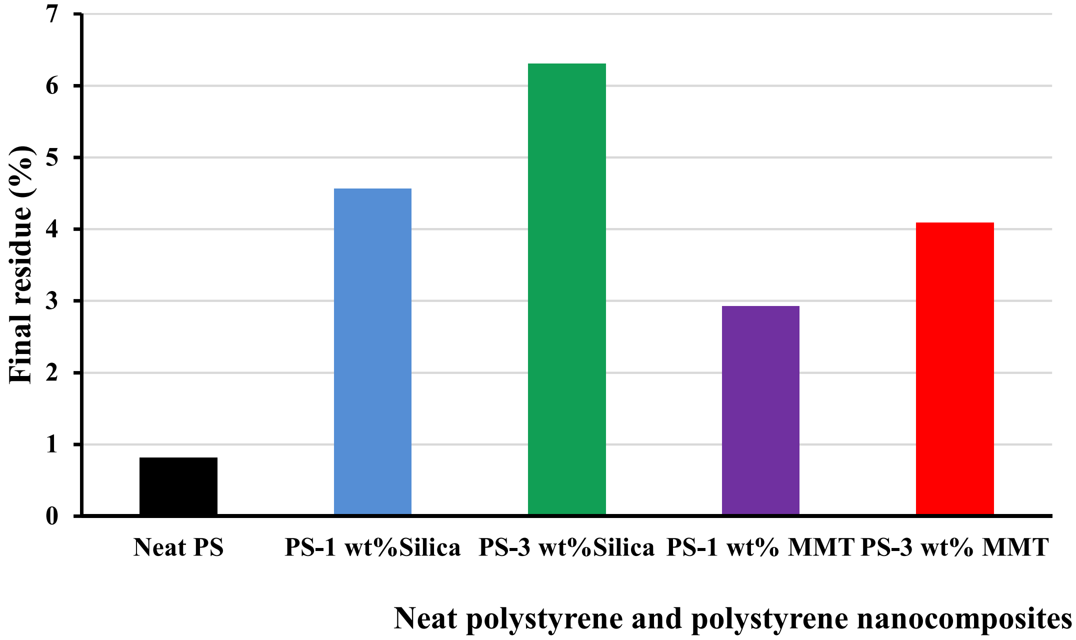

Figure 10 Final char residue (in percentage) for polystyrene and polystyrene nanocomposites

The high temperature residuals in polystyrene nanocomposites compared to neat polystyrene in Figure 8 indicate that there has been a significant retention of mass. The final mass of samples after TGA tests and percentage char yield values are summarized in Table 6 and re-drawn as a bar graph in Figure 10. There has been 72-87 % increase in char yield for the nanocomposites compared to neat PS. Extensive charring of the polymer material is the eventual target in fire retardancy. It would allow for the formation of char in presence of a heat source and limit potential production of combustible products thereby ensuring safety [21]. Char also acts as barrier between the neat polymer and the source of heat [39].

Table 6 Mass retention and percentage of char yield of polystyrene and polystyrene nanocomposites

Sample name	% increase in char formation
PS	Basis
PS-1wt% Silica	82.18 %
PS-3wt% Silica	87.1 %
PS-1wt% MMT	72.20 %
PS-3wt% MMT	80.12 %

Overall, the polystyrene-silica and polystyrene-nanoclay (MMT) nanocomposites have shown improved performance in terms of thermal stability, flame retardancy and char production.

Differential scanning calorimetry

When a neat polymer or polymer nanocomposite undergoes phase change, it becomes evident by a step change in the heat flow versus temperature plot of DSC. For the current study, DSC has been performed to determine the glass transition temperature - the temperature beyond which polymers transform from solid phase to semi-liquid or rubbery phase [40]. Therefore, it essentially gives the temperature range for the applicability of a material. For our current purpose, the inflection points of heat capacity jump in the heat flow versus temperature plot (Figure 11) have been taken as the glass transition temperature [27]. The DSC curves, in general, show a slight rise in heat flow before reaching to the endotherm corresponding to glass transition temperature, T_g and the values have been listed in Table 7. The glass transition temperature, T_g for the pure polystyrene as shown by the endotherm was 81 °C. For the nanocomposites, the T_g varied between 85-106 °C and reached a maximum value of 106 °C for PS-1 wt% silica nanocomposite (Table 7).

Nanofillers may sometimes show reduction in T_g when agglomeration occurs [26]. The agglomeration results in reduction in interphase volume which hampers the construction of percolating network [41]. As evident from the DSC plots for this study, there has not been any reduction in T_g for most of the nanocomposites except for PS-3 wt% MMT. The increase in T_g for PS-silica and PS-MMT nanocomposites indicate that the nanofiller silica and nanoclay have been well dispersed in the polymer matrix. For the PS-3 wt% MMT; however, there has been agglomeration as indicated by the lower T_g value. It implies that increasing the nanofiller loading, especially for the nanoclay composites; there is a possibility of generating agglomeration that can hamper the interphase volume.

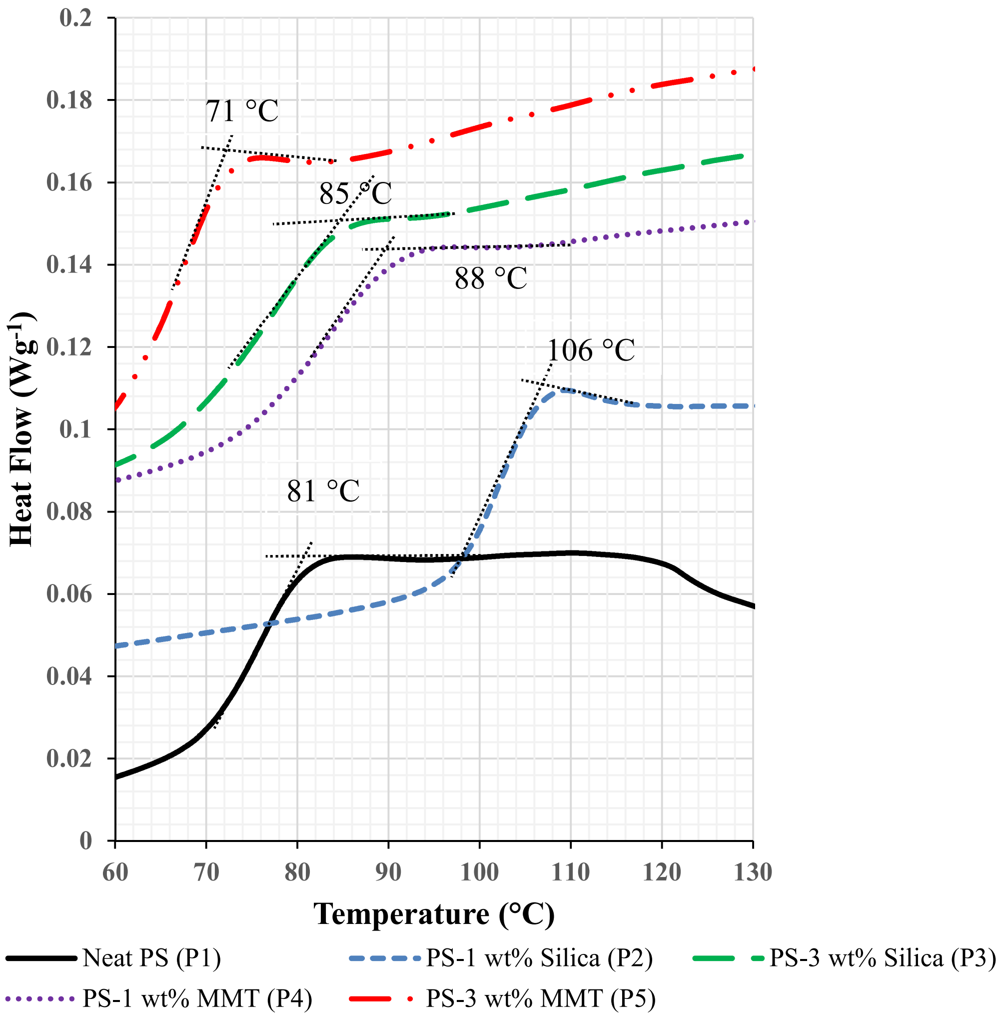

Figure 11 Heat flow versus temperature plot using differential scanning calorimetry

Table 7 Glass transition temperature (T_g) determined by differential scanning calorimetry

Sample name	Glass transition temperature, T_g (ºC)
Neat PS	81
PS-1wt% Silica	106
PS-3wt% Silica	85
PS-1wt% MMT	88
PS-3wt% MMT	71

3.4.2 Mechanical analysis

Dynamic mechanical analysis

Due to the viscoelastic properties of polymers, their behavior can be dictated by the relationship between stress and strain [37]:

$E^* = \sigma$ (stress) $/\varepsilon$ (strain);

where E^* is the complex modulus of elasticity.

In fact, in dynamic mechanical analysis, a sinusoidal strain is applied to the sample and the stress is measured or vice versa.

Complex modulus of elasticity can also be presented as:

$E^* = E' + i^*(E''); i^2 = -1;$

where, the real part of the E* is termed as the storage modulus (E') and the imaginary part is the loss modulus (E'').

Storage modulus (E') is measured as the elastic response of a material, which corresponds to stiffness while loss modulus (E'') represents the viscous response of a material, thereby representing damping [42, 43]. Because of the viscous nature of the material, there exists a phase shift between the stress and strain; the tangent of which is termed as the damping factor or mechanical loss factor (tanδ). This is expressed as the ratio of E'' to E' [37, 44].

As mentioned before, glass transition temperature is the temperature beyond which the polymer turns into a more rubbery phase from the solid state. The storage modulus reduces significantly as opposed to loss modulus, which reaches its maximum at glass transition temperature, T_g. The peak tanδ value is taken as the measure of the T_g. T_g is also known as α transition. At the α-transition (T_α or T_g), the larger segments of polymer become mobile. At lower temperature, β-transition occurs due to side group or localized backbone motion in polymers [26, 45].

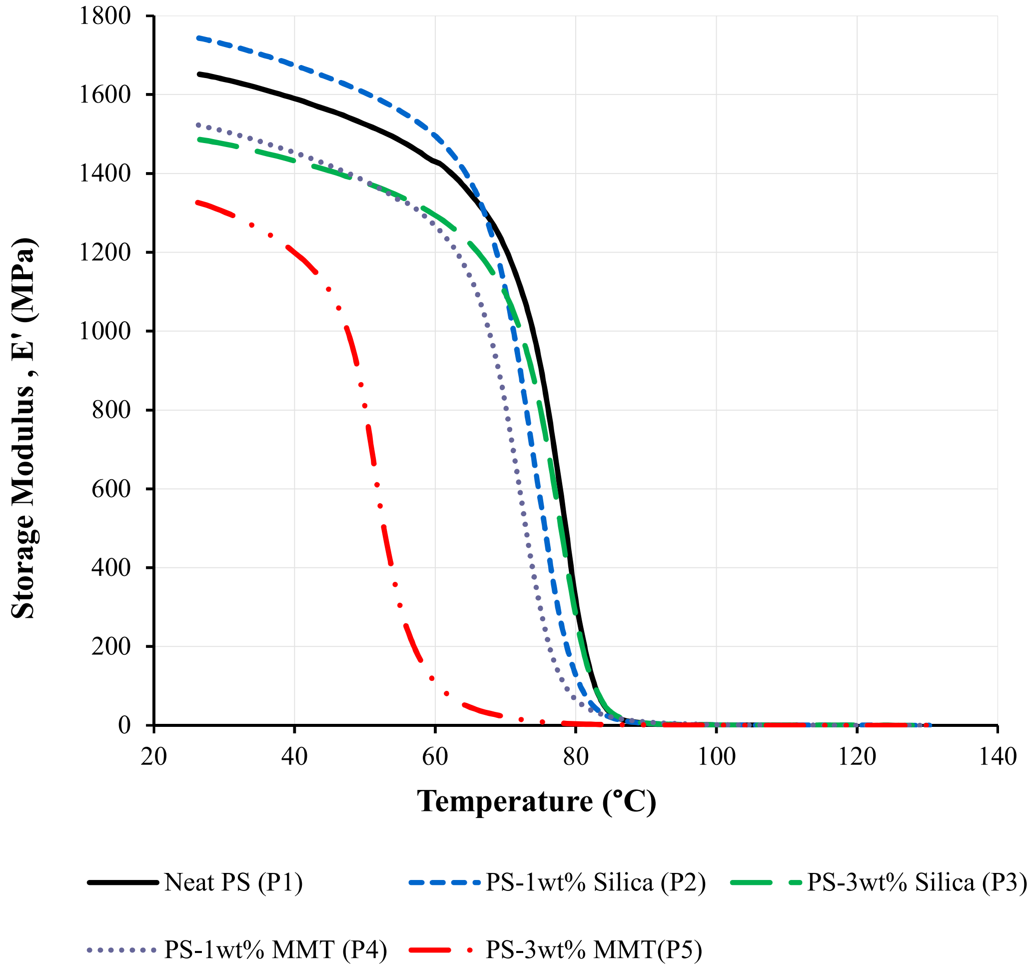

Figure 12 Storage modulus (E') as a function of temperature for polystyrene and polystyrene nanocomposites

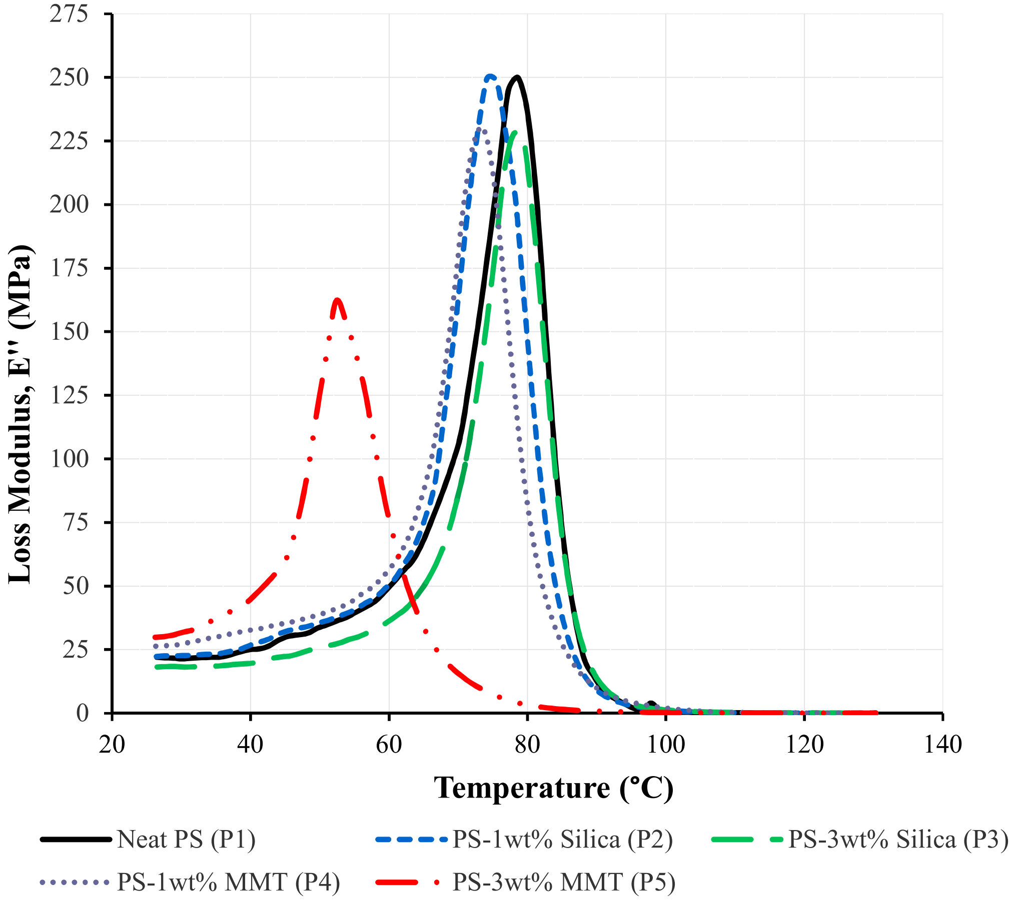

Figure 13 Loss modulus (E'') as a function of temperature for polystyrene and polystyrene nanocomposites

Figure 12 and Figure 13 demonstrate the variation of storage modulus (E') and loss modulus (E'') as a function of temperature at a constant frequency of 1 Hz. In comparison to neat polystyrene, both E’ and E’’ of polystyrene nanocomposites reduce with the greatest reduction being observed for the PS-3 wt% MMT. The reduction in storage and loss modulus indicates agglomeration of nanofillers in polymer nanocomposite, which weakens the interaction between polymer and filler [27]. The PS-3wt% MMT has more agglomeration compared to the other composites. This result is also supported by the glass transition temperature values obtained from the tanδ values in DMA.

From observing the glass transition temperature and comparing it to the value obtained from DSC, the variation of tanδ was plotted as a function of temperature in Figure 14. It shows α transition corresponding to glass transition temperature and β transition corresponding to side group motion. The peak values of $(\tan\delta)_{max}$ have been deemed as the glass transition temperature and are listed in Table 8.

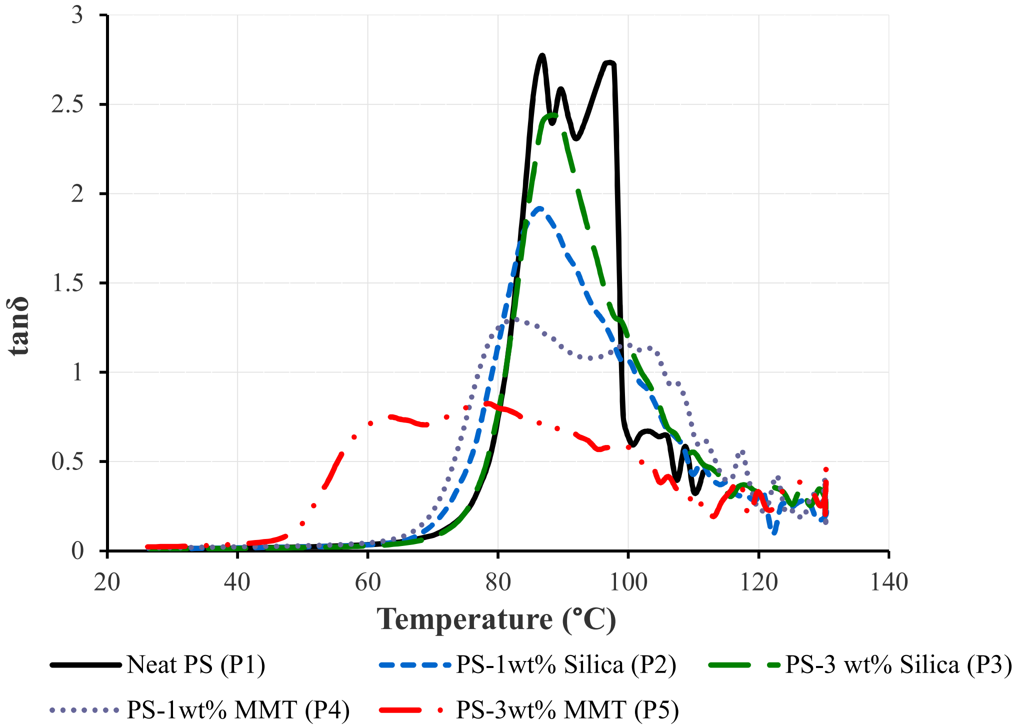

Figure 14 tanδ as a function of temperature for polystyrene and polystyrene nanocomposites

The T_g value of the nanocomposites either remained almost the same or slightly increased for most of the samples in comparison to the neat polystyrene except for PS-3 wt% MMT nanocomposite. The T_g reduced by 9.3% which indicates agglomeration. The results obtained from DMA were comparable to the results obtained from DSC. From

Table 8, it can be observed that the T_g were similar for both the neat polystyrene and the nanocomposites except for PS-1 wt% silica nanocomposite, which shows higher value (106 °C) of T_g. However, the T_g, if taken from the first endotherm of the DSC reading gives a value of around 83 °C which is comparable to the value obtained in DMA test.

Table 8 Storage modulus and glass transition temperature of polystyrene and polystyrene nanocomposites by dynamic mechanical analyzer (DMA) and differential scanning calorimetry (DSC)

Sample name	E' at glassy state (T=40 °C) **(MPa)**	E' at rubbery state (T=120°C) **(kPa)**	$(\tan\delta)_{max}$	Glass transition temperature, T_g (DMA)	Glass transition temperature, T_g (DSC)
Neat PS	1590	242	2.77	86.8	81
PS-1wt% Silica	1674	167	1.92	86.5	106
PS-3wt% Silica	1430	143	2.44	88.1	88
PS-1wt% MMT	1452	145	1.29	83.2	85
PS-3wt% MMT	1200	204	0.82	78.7	71

Nanoindentation

The load displacement curves in Hystiron TI 950 triboindenter were generated from the quasi-static trapezoid nanoindentation loading-holding-unloading cycles.

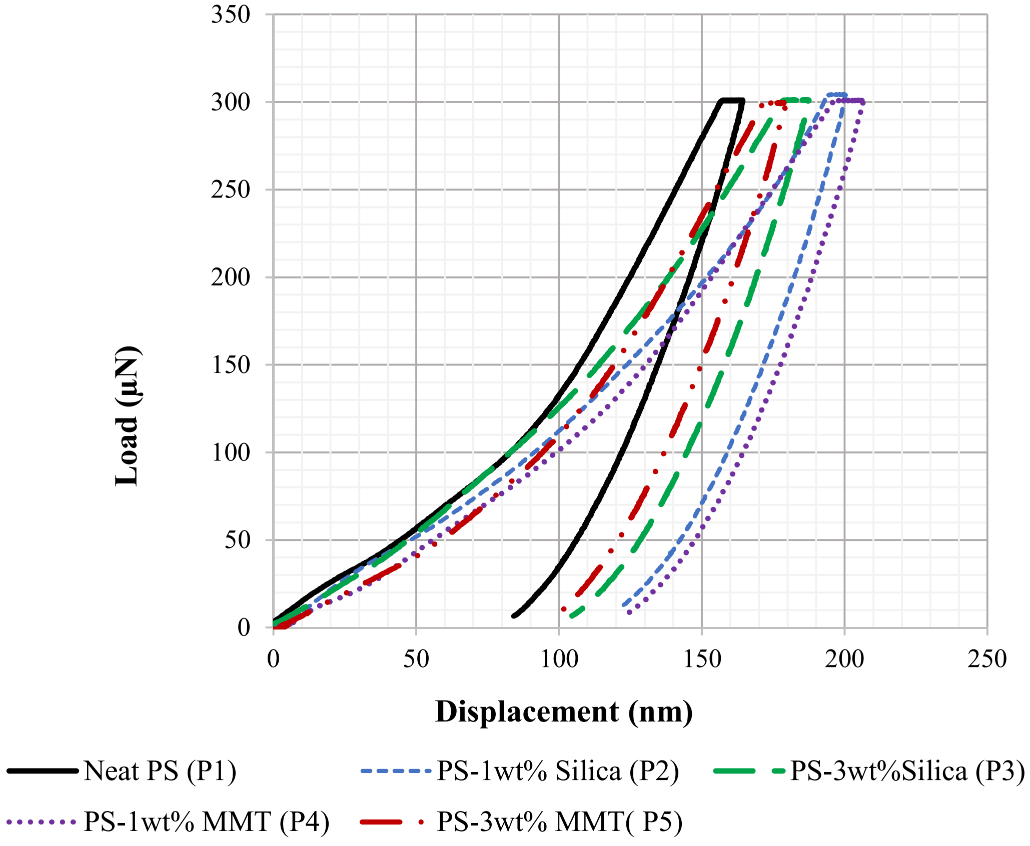

Figure 15 Load displacement data for polystyrene and polystyrene nanocomposites at room temperature

The load displacement data was obtained at a constant loading of 300 µN and the maximum displacement range, as shown in Figure 15, is in the range of 164-206 nm. The slope of the unloading curve in the load displacement plots as shown in Figure 15, can be termed as stiffness (S) of the polymer nanocomposites and relates to reduced modulus (E_r) according to the following equation [46]:

$$S = \frac{dP}{dh} = 2\ E_r \left(\frac{A}{\pi}\right)^{0.5}$$

Here, P is the loading, h is the displacement, S is the initial unloading stiffness, E_r is the reduced modulus or Young's modulus, and A is the contact area.

The ratio of peak indentation to contact area is defined as the measure of hardness [46]:

$$\text{Hardness, } H = \frac{Pmax}{A}$$

Table 9 Average Young's modulus and average hardness of polystyrene and polystyrene nanocomposites

Sample code	Sample name	Average Young's modulus, E_r (GPa)	Average hardness, H (GPa)
P1	Neat PS	6.1	0.42
P2	PS-1wt% Silica	5.4	0.31
P3	PS-3wt% Silica	5.4	0.33
P4	PS-1wt% MMT	5.4	0.31
P5	PS-3wt% MMT	5.6	0.37

The hardness of the neat polystyrene and the composites are listed in Table 9. The hardness of the neat polystyrene is higher than other nanocomposites and it is made apparent by the difference in the depth obtained at the maximum load. For the maximum load of 300 μN, the hardest material, neat polystyrene has a displacement of 84 nm whereas the softer nanocomposites have a displacement ranging between 97-124 nm (Figure 15). The addition of nanofillers into the polymer matrix thus reduces hardness.

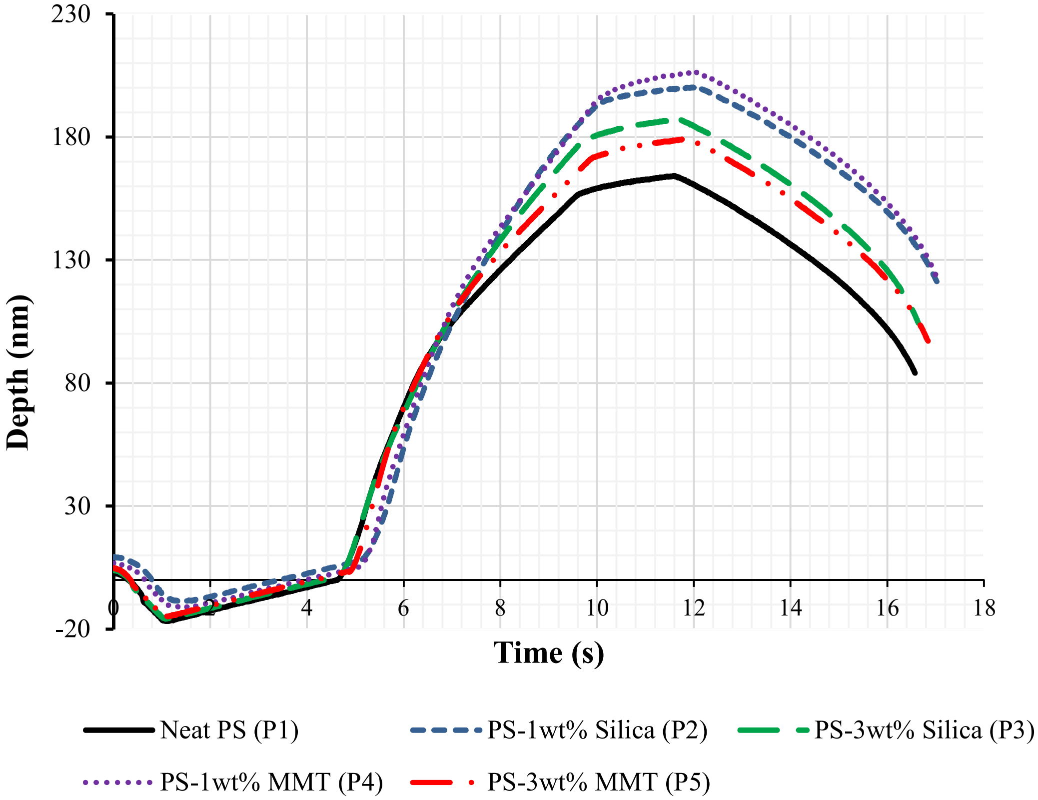

Figure 16 Depth versus time (creep data) for polystyrene and polystyrene nanocomposites

The decrease in hardness with the addition of nanofillers in the polymer nanocomposites is also confirmed by the nanoindentation creep displacement versus time data at room temperature (

Figure **16**). The creep depth increased for the nanocomposites in comparison to neat polystyrene, *e.g.,* at t = 10 s, the creep depth for neat polystyrene is 159.3 nm whereas the creep depth varies between 172-194 nm for the nanocomposites. This indicates the reduction of creep resistance.

3.5 Conclusions

The effects of addition of nanoparticles on thermal stability of the polymer, potential flame-retardant mechanism, and changes in mechanical properties have been investigated. For this purpose, neat polystyrene, polystyrene-nanoclay (1 and 3 wt% in loading), and polystyrene-silica nanocomposites (1 and 3 wt% in loading) have been prepared via *in-situ* polymerization method. TGA/DTG and DSC have been used for thermal characterization of the samples. TGA/DTG showed one reaction degradation pathway. There has been a significant reduction of peak mass loss rate (PMLR) of 22.67% for PS-1 wt% silica nanocomposite and 15% for PS-3wt% silica nanocomposite. The high temperature mass residuals indicate char formation and the composites have shown about

72-87% improvement in char yield in comparison to neat PS. The addition of nanofillers in 1 and 3 wt% in the polymer matrix has shown improved thermal stability and char formation, both of which are essential for better flame retardancy.

For mechanical analysis, dynamic mechanical analysis (DMA) and nanoindentation were performed. The DMA showed that there was reduction in storage and loss modulus for the composites with temperature when compared to neat PS, which is indicative of agglomeration. The greatest agglomeration was observed for PS-3wt% MMT, which was also confirmed by the glass transition temperature (T_g) obtained by the $(\tan\delta)_{max}$ and the DSC plots. The hardness of the nanocomposites were reduced in comparison to the neat polymer as per the nanoindentation results. However, this is not an elaborate calculation that can depict whether this reduction on hardness would impact the product quality and its application. In conclusion, the addition of nanosilica and nanoclay in small loading can significantly help improve thermal stability and mechanical properties. However, as the nanofillers loading increases the tendency to agglomerate and reduction in hardness were observed.

4. FIRE REACTION STUDIES*

4.1 Synopsis

Using nanofiller additives in the polymer matrix to form nanocomposites is a potential way of reducing the flame spread and enhancing flame retardancy of polymeric materials during fire. To understand the fire reaction properties and the relative performance of flame-retardant additives in polymer during well-developed fire, neat polystyrene, polystyrene-silica and polystyrene–nanoclay (MMT) have been tested in a cone calorimeter. The neat polystyrene and the polystyrene nanocomposites have been prepared via an *in-situ* polymerization method. An external heat flux of 50 kW m^{-2} was applied in the test, and parameters such as heat release rate, peak heat release rate, time to ignition, smoke toxicity, CO and CO_2 yield have been investigated. Both neat polystyrene and polystyrene nanocomposites have shown the trend of a thermally thick charring polymer in the heat release rate over time data. The nanocomposites had an overall better flame retardancy than the neat polystyrene in terms of lower peak heat release rate, lower

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* "Fire reaction properties of polystyrene-based nanocomposites using nanosilica and nanoclay as additives in cone calorimeter test." by L Ahmed, B. Zhang, R. Shen, R. J. Agnew, H. Park, Z. Cheng, M. S. Mannan and Q. Wang, 2018. Journal of Thermal Analysis and Calorimetry, Copyright [2018] by Springer Nature. Part of this section is reprinted with permission from Springer Nature.

average mass loss rate and enhanced char formation. The nanocomposites had also reduced smoke emission with lower CO and CO_2 yield compared to the neat polystyrene. The overall flame retardancy was enhanced as the nanofiller loading was increased for both the nanosilica and MMT nanocomposites.

4.2 Introduction

Due to advances in polymer science, we see application of polymers in our everyday life. Use of polymers or plastics has become almost ubiquitous and so has the risk of being exposed to flame spread by polymeric materials during a fire incident. Polymers act as potential source of fuel and a means of rapid spread of fire. In fact, plastic commodities can be a significant contributor to household or structure fires [47] and every year household fires result in property damage worth 7.9 billion US dollars in USA [48]. Research effort has, therefore, been directed toward developing an effective flame-retardant system that can reduce the possibility of rapid fire spread and aid in controlling the fire hazard. For the current study, neat polystyrene (PS) has been selected as the base polymer which has wide-spread application owing to its ease of processing and excellent properties as low density, mechanical stability and thermal stability. However, polystyrene is highly flammable and drips severely during combustion [32] which necessitates the study of impact of potential flame retardant additives in improving the flame retardancy of the polystyrene composites.

Flame retardant additives function by interfering with the polymer combustion process and thus reducing the flame spread [47, 49]. Among the different classes of flame retardants, nanometric particles are relatively new and these additives enhance mechanical, flammability and thermal properties when dispersed in polymer matrices. The principal mechanism of fire retardancy for nanocomposites occurs in the condensed phase and the fire retardancy performance may vary depending upon the geometry and chemical structure of the nanometric particles. Some common nanoparticles are: layered materials (*e.g.,* nanoclay), particulate materials (*e.g.,* polyhedral oligosilsesquioxane (POSS)) and fibrous material (*e.g.,* carbon nanotubes) [15]. Unlike many of the previous flame retardant additives in use, these are relatively more environment-friendly and non-toxic [47] and therefore, are ideal candidates for flame retardancy studies. As potential fire retardant nanofiller candidates for the PS in this study; montmorillonite and nanosilica have been chosen. Montmorillonite (MMT) is a smectite type of layer of lattice silica-alumina clay that is composed of stacks of negatively charged nanolayers separated by a balance of positive cations. The clay layer is made up of tetrahedral-octahedral-tetrahedral structure [33, 34]. According to literature, polymer-nanoclay composites have demonstrated improved thermal, mechanical properties along with flame retardancy and gas permeability [35]. These improved physical behaviors are due to the interfacial intercommunication between the polymer matrix and the silicate layers of MMT in the nanocomposites. MMT is also known to generate char and reduce heat release rate of the nanocomposites in comparison to neat polymer [50]. Nanosilica is another noteworthy inorganic additive that has shown improved thermal, mechanical and water-resistance properties [27]. A good dispersion of nanosilica in the polymer matrix and particle diameter in the nanoscale are responsible for providing large interfacial area [36]. During fire, silica nanoparticles in a polymer nanocomposite accumulate in the vicinity of the polymer surface and thereby reduces flame spread by creating an insulating char layer and diluting the concentration of polymer which, otherwise would act as a source of fuel [51]. Thus, it is hypothesized that both nanosilica and nanoclay flame retardant additives would enhance the flame retardancy of the polystyrene and therefore, both have been chosen as ideal flame-retardant filler candidates for preparing and studying the polystyrene-nanocomposites.

To understand the full scenario of the performance of the flame-retardant polymer nanocomposite system, it is important to explore the aspect of a real fire scenario. Cone calorimeter is a medium-scale test method predominantly used to give insight to fire reaction properties during a well-developed fire scenario. It is a well-recognized instrument for testing of fire properties and is included in testing methods prescribed by the International Standards Organization (ISO-5660) and the American Society for Testing and Materials (ASTM E-1354). It functions upon the principle that oxygen consumption is proportionally related to the heat release rate [12]. Cone calorimeter illustrates the fire behavior of a material using a relatively smaller size specimen which makes it a more economic test method. The limiting factors are that it does not cover flame spread and generates data for one-dimensional burning. Despite the limitations, cone calorimeter can provide reasonable insight into the material's fire performance in a developing fire [13] and therefore, has been used as a standard test method to measure fire reaction properties of flame retardant polymeric materials.

The behavior of any material in fire is typically represented by the ability to ignite, the rate of heat release, flame spread, emission of flammables and toxic gases. While a single fire test in a cone calorimeter is not capable of illustrating the whole range of fire scenario; by careful manipulation of the parameters measured in a cone calorimeter, useful information can be obtained for understanding the performance of flame retardant materials. With the aim of understanding and interpreting the cone calorimeter results, Hull *et al.* (2007) presented guidance on use of cone calorimeter with respect to parameters such as heat flux, temperature, ventilation, test setup. The difficulties in correlating the results of cone calorimeter with other standard tests such as limiting oxygen index (LOI), UL94 (the standard for safety of flammability of plastic materials for parts in devices and appliances testing [52]) have been addressed as well [13]. Shen *et al.* (2017) explored the flammability properties of the poly (methyl methacrylate)-silica crosslinked and non-crosslinked samples and primarily found that at higher loading, the nanocomposites show negative performance in terms of soot production and ignitability; however, simultaneously demonstrates reduction in heat release rate, total heat release and mass loss rate [29]. Mouritz *et al.* (2006) investigated the link between heat release rate (HRR) and other fire reaction properties over various levels of heat flux in a cone calorimeter. Thermoset matrix composites augmented with both combustible and noncombustible fibers were used for the purpose of the study. A linear relationship was observed between HRR and other fire reaction properties, such as specific extinction area (SEA), mass loss rate, total mass loss and CO yield; however, no correlation was obtained for HRR and time to ignition [30]. Li (2000) investigated the smoke suppressant method of metal oxides on poly (vinyl chloride); which is a good flame retardant but generates black smoke and therefore poses fire hazard. In this study, it was found by cone calorimeter analysis that the metal oxides (CuO, MoO_3 and Fe_2O_3) in PVC enhance SEA in smoldering mode whereas reduces SEA in flaming mode. The metal oxides reduce the amount of aromatic compounds which are generally responsible for the smoke production and thus shows a reduction in the SEA [31].

It is apparent that though there have been studies in literature to investigate the fire reaction properties of individual nanocomposite systems; there is lack of systematic study to compare the performance of different nanofillers on fire reaction properties while making a connection to the thermal and mechanical properties to provide a holistic view of the system. To fill up the gap in literature, the impact of nanosilica and nanoclay loading on the thermal and mechanical properties of polystyrene has been investigated in the first part of the study [47] as described in section 4. It was observed that the addition of nanofiller improves thermal stability in terms of lower peak mass loss rate, higher onset degradation temperature and better char yield. The increase in nanofiller loading; however, reduced hardness and the impact of this reduced hardness can be further analyzed to understand how it affects the product quality and performance. However, our focus is more directed toward understanding the thermal and flammability properties of the flame-retardant nanocomposites in comparison to the neat polymer. To obtain the full scenario of the performance of the flame-retardant polymer nanocomposite system, it is important to explore the aspect of a real fire scenario. Small-scale tests using thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) in the previous study gave insight into the thermal degradation pattern of the nanocomposites and the neat polymer; but these methods could not comprehend the impact of HRR, time to ignition, smoke release and other parameters that affect the flame spread and the corresponding human reaction to the fire. Therefore, the aim of the present study is to extend the scope of the previous study to understand the impact of different types and loadings of nanofiller additives, namely nanosilica and nanoclay on the fire reaction properties of the neat polystyrene using cone calorimeter. By tying the analysis of fire reaction properties of flame retardant nanocomposite system with the past investigation on thermal and mechanical attributes; this study can contribute to developing our understanding of how the flame-retardant additives can be effectively used in fire control and therefore, saving lives and properties.

4.3 Experimental

4.3.1 Materials

Styrene and 1, 1'-azobis (cyclohexanecarbonitrile) (ABCN) were used as the monomer and the initiator respectively. Surface treated nanosilica (KH570) with a diameter of 20-30 nm and montmorillonite (MMT) or nanoclay organically modified with aminopropyltriethoxysilane were used as flame retardant nanofillers. Surface treatment of nanosilica with KH570 enhances the silica surface with vinylidene groups ($RC=CH_2$) that participates in free-radical polymerization [16]. Styrene and nanoclay were bought from Sigma Aldrich. Nano-silica was purchased from US Nano and the initiator ABCN was bought from PolySciences.

4.3.2 Synthesis

In-situ polymerization method as described in Ahmed *et al.* (2017) has been followed for preparing the neat polystyrene and the polystyrene nanocomposites [53]. A measured amount of monomer styrene was taken in a polytetrafluoroethylene (PTFE)/silicone septum capped glass vial with a magnetic stirrer inside. Later specifically massed nanofiller was mixed in the monomer to produce 1 or 3 wt% of polymer nanocomposites. The addition of nanofiller into the monomer for preparing the polymer nanocomposites was followed by vortex mixing for about 30 seconds, regular mixing for 30 minutes and sonication for 20 minutes to establish complete mixing and degasification of any dissolved oxygen. Later, 2 wt% of the initiator was added to the monomer solution. For preparing the neat polystyrene, the aforementioned steps were omitted and the initiator was directly added to the monomer.

To inert the solution, nitrogen was bubbled through the vessel for 30 minutes after adding the initiator. The reaction vessel was then transferred to a mineral oil bath maintained at 70±1 ºC and kept there for approximately 4 hours before solution gelling started and the solution became thick and viscous enough to be transferred to the mold for casting.

4.3.3 Casting into the mold

For casting the solution gel into the approximate dimension of 100 mm × 100 mm × 5 mm sample, a specialized mold described in literature [16, 29] was used. The mold was built with two parallel pairs of glass plates and a silicone tube wrapped metal frame held in between the glass plates. The whole mold structure was tightly clamped using clips and the cavity formed between the glass plates thus held was used as the curing mold. A suction pump was used to get rid of potential bubbles from the monomer solution and then it was poured in the cavity of the mold. The top side of the mold was then sealed with another piece of silicon tubing and the whole setup was immersed in an oil bath at 70±1 °C for 40 hours. After retrieving the mold from the oil bath and removing the rectangular samples formed, they were further cut to create a surface area of 88.36 cm^2 (100 mm × 100 mm) suitable for the cone calorimeter test. The thickness of the samples varied between 3.4 mm to 4.4 mm.

4.3.4 Characterization

For understanding the fire reaction properties of the polystyrene-silica and polystyrene-nanoclay nanocomposite samples with respect to neat polystyrene, cone calorimeter provided by Fire Testing Technology Limited (FTT) was used in this study. The incident heat flux from cone heater was 50 kWm^{-2} for all the tests and the surface exposed to incident heat flux was 88.36 cm^2 (100 mm × 100 mm). Higher heat flux of 50 kWm^{-2} was chosen since it would provide better reproducibility of data and would correspond to fully developed fire and clearly defined ignition [54]. The ambient temperature, ambient pressure and relative humidity were 26.1-27.6 °C, 97.9 kPa, and 33-34% respectively during the test. The samples were all placed in horizontal position.

4.4 Results

Cone calorimeter provides a thorough representation of fire reaction properties for a well-developed fire scenario. Cone calorimeter data can be utilized to determine comparative fire performance of different materials, generate data for simulating real-scale fire behavior and also determine parameters required for regulatory purposes, such as heat release rate, total heat evolved, fire growth rate index (FIGRA) [13]. Among these fire reaction properties, heat release rate is deemed as the most critical since this acts as the driving force for fire spread [30]. Other parameters tested in cone calorimeter include time to ignition (t_{ign}), effective heat of combustion, total heat release (THR), smoke obscuration (specific extinction area, SEA), mass loss rate (MLR), carbon-dioxide (CO_2) and carbon monoxide (CO) yield.

The cone calorimeter results for the neat polystyrene and polystyrene nanocomposites are summarized in Table 10.

Table 10 Ignition and heat properties of polystyrene and polystyrene nanocomposites in cone calorimeter test

Sample code	Sample name	Effective heat of combustion (MJ kg^{-1})	Time to ignition, t_{ign}(s)	Flame out time (s)	Average mass loss rate, MLR_{avg} (g s^{-1} m^{-2})	Total heat release, THR (MJ m^{-2})
P0	Neat PS	29.6	10	471	24.3	130.2
PS01	PS-1wt% Silica	29.8	7	596	19.4	106.3
PS03	PS-3wt% Silica	33.2	8	690	14.9	121.9
PM01	PS-1wt% MMT	31.6	18	534	23.9	137.4
PM03	PS-3wt% MMT	30	11	611	16.5	136.7

4.4.1 Time to ignition and ignitability

Time to ignition (t_{ign}) is taken as the time required for ignition and sustenance of the flame over the whole of the sample surface. It is a measure of ignitability, *i.e.,* if a sample has lower time to ignition, it is deemed as more flammable [30]. From Table 10, it is observed that the time to ignition increases for PS-1wt% MMT (PM01) and PS-3wt% MMT (PM03) with respect to neat polystyrene and decreases for PS-1wt% silica (PS01) and PS-3wt% silica (PS03) nanocomposite. The reduction in time to ignition (t_{ign}) for the nanocomposites in comparison to the neat polystyrene can be associated with the lower thermal stability of the nanofillers in comparison to the neat polystyrene and the compensation of the polystyrene due to the addition of the fillers [55]. Another possible explanation is that the surface treatment used for the nanofiller decomposes at relatively lower temperature and hence initiates flame faster than it would for neat polystyrene [56]. However, different parameters, such as material thickness, density, and thermal conductivity (especially for the thin samples) play a role in determining the time to ignition [57] and hence, it is not always a reliable parameter for comparison. In fact, time to ignition is not a representation of flammability, rather it corresponds to the minimum mass loss associated with sustained combustion of flame. It is also independent of the irradiation applied and acts like an intrinsic property in cone calorimeter [13]. It is, therefore, more pragmatic to rely on other fire reaction properties, such as heat release rate that determines the flame spread as a more reliable means of explaining fire reaction properties.

4.4.2 Heat release rate (HRR)

Heat release rate (HRR) is the means of quantifying the release of thermal energy per unit area for a material that is subject to fire at constant temperature or a constant heat flux. It is expressed by the unit of kilowatt per square meter (kWm^{-2}) [58]. Heat release rate (HRR) is considered as the most critical factor in determining the flame spread and is also known to have relationship with other important fire reaction properties, such as specific extinction area (SEA), mass loss rate (MLR), total mass loss, CO_2 and CO yield. According to literature, no correlation was obtained for HRR and time to ignition [30].

The changing trend of the HRR is representative of the burning behavior of the polymeric material and other relevant factors [59], and therefore, the HRR trend with respect to time is observed for analysis of fire reaction properties in the cone calorimeter. For the current study, the HRR behavior for incident heat flux of 50 kWm^{-2} for the neat polystyrene and polystyrene nanocomposites with respect to time has been represented in Figure 17. From the plot, it can be observed that the there is an initial delay period, which can be due to the fact that the material’s temperature is initially lower than the pyrolysis temperature of the nanocomposites [30]. After the initial delay period, there is a rapid rise in the HRR until it reaches the peak heat release rate (PHRR).

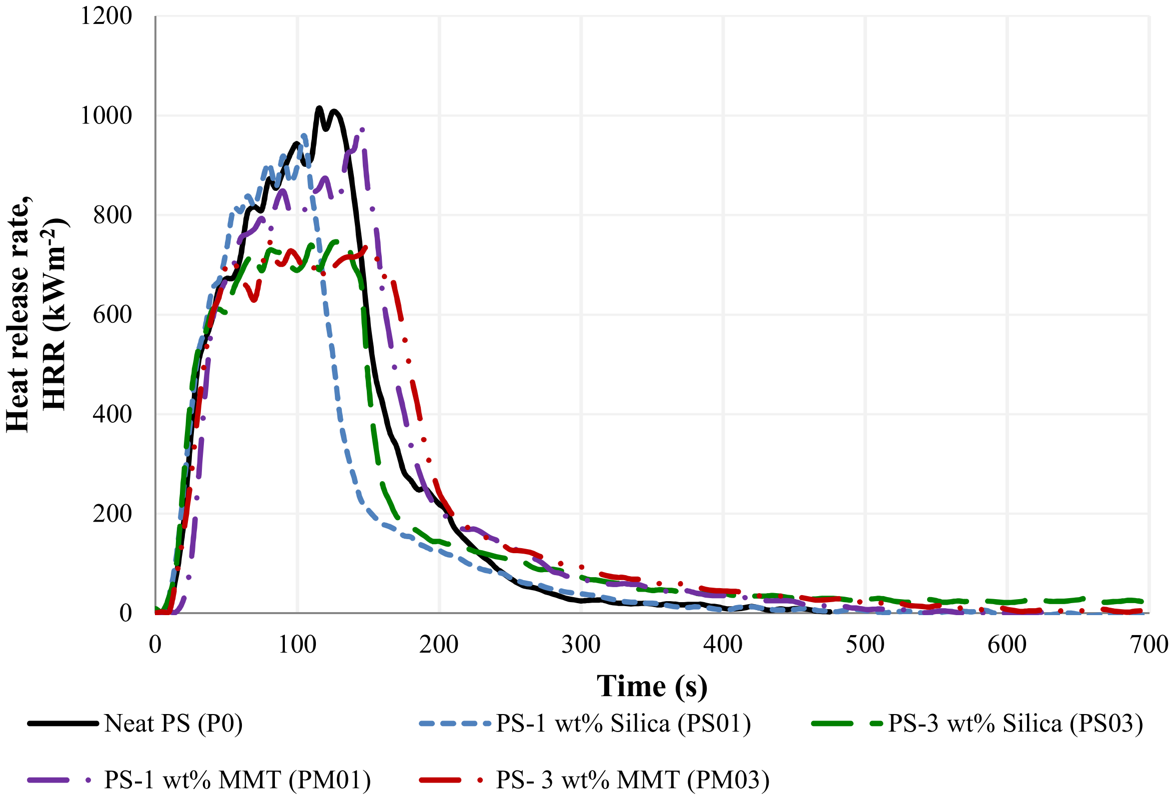

Figure 17 Heat release rate (HRR) with respect to time for neat polystyrene and polystyrene-nanocomposites at external heat flux = 50 kWm^{-2}

As seen from Table 10, after the initial delay period is over, the decomposition of neat PS (P0) is initiated and reached its critical concentration of burning at t_{ign} = 10 s. Similarly, the PS-1 wt% silica (PS01), PS-3wt% silica (PS03), PS-1wt% MMT (PM01), and PS-3wt% MMT (PM03) went through an initial delay period followed by sustained ignition at t_{ign} = 7 s, 8 s, 18 s, and 11 s respectively.

The maximum amount of heat released by a material during combustion is represented by the PHRR which acts as the determining factor for maximum temperature and the rate of fire spread [30]. PHRR also depends on the test setup and may appear to have different shapes, *e.g.,* the PHRR can be single, sharp peaks for thin samples where all of the sample is pyrolyzed at once whereas PHRR can be more diffuse for relatively thicker samples [55, 57].

Table 11 Peak heat release rate (PHRR) data for neat polystyrene and polystyrene nanocomposites

Sample code	Sample name	Peak heat release rate, PHRR (kWm^{-2})	Reduction in PHRR compared to neat PS (Δ%)	Time to PHRR, t_{PHRR} (s)
P0	Neat PS	1014	-	115
PS01	PS-1wt% Silica	958.7	5.5%	105
PS03	PS-3wt% Silica	745.3	26.5%	130
PM01	PS-1wt% MMT	981.6	3.2%	145
PM03	PS-3wt% MMT	746.5	26.4%	80

The peak heat release rate (PHRR) values for the neat polystyrene and polystyrene nanocomposites have been listed in Table 11. For the neat polystyrene (P0), the PHRR of

1,014 kWm^{-2} occurs at t =115 s (time to reach PHRR as listed in Table 11). Subsequently, the HRR decreases and become negligible towards t = 471s (flame out time as listed in Table 10). Similarly, for the PS-1wt% silica (PS01), PS-3wt% silica (PS03), PS-1wt% MMT(PM01), and PS-3wt% MMT (PM03); the PHRR reached the values of 958.7 kWm^{-2}, 745.3 kWm^{-2}, 981.6 kWm^{-2}, and 746.5 kWm^{-2} respectively at t = 105 s, 130 s, 145 s and 80 s.

It can be observed, that there has been a reduction in PHRR for the nanocomposites compared to neat polystyrene samples and as the loading of nanofillers increases from 1 to 3 wt%, the PHRR appear to become more diffuse and broader with lower maxima implying that the samples are burning less intensely while taking longer to burn [60]. The maximum reduction is observed for PS-3wt% silica (ΔPHHR = 26.5%) and PS-3wt% MMT (ΔPHHR = 26.4%). The reduction in PHRR for the nanocomposites compared to the neat polystyrene represents char enhancement and better thermal stability [61] and hence, can be a good indicator of flame retardancy.

After the PHRR is reached, there is a continuous reduction of HRR with time for both the neat PS and PS nanocomposites until HRR finally diminishes as the nanocomposites are completely decomposed (Figure 17). For the neat PS, the sample is consumed after 471 seconds whereas for the PS nanocomposites, it takes longer time to reach the burnout condition. The flame out time as seen from Table 10 are 596 s, 690 s, 534 s, and 611 s for the PS-1 wt% silica (PS01), PS-3wt% silica (PS03), PS-1wt%

MMT(PM01), and PS-3wt% MMT (PM03) respectively which is higher than the flame out time for neat PS (t_{flameout} = 471 s). The longer burn out time for the nanocomposites is an indicator that the neat PS is consumed faster than the nanocomposites.

The reduction in HRR after the peak value has been explained to have happened due to formation of char layer and the reduction in decomposition rate of the corresponding material [30]. In fact according to Schartel *et al.* (2007), thermally thick charring samples shows the trend of increasing HRR until it reaches peak value where the peak heat release rate equals the steady or mean HRR and then as the char builds up, the HRR reduces continuously [13]. This confirms that both neat polystyrene and polystyrene nanocomposites form char as they thermally decompose. However, the nanocomposites show reduction in PHRR and longer burnout time in comparison to the neat PS which are indicator of better flame retardancy.

4.4.3 Mass loss rate and char yield

The ratio of residue to the initial mass portrays the char yield which is an important parameter for describing the burning behavior of polymer and polymer nanocomposites. Char formation is an effective way to limit production of combustible products and producing barrier between the polymer (fuel source) and the ignition source [53].

Heat available per unit mass loss can be used as a means for predicting the possibility of char formation. The integral of HRR corresponding to time gives total heat released (THR) and the THR at the termination of the test is the total heat evolved (THE). For a constant effective heat of combustion, the HRR is controlled by the mass loss rate and the THR is dependent on total mass loss. THE is also dependent on effective heat of combustion and combustion efficiency [13]. From Table 10 it is apparent that there has been a reduction of total heat evolved (THE) for PS-1wt% silica and PS-3wt% silica nanocomposites compared to neat polystyrene. Flame inhibition by the nanofillers is responsible for reduction in THE, which implies reduction in the production of effective heat of combustion of the volatiles and heat of combustion. To have a better understanding of the mass loss behavior and possible char formation, the percentage of mass loss as a function of time is shown in Figure 18.

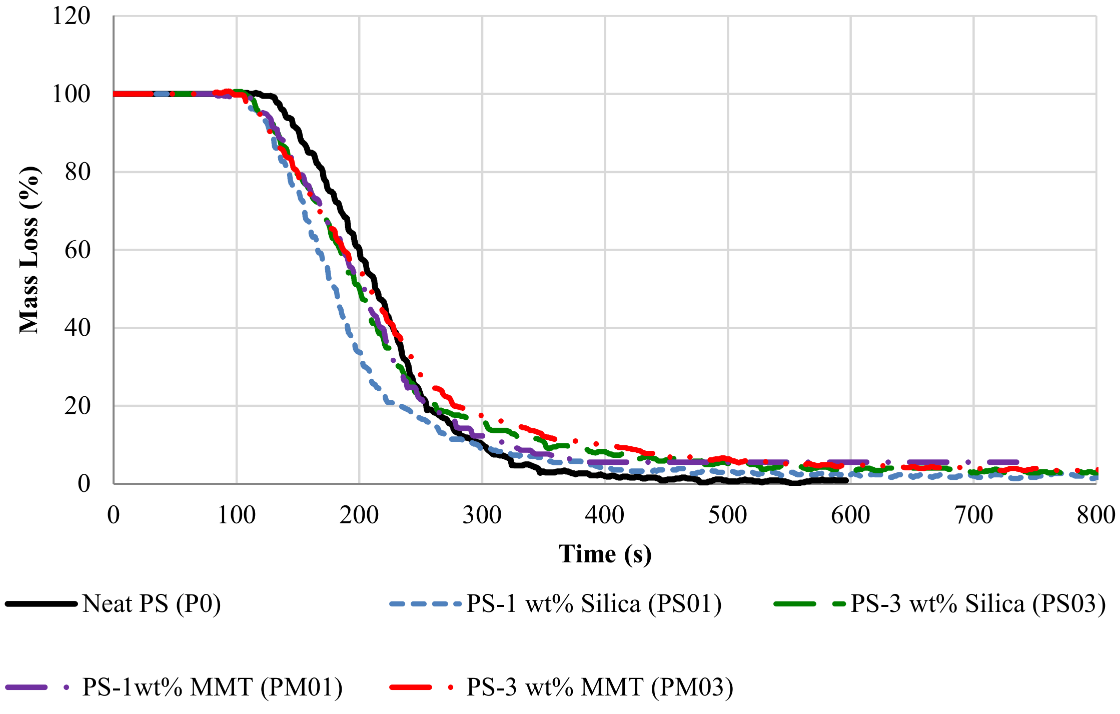

Figure 18 Mass loss data for polystyrene and polystyrene nanocomposites

The mass loss behavior of the polystyrene and the polystyrene nanocomposites follow similar trend as observed in Figure 18; however, the mass loss rate (MLR) reduces gradually for the nanocomposites as compared to the neat polystyrene evident by the steeper slope of the curve for the neat polystyrene. There is also reduction in mass loss for nanocomposites compared to the neat polymer implying that most of the nanofiller/flame-retardant has been contained in the condensed phase creating char formation [13]. The char formation as seen from the residual mass from the mass loss data in Figure 18 has been re-plotted as a bar chart in Figure 19. It is observed that the polystyrene itself generates char; however, greater char formation is seen for the polystyrene-nanocomposites.

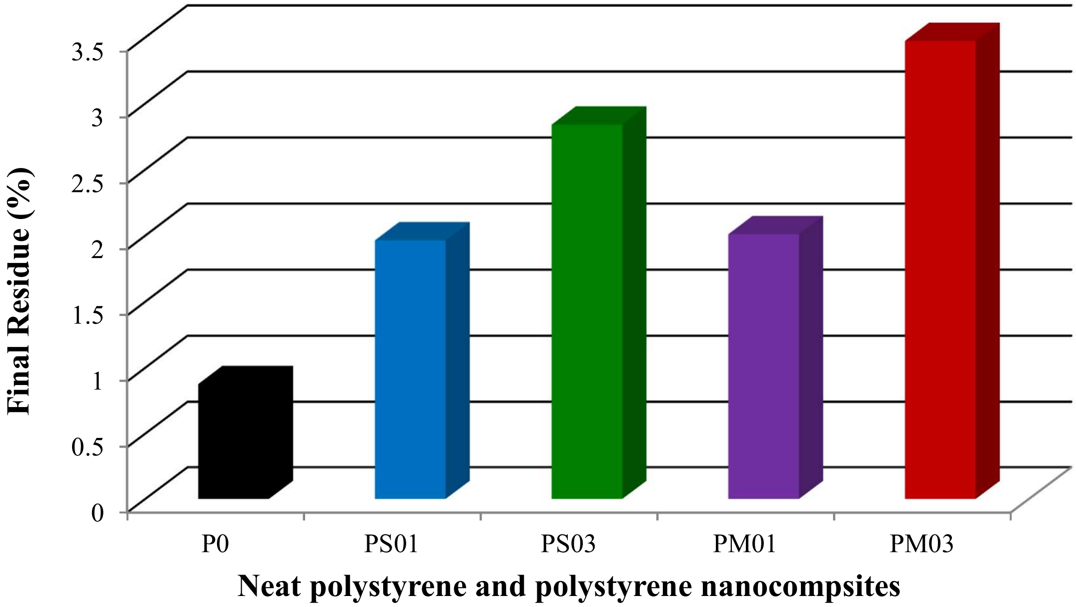

Figure 19 Char turnout for polystyrene and polystyrene nanocomposites

Table 12 Mass containment and percentage of char production of polystyrene and polystyrene nanocomposites

Sample code	Sample name	Percentage increase in char formation (%)
P0	Neat PS	-
PS01	PS-1wt% Silica	55.4
PS03	PS-3wt% Silica	69.1
PM01	PS-1wt% MMT	56.4
PM03	PS-3wt% MMT	74.8

There has been overall 55-75% increase in char formation (Table 12) for the nanocomposites which re-establishes the fact that the nanosilica and nanoclay fillers added in small loading can enhance the char building capability and hence the flame retardancy of the polystyrene. The maximum char yield is obtained for PS-3wt% MMT: a 75% increase in char buildup in comparison to neat polystyrene. This is similar to the 80% increase in char yield for the polystyrene-3wt% MMT nanocomposites with respect to neat polystyrene as observed in literature [53].

The images of the polystyrene and polystyrene nanocomposites after the cone calorimeter tests in **Figure 20** also reveals clear visual indication that the nanocomposites have more char yield compared to the neat polystyrene. It is observed that the polystyrene-silica nanocomposites yield whitish char while the polystyrene-MMT nanocomposites yield black char. Higher loading of 3 wt% show higher char content compared to the 1 wt% loading for both polystyrene-silica and polystyrene-MMT nanocomposites which is comparable to the results observed in Table 12. The higher char yield for the nanocomposites indicate that fragments of polystyrene entrapped within the char layer form an insulating barrier which slows down the process of degradation products of polymer fueling the flame [62].

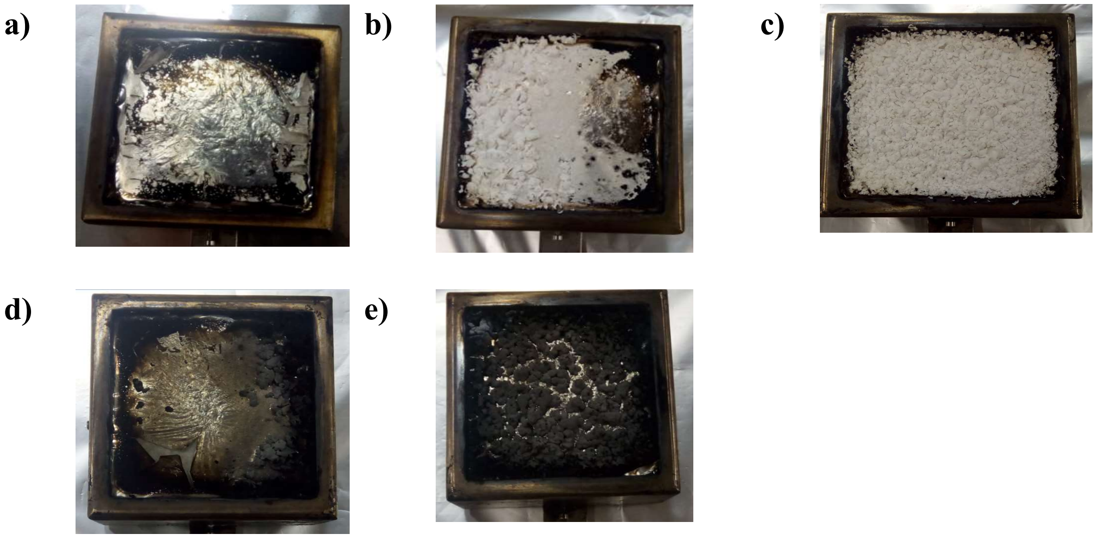

Figure 20 Images of polystyrene and polystyrene nanocomposites residue after cone calorimeter test (heat flux = 50 kWm^{-2}, horizontal setting): a) neat PS (P0), b) PS-1wt% silica (PS01), c) PS-3wt% silica (PS03), d) PS-1wt% MMT (PM01), and e) PS-3wt% MMT (PM03)

4.4.4 Smoke property

Smoke is an aftermath of incomplete combustion and is an important parameter that impacts human survivability in a fire scenario. Specific extinction area (SEA) is one terminology used to describe the smoke obscuration area in terms of mass loss [57] and the corresponding unit is $m^2\ kg^{-1}$. Average SEA is used to assess the release of smoke per unit time for combustion of different products and is used as a means of defining effective optically obscured area 1 kg of mass loss of the sample [30]. To account for the impact of heat release rate on the smoke production, another parameter named smoke parameter (SP) is used. Smoke parameter is defined as the product of average specific extinction area (SEA) and peak heat release rate (PHRR) [57]. Total smoke release (TSR) is the total smoke parameter during the test normalized for the surface area of the material or sample. Table 13 summarizes the TSR, SEA and SP values for the polystyrene and polystyrene nanocomposites.

The neat polystyrene has relatively higher TSR values than all the nanocomposites except for PS-3wt% MMT. It indicates that the nanocomposites have better smoke suppression than the neat polystyrene. The SEA value for the neat polystyrene is relatively higher (483 $m^2\ kg^{-1}$) as observed in Table 13 than that for the PS-1wt% silica (SEA = 135 $m^2\ kg^{-1}$), PS-1wt% MMT (SEA = 236 $m^2\ kg^{-1}$) and PS-3wt% MMT (SEA = 446 $m^2\ kg^{-1}$)

nanocomposites and the SEA value is relatively higher for the PS-3wt% silica (529 $m^2 kg^{-1}$).

Table 13 Smoke obscuration properties of polystyrene and polystyrene nanocomposites

Sample code	Sample name	Peak heat release rate, PHRR (kWm^{-2})	Specific extinction area, SEA ($m^2 kg^{-1}$)	Smoke parameter, SP = SEA*PHRR ($MW m^{-2}$)	Total smoke release, TSR ($m^2 m^{-2}$)
P0	Neat PS	1014	483	577	3210
PS01	PS-1wt% Silica	959	135	129	2453
PS03	PS-3wt% Silica	745	529	129.5	2976
PM01	PS-1wt% MMT	982	236	486	2976
PM03	PS-3wt% MMT	746.5	446	232	3570

However, SEA is limited by the fact that it does not account for the impact of PHRR and the rate at which smoke is being produced. In fact, the fire will not spread over a large area and hence the smoke obscuration will be lower if the PHRR value is lower than a certain value. Smoke parameter (SP) accounts for the peak heat release value by multiplying it with the SEA thus giving a better representation of the smoke generation by a fire [57]. From the SP values listed in Table 13, it is observed that there is a reduction in SP for the nanocomposites compared to the neat polystyrene. In fact, when the impact of

PHRR is accounted for in the SP; the smoke production is seen to be reduced for all of the nanocomposites compared to the neat polystyrene. This is an important assessment required for determining the possible visual obscurity occurring during the fire resulting from the burning polymeric materials; which can impact human evacuation and rescue effort.

Smoke production rate (SPR) is related to the specific extinction area (SEA) and mass loss rate (MLR) as follows [31]:

$$\mathrm{SPR} = \mathrm{SEA} \times \mathrm{MLR}$$

In terms of SPR, the nanocomposites again show lower SPRs compared to neat polystyrene, which can be attributed to the reduction in mass loss rate (Figure 21) [63]. Overall, the nanocomposites generate less smoke compared to the neat polystyrene indicating that the nanofillers can be an environmentally friendly choice for mitigating the fire hazard of polymeric materials.

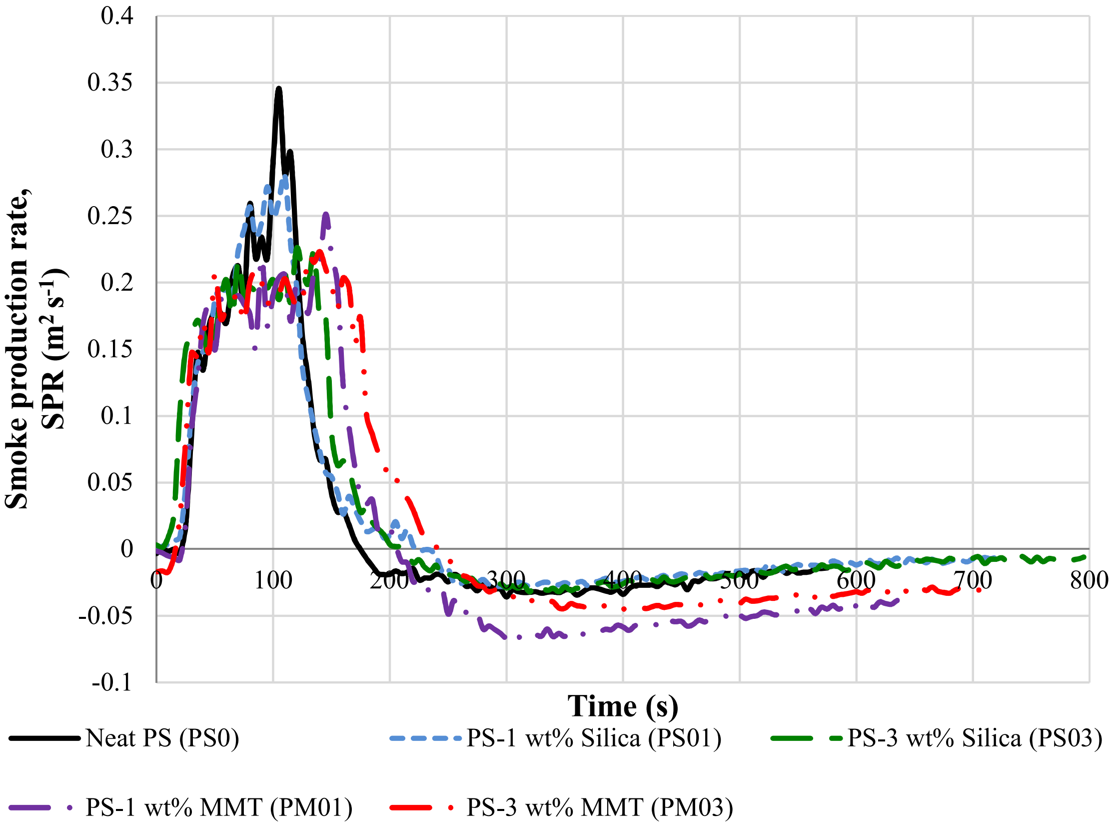

Figure 21 Smoke production rate (SPR) for the neat polystyrene and polystyrene nanocomposites

4.4.5 CO and CO_2 yield

All polymers and polymer composites release CO as a result of incomplete combustion of volatiles at the interface of fire and composite. CO_2 resulting from complete combustion also create difficulty in breathing for people. Particularly, CO is more dangerous since it is lethal at relatively lower concentration and can kill a person exposed to a concentration of 1,500 ppm of CO for an hour [30].

The CO and CO_2 generation can be an important measure considering the impact of them on human evacuation and rescue effort. The human fatality increases if the burning material generates large amount of CO, CO_2 *etc.* It would be beneficial if the burning material in fire would generate lesser amount of these gases.

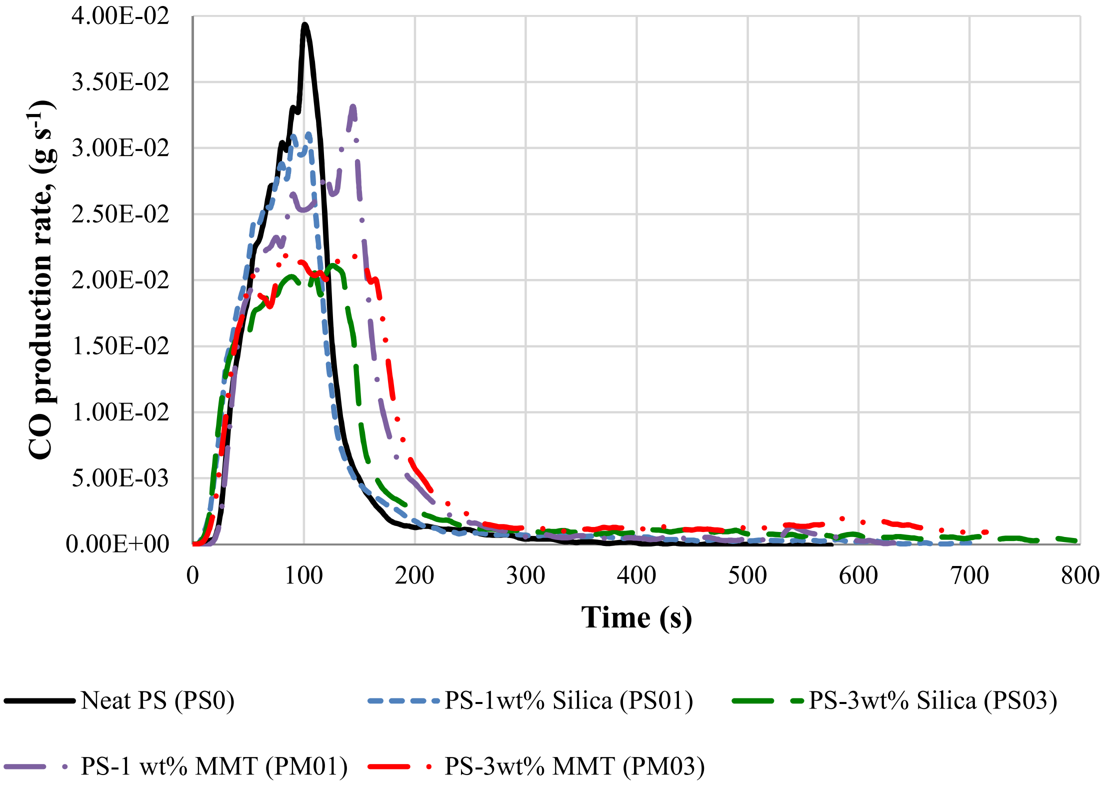

Figure 22 CO production rate with respect to time for neat polystyrene and polystyrene nanocomposites

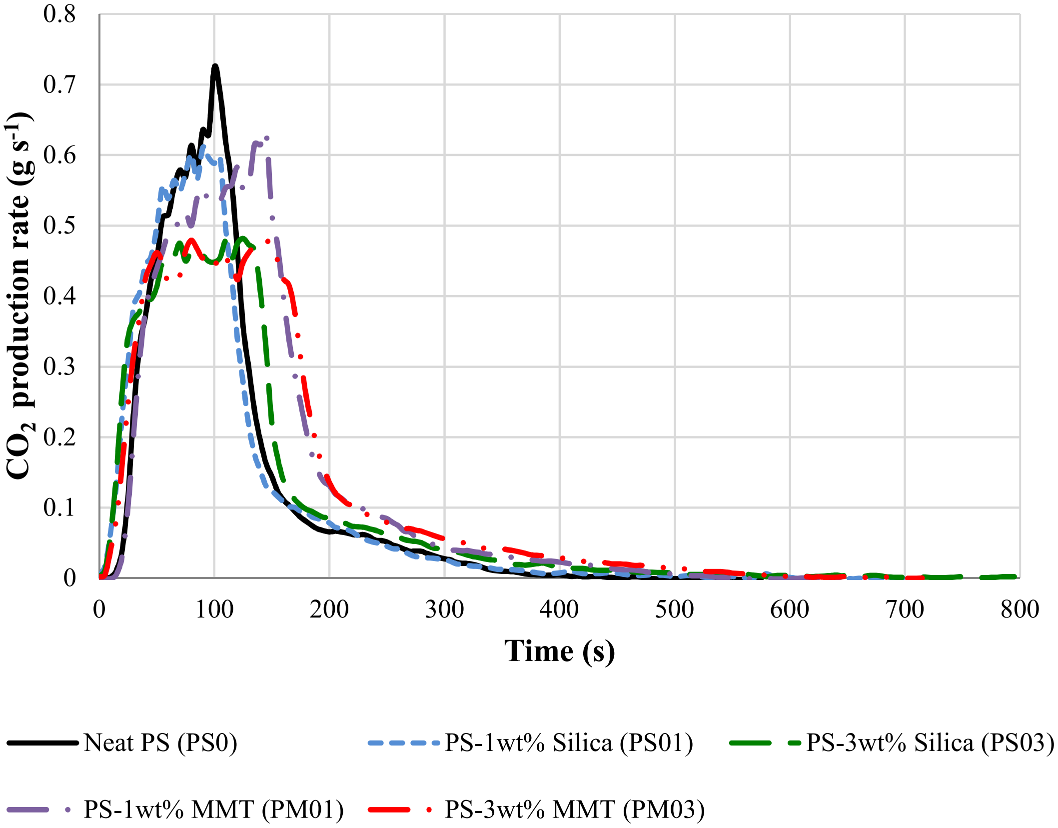

Figure 23 CO_2 production rate with respect to time for neat polystyrene and polystyrene nanocomposites

Figure 22 and Figure 23 show the CO and CO_2 release rates for neat polystyrene and polystyrene nanocomposites as a function of time. Heat release rate can be associated with increase in CO and CO_2 yield since it represents the measure of decomposition rate for the volatiles. Hence, the increase in HRR should be accompanied by increase in the yield of CO and CO_2 gas [30]. In fact, the results in Figure 22 and Figure 23 show that the observed trend for the CO and CO_2 production rate with time resembles the trend for the HRR data in Figure 17. After t = 100 s, both the CO and CO_2 emission rates drop to lower values for the neat polystyrene. In comparison to the neat polystyrene, the CO and CO_2 production rate for the nanocomposites decline. The reduction in CO evolution during combustion helps reduce the toxicity of the smoke [64].

4.4.6 Flame retardancy performance

Table 14 enlists commonly used fire performance parameters used in cone calorimeter analysis, such as fire performance index (FPI), fire growth rate index (FIGRA) and maximum average rate of heat emission (MARHE).

Table 14 Fire performance parameters in cone calorimeter analysis for polystyrene and polystyrene nanocomposites

Sample code	Sample name	Fire performance index, FPI (s m^2 kW^{-1}) × 10^3	FIGRA (kW m^{-2} s^{-1})	MARHE (kWm^{-2})	Reduction in MARHE (Δ%)
P0	Neat PS	9.9	8.8	684	-
PS01	PS-1wt% Silica	7.3	9.1	642	6.2
PS03	PS-3wt% Silica	10.7	5.7	583	14.8
PM01	PS-1wt% MMT	18.3	6.8	637	7
PM03	PS-3wt% MMT	14.7	9.3	582	13.7

Fire performance index (FPI) represents the degree of fire hazard of a material and is calculated as the ratio between the time to ignition (t_{ign}) and peak heat release rate (PHRR):

FPI = $\frac{\mathbf{tign}}{\boldsymbol{PHRR}}$ (s m^2 kW^{-1}) [65].

It is related to the time to reach flashover [66]. All the nanocomposites show improvement in terms of increased FPI compared to the neat polystyrene.

The fire growth rate index (FIGRA) is defined as the ratio of maximum of quotient of HRR and the time and it can estimate the size of the fire as well as fire spread [67, 68]. It can be represented as the maximum quotient of heat release rate with respect to time.

FIGRA = maximum quotient of HRR/t

= PHRR/t_{PHRR}

where, t_{PHRR} = time to reach to peak heat release rate (PHRR)

From Table 14, it is observed that there is no clear trend for FIGRA for the neat polystyrene and the polystyrene nanocomposites.

Average rate of heat emission can be defined as the cumulative heat emission per unit time and the peak value is considered as maximum average rate of heat emission (MARHE). MARHE is a good parameter that can measure the tendency of the fire spread during a fire scenario [68]. The MARHE values for the nanocomposites show a notable reduction of 6-14% with respect to the neat polystyrene. Both FIGRA and MARHE have been used for regulatory purposes and therefore, have been defined in relevant standards.

However, indices such as FIGRA and MARHE oversimplify information by combining several parameters into a single number. The value of these indices on the HRR and cone calorimeter setup and they are not deemed as parameters that can explain physical meaning of the fire behavior [13]. It would be more meaningful to involve parameters such as HRR, PHRR, MLR and THR to help evaluate the performance of the materials as flame retardants. The PHRR describes the flame spread and lower peak value demonstrates lower flame spread. Similarly, the MLR data provide useful information in terms of polymer degradation or consumption and char yield. However, to have a better understanding of the fire performance of the nanocomposites with respect to neat polymer, it is important to look at the combined impact. To observe the flame retardancy performance of the nanocomposites compared to neat polymer, the plot of peak heat release rate (PHRR, kWm^{-2}) as a function of THR × MLR_{avg} ($g\ MJ\ s^{-1}\ m^{-4}$) have been shown in Figure 24.

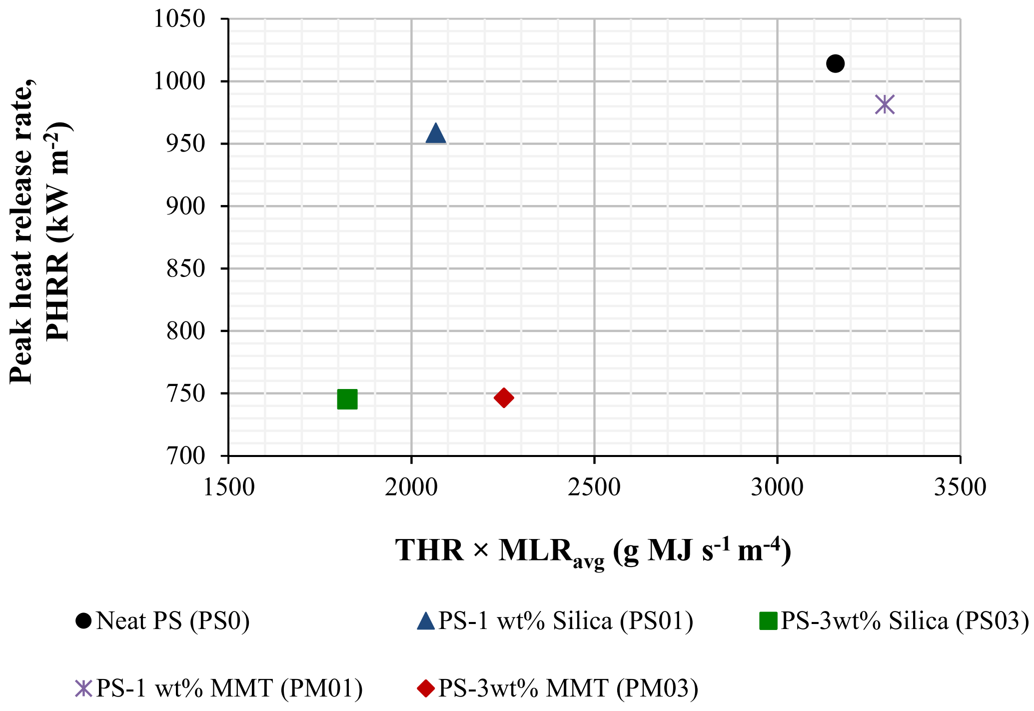

Figure 24 Peak heat release rates, PHRR (kWm^{-2}) with respect to THR × MLR$_{avg}$ (g MJ s^{-1} m^{-4}) for fire performance evaluation of polystyrene and polystyrene nanocomposites

It is observed that compared to the neat polystyrene, the nanocomposites demonstrate lower PHRR at lower THR × MLR$_{avg}$. In other words, the nanocomposites perform better as fire retardants in terms of lower peak heat release, longer time for burning for lower MLR$_{avg}$ and lower fire load for THR [29].

4.5 Discussions

With the intent of comparing the fire performance of the nanocomposites in terms of type and loading of the nanofillers; neat PS, PS-silica (1 and 3 wt% loading) and PS-MMT (1 and 3 wt% loading) were synthesized and tested in the cone calorimeter. Inorganic flame retardant additives such as nanosilica and MMT tend to improve flame retardancy of polymeric material by modifying the physical burning process and/or the chemistry in the condensed phase [51]. It was, therefore, hypothesized that addition of nanosilica and nanoclay to the polystyrene matrix would improve flame retardancy performance of the nanocomposites compared to the neat PS in the cone calorimeter analysis and the results would be comparable to the smaller-scale thermal studies conducted previously [47].

In an ideal case of a cone calorimeter analysis of flame retardant system; it is likely that the system will show increase in time to ignition, reduction in total and peak heat release rates along with reduction of mass loss rate and enhancement in char yield [50]. As per the cone calorimeter analysis on the current systems, it was observed that PS-MMT nanocomposites only showed increase in time to ignition compared to the neat PS. Increase in time to ignition is deemed as favorable since it is a measure of ignitability. From that point of view, MMT seemed to perform better than silica. However, HRR is a more reliable parameter for comparing fire retardancy performance and the HRR trends represent burning behavior of polymers [69]. From the HRR curves in Figure 17, it is evident that both PS-silica and PS-MMT nanocomposites show improvement in terms of reduced PHRR. In fact, maximum reduction in PHRR is observed as the nanofiller loading was increased from 1 to 3 wt% for both PS-silica and PS-MMT nanocomposites (ΔPHHR = 26.5% for PS-3wt% silica and ΔPHHR = 26.4% for PS-3wt% MMT). As the loading increased; the PHRR appeared to become more diffuse and broader with lower maxima implying that the samples were burning less intensely while taking longer time to burn [60]. This was confirmed by the longer flame out time for the nanocomposites compared to neat PS as shown in Table 10 with flame out time being lingered with higher loading of nanofillers. The reduction in PHRR acted as a measure of better flame retardancy for the nanocomposites as it represents char enhancement and better thermal stability [61].

The effective heat of combustion remained almost unaltered for both the neat PS and PS nanocomposites (31±2.4 MJ kg^{-1}). Simultaneously, similar trends for the heat release rate curves (Figure 17) and the mass loss rate curves (Figure 18) for both neat PS and PS-nanocomposites suggested that the physical and chemical processes in the condensed phase were responsible for the reduction of heat release rates of the nanocomposites instead of the processes in the gas phase [36]. This proves the hypothesis that both silica and MMT nanocomposites function in the condensed phase to promote flame retardancy to PS.

Flame inhibition by the nanofillers is responsible for reduction in THE; and the PS-silica nanocomposites showed reduction in THE (Table 10). There is also reduction in mass loss for both types of nanocomposites compared to the neat polymer implying that most of the nanofiller/flame-retardant is contained in the condensed phase creating char formation [13]. According to the calculation from the mass loss data, there is overall 55-75% increase in char formation (Table 12) for the nanocomposites which re-establishes the fact that the nanosilica and nanoclay fillers added in small loading can enhance the char building capability. The higher char yield for both the silica and MMT nanocomposites implies that fragments of the polymer are entrapped within the char layer forming an insulating barrier which slows down the process of degradation products of polymer fueling the flame [62] and thereby translates into better flame retardancy. PS-3wt% MMT showed a maximum of 75% increase in char buildup in comparison to the neat polystyrene. This was comparable to the 80% increase in char yield for the polystyrene-3wt% MMT nanocomposites with respect to neat polystyrene as per the TGA test in literature [47]. It can be assumed that the protective char layer attained at higher loading for the MMT nanocomposites are efficient since the clay sheets are clustered nearer [62].

In addition to the analysis of relative performance of the nanosilica and nanoclay for flame retardancy and char yield; it was intended that the cone calorimeter analysis would complement the previous study by incorporating performance for smoke toxicity, CO and CO_2 yield that directly impact human survivability in a fire. From the SP values listed in Table 13, it is observed that there is a reduction in SP for the nanocomposites compared to the neat polystyrene. In fact, when the impact of PHRR is accounted for in the SP; the smoke production is seen to be reduced for all of the nanocomposites compared to the neat polystyrene; especially when the loading is increased from 1 to 3 wt%. This is an important assessment required for determining the possible visual obscurity occurring during the fire resulting from the burning polymeric materials; which can impact human evacuation and rescue effort. The nanocomposites even generated lesser amount of CO and CO_2 than the neat PS and the performance improves as the loading is increased from 1 to 3 wt%. This reduction in CO evolution during combustion helps reduce the toxicity of the smoke [64] and signals the importance of using nanofiller additives as a cleaner alternative in the fire protection technology.

The enhancement in fire performance with increasing in loading is also observed in terms of lower peak heat release, longer time for burning for lower MLR_{avg} and lower fire load for THR. It is apparent that both silica and MMT perform better to promote flame retardancy in neat PS. Although a clear distinction in performance between the two types of fillers could not be made; it is evident that the flame retardancy performance is enhanced as the loading is increased from 1 to 3 wt%. Improvement is observed in terms of reduction on PHRR, MLR, SP, CO and CO_2 production and enhancement in char yield. Since the experiments were limited to 0, 1 and 3 wt% loading, further research can help predict the optimum loading required for having the best fire performance for the nanocomposites while retaining the original properties of the polymer. The overall conclusion is that both nanosilica and nanoclay enhance the fire retardancy performance in polystyrene as the loading is slightly increased from 1 to 3 wt% and can be environment friendly alternative for fire retardancy application that emit lesser smoke, CO and CO_2 than the neat PS during a fire.

4.6 Conclusions

For studying the impact of type and loading of flame retardant nanofillers on the fire reaction properties of polymer; neat polystyrene, polystyrene-silica and polystyrene-MMT have been prepared by *in-situ* polymerization method. To generate full-scale fire scenario and understand corresponding human reaction to parameters such as smoke generation, CO formation; cone calorimeter tests have been conducted on the above-mentioned samples. The heat release rate (HRR) data over time for both the neat polystyrene and polystyrene nanocomposites followed the trend of a thick char-forming polymer. The nanocomposites had reduced peak heat release rate (PHRR) compared to the neat polystyrene, the maximum 26% reduction in PHRR obtained for the PS-3wt% silica and PS-3wt% MMT nanocomposites. A better flame retardancy for the nanocomposites was observed in terms of 55-75% enhanced char formation, which was comparable to the visual observation of char formation after the cone calorimeter test. The nanocomposites had reduced smoke emission, as well as reduced CO and CO_2 yield with respect to the neat polystyrene. The smoke parameters (SP) reduced for all nanocomposites compared to the neat polystyrene (SP=577 MWm^{-2}), the greatest reduction being observed for PS-1wt% silica nanocomposite (SP=129 MWm^{-2}). The nanocomposites had an overall better fire performance in terms of lower peak heat release rate, longer time for burning for lower average mass loss rate (MLR_{avg}) and lower fire load for total heat release (THR) and there was an overall tendency to have enhanced fire performance as the nanofiller loading was raised from 1 to 3 wt%. Further research can provide direction as to how to determine the optimum loading for the nanofillers that can generate adequate flame retardancy without compromising the useful properties of the neat polymer.

5. SUMMARY, CONCLUSIONS AND FUTURE WORK

5.1 Summary and conclusions

Application of nanofiller additives in the polymer matrix to form nanocomposites is one potential method of solving the problem of fire spread in polymeric materials. With the objective of comparing the effect of types and loading of flame retardant nanofillers in polymer nanocomposites; the thermal, mechanical and fire reaction properties have been investigated. For this purpose, neat polystyrene (PS), PS-silica and PS-montmorillonite (MMT) have been prepared via *in-situ* polymerization method. Different characterization methods, such as thermogravimetric analysis, dynamic analysis, cone calorimetry have been employed to investigate the properties of the neat polystyrene and polystyrene nanocomposites. Some of the important findings are summarized below:

1) Thermal analysis in TGA revealed that both neat polystyrene and polystyrene nanocomposites follow similar degradation mechanism; however, the nanocomposites showed improved thermal stability in terms of higher onset of degradation temperature and lower peak mass loss rate. It can be attributed to the delayed kinetics of degradation from the addition of nanofiller additives.

2) High temperature residuals in nanocomposites compared to neat polystyrene indicated retention of mass in form of char. There has been 72-87% increase in char yield compared to neat PS. Char formation is indicative of better flame retardancy for the nanocomposites since char layer protects the unburned material beneath and slows down the heat release rate.
3) Rheological tests in dynamic mechanical analyzer showed reduction in storage and loss modulus for polystyrene nanocomposites, the highest reduction being for PS-3wt% MMT. Reduction in storage and loss modulus indicated agglomeration that weakens the interaction between polymer and filler. The glass transition value obtained using DSC and DMA showed consistency in terms of agglomeration in PS-3wt% MMT. Higher loading, may therefore introduce agglomeration.
4) Test in nanoindentation indicated that addition of nanofiller introduces hardness and as the nanofiller loading increases, hardness reduces more.
5) Reaction of nanocomposites in a well-developed fire scenario has been tested in the cone calorimeter at a heat flux of 50 kWm^{-2}. The heat release rate data over time followed the trend of a thick char producing polymer for both neat polystyrene and polystyrene nanocomposites. The maximum amount of heat liberated as represented by peak heat release rate was reduced for the nanocomposites; the maximum reduction of ~26% being observed for the PS-3wt% silica and PS-3wt% MMT.

6) Reduction in mass loss for the nanocomposites in comparison to the neat polystyrene implied that char has been retained in the condensed phase. An enhanced char yield of 55-75% was observed for the nanocomposites which was comparable to the char yield as observed in the small scale TGA tests. The maximum char was formed for PS-3wt% MMT. The visual observation of char formation after the cone calorimeter test was also consistent with the char yield calculation from the mass loss data.
7) Human survivability during fire is impacted by smoke and toxic gas generation. The nanocomposites have shown reduction in smoke parameter that considers impact of PHRR on smoke obscurity. The nanocomposites also generated less CO and CO_2 in comparison to the neat polystyrene implying that the nanofiller additives can be an environment friendly alternative for protection against fire.
8) There was improvement for the nanocomposites in terms of reduced MARHE. Overall, the performance of the nanocomposites was enhanced in terms of lower PHRR, longer burning time for lower MLR and lower fire load for THR.

Overall, the nanofiller additives namely, nanosilica and nanoclay have shown better flame retardancy performance in terms of enhanced thermal stability and char yield, lower smoke emission and lower mass loss rate. The performance tended to improve as the loading was increased from 1 to 3 wt%. However, there was a trade-off observed between the increased loading and the chances of increased agglomeration. Higher loading also impacted hardness. Further study is, therefore, needed to determine the optimum loading that can render maximum thermal stability and fire reaction properties while maintaining necessary mechanical properties of the polymer nanocomposite system.

5.2 Future work

The current study portrays a holistic view of the flame-retardant nanocomposite system for flame retardancy and depicts the role of type and loading of nanofiller loading on thermal, mechanical and fire reaction properties. There is however, scope for further analysis that can strengthen the fundamental research on flame retardancy.

1) **Optimal loading for flame retardancy performance:** It was observed that the flame retardancy and fire reaction properties, such as char yield, smoke and toxicity, peak heat release rate and mass loss rate improved as the nanofiller loading was increased from 1 to 3 wt%. Simultaneously, it was observed that agglomeration was induced and hardness was reduced as the loading increased. Further research can be conducted to identify the optimal loading required for attaining the best thermal, mechanical and fire reaction properties for the polymer nanocomposite system.

2) **Elemental analysis of char residue:** Char formation is the ultimate goal of the flame retardancy that ensures that combustible volatiles do not transfer to the gas phase and so that subsequently the heat release rate gets reduced. Elemental analysis of char residue formed after cone calorimeter test can help identify the components of char. Fourier-transform infrared spectroscopy (FTIR) on the char samples obtained after the cone calorimeter analysis can be used to analyze the characteristic peaks and then identifying different elements of char. This analysis can also help reveal the possible steps of degradation mechanism of polymers [70]. In-depth knowledge about the structure-property relation of the char can expand our understanding on how the char layer functions and contributes to fire retardancy.

3) **Synergism for enhanced flame retardancy:** For the current study, nanocomposites have been synthesized using one type of filler at a time for making a nanocomposite. However, the concept of synergism can be used to synthesize polymer nanocomposites using multiple types of nanofillers. In literature, the impact of using two or more types of flame retardant additives synergistically have been studied [71] and in many cases, these synergisms resulted in enhanced thermal stability and char formation. The impact of synergism on the overall flame retardancy can be a future direction for this study.

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