# EFFECTS OF NANOADDITIVES AND DIFFERENT CONVENTIONAL FLAME RETARDANTS ON THE FLAMMABILITY OF POLYSTYRENE

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# EFFECTS OF NANOADDITIVES AND DIFFERENT CONVENTIONAL FLAME RETARDANTS ON THE FLAMMABILITY OF POLYSTYRENE

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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# ABSTRACT

# EFFECTS OF NANOADDITIVES AND DIFFERENT CONVENTIONAL FLAME RETARDANTS ON THE FLAMMABILITY OF POLYSTYRENE

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In this thesis, there were four purposes. The first one was to investigate effects of *nanoclays* (NC) on the flammability behavior of polystyrene (PS). The second purpose was to investigate contribution of nanoclays to the flame retardancy performance of conventional phosphorus based flame retardant; *triphenyl phosphate* (TPP) and its synergist *melamine cyanurate* (MCA). For the third purpose contribution of nanoclays to the flame retardancy performance of another conventional halogenated flame retardant; *brominated epoxy polymer* (BE) and its synergist *antimony trioxide* (AO) was investigated. As the fourth purpose, effects of another nanoadditive; *carbon nanotubes* (CNTs) on the flammability behavior of PS with and without BE-AO flame retardant system was investigated.

Materials were prepared via "solution mixing" method, while test specimens were shaped by compression and injection molding. Flammability behaviors were investigated by Mass Loss Cone Calorimeter (MLC), Limiting Oxygen Index (LOI) and UL-94 Vertical Burning tests. Other characterization techniques required in this thesis were; X-ray diffraction analyses, scanning and transmission electron microscopy, thermogravimetric analyses and tensile tests.

It was revealed that use of nanoclays improved flame retardancy of PS significantly, mainly with "condensed phase" mechanism via formation of strong char barrier layers inhibiting mass and heat transfer.

When nanoclays were used together with conventional flame retardant systems TPP-MCA and BE-AO, flame retardancy parameters improved further, this time due to the "synergistic action" of "condensed phase mechanism" of nanoclays and "gas phase mechanism" of the conventional systems.

Use of carbon nanotubes also resulted in improvements in the flame retardancy of PS. However, "condensed phase mechanism" of CNTs were not as effective as the NCs, which might be due to the lower performance of 1D geometry (CNTs) compared to higher efficiency of 2D geometry (NC) in barrier formation.

As an additional purpose, effects of mixing methods in the production of PS-Nanoclay composites were also investigated. It was seen that compared to "*solution mixing*" use of "*in-situ polymerization*" resulted in poorer flame retardancy parameters that might basically be due to residual monomers or oligomers left during polymerization.

**Keywords:** Flame Retardancy, Nanoclays, Carbon Nanotubes, Polystyrene, Mass Loss Cone Calorimetry

# NANOKATKI MALZEMELERİ VE FARKLI GELENEKSEL ALEV GECİKTİRİCİLERİN POLİSTİRENİN ALEVLENME DAVRANIŞINA ETKİLERİ

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Bu tezin dört amacı vardır. Bunlardan ilki, *nanokillerin* (NC) *polisitren*'in (PS) alevlenme davranışına olan etkilerini araştırmaktır. İkinci amaç ise nanokillerin geleneksel fosfor bazlı alev gecitirici; *trifenil fosfat* (TPP) ve sinerjisti *melamin siyanürat*'ın (MCA) alevlenme dayanımı performansına katkılarını araştırmaktır. Üçüncü amaç olarak, nanokillerin bir başka geleneksel halojenli alev gecitirici; *bromlu epoksi polimer* (BE) ve sinerjisti *antimon trioksit*'in (AO) alevlenme dayanımı performansına katkıları araştırılmıştır. Dördüncü amaç olarak ise, bir başka nanokatkı malzemesi; *karbon nanotüpün* (CNT) tek başına ve BE-AO alev geciktirici sistemi ile birlikte PS'nin alevlenme davranışına olan etkileri araştırılmıştır.

Malzemeler "çözelti karıştırma" yöntemi ile üretilmiştir, test numuneleri ise basınçlı kalıplama ve enjeksiyon kalıplama yöntemleri ile şekillendirilmiştir. Alevlenme

davranışları, Kütle Kaybı Konik Kalorimetre (MLC), Oksijen Limiti İndeksi (LOI) ve UL- 94 Dikey Yanma testleri ile incelenmiştir. Bu tez için gerekli olan diğer karakterizasyon teknikleri ise; X-ışını kırınımı analizi, taramalı ve geçirimli elektron mikroskobu, termogravimetrik analiz ve çekme testleridir.

Nanokillerin PS'nin alevlenme dayanımını kütle ve ısı transferine engel olan güçlü kül bariyer katmaları oluşumu sağlayan "katı faz" mekanizması ile önemli ölçüde geliştirdiği gözlenmiştir.

Nanokillerin geleneksel alev geciktirici TPP-MCA ve BE-AO sistemleri ile birlikte kullanımında, alevlenme dayanımı parametrelerinin daha da iyileştiği gözlenmiştir. Bunun nedeni nanokillerin "katı faz mekanizması" ile geleneksel alev geciktiricilerinin "gaz fazı mekanizması"nın birlikte yarattığı "sinerjik etki"den kaynaklanmaktadır.

Nanokatkı malzemesi olarak karbon nanotüplerin kullanımı da PS'nin alevlenme dayanımında iyileşmelere neden olmuştur. Fakat CNT'nin "katı faz mekanizması"nın, NC kadar etkili olmadığı gözlenmiştir. Bunun nedeni olarak, bariyer oluşumu için çok etkin olan 2D geometriye (NC) kıyasla, 1D geometrinin (CNT) daha az etkin olması gösterilebilir.

Bu tezde ek amaç olarak, PS-nanokil kompozitlerinin üretiminde kullanılan karıştırma yöntemlerinin etkisi incelenmişitir. "*çözelti karıştırma*" yöntemine kıyasla "*yerinde polimerizasyon*" yönteminin alevlenme dayanımı parametrelerine etkisinin daha zayıf olduğu görülmüştür. Bunun temel nedeni polimerizasyon sırasında sistemde kalan monomer ve oligomerler olabilir.

Anahtar Kelimeler: Alevlenme Dayanımı, Nanokil, Karbon Nanotüp, Polistiren, Kütle Kaybı Konik Kalorimetre

# Dedem'e

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# **CHAPTER 1**

# INTRODUCTION

# 1.1 Polystyrene and Nanocomposites

# 1.1.1 Polystyrene (PS)

Polystyrene is an aromatic polymer composed of a long chain hydrocarbon wherein alternating carbon centers are attached to phenyl groups. Polystyrene is produced by free radical polymerization, from the monomer styrene. In the polymerization one carbon-carbon double bond (in the vinyl group) is replaced by a much stronger carbon-carbon single bond. In general, polymerization of polystyrene occurs with a few thousand monomers, leading to a molecular weight varying in between 100000 to 400000. Mechanical properties of polystyrene is highly dependent on its average molecular weight, the strength improves with increasing chain length but the melt viscosity increases as well, making processing difficult.



Figure 1.1 Structure of Polystyrene

Polystyrenes can be *atactic* or *syndiotactic* depending on where the phenyl groups on the polymer chain are attached to. *Atactic* polystyrenes are the most commercially

important forms. In atactic polystyrenes phenyl groups are randomly distributed along each side of the polymer chains, creating an amorphous structure. In syndiotactic polystyrenes, phenyl groups are positioned on alternating sides of the hydrocarbon backbone forming a highly crystalline structure. Syndiotactic polystyrenes are not commercially produced due to processing difficulties as a result of increased brittleness and long polymerization times.

Polystyrene is a commodity polymer, manufactured on a very large scale. Even tough, its brittle nature limits its use in high performance engineering applications; its transparency, ease of coloring and production makes it useful in applications including packaging, light covering and transparent parts of electric appliances. Also, foamed polystyrenes are highly used as insulation materials. In such uses, decreased vapor permeability, low oxygen diffusion and flame retardancy are required.

Polystyrene is a relatively inert polymer, fairly resistant to alkalis, halide acids, oxidizing and reducing agents. Still, they are soluble in large variety of solvents. Polystyrene having high refractive index (1.60); possess excellent optical properties in terms of transparency, color and clarity. It is a good electrical insulator, having a low dielectric loss factor at moderate frequencies. However, they have poor mechanical properties due to their brittleness and low heat-deflection temperature of 82-88°C and they also tend to craze and turn yellow at outdoor exposure.

Polystyrene is very flammable and burn with a smoky flame. They depolymerize when heated above 300°C and release highly flammable, volatile, monomeric and oligomeric fragments in large quantities [1]. Their high flammability and dripping limits its use in some applications. Many of these defects can be overcome via introduction of proper additives into the system or by copolymerizing.

# **1.1.2** Nanocomposites with Nanoclays

Polymer matrix nanocomposites are new class of composites which attracted great interest in recent years. They are composed of dispersed particles of which at least one dimension is in the nanometer range. Outstanding changes observed in properties with alteration of particle size from micro to nano scale even with small loadings. Improved mechanical strength, thermal stability, flame retardancy, wear resistance, optical and electrical properties are achieved compared to micro scale particle addition. These improvements are gained as a result of high aspect ratio and large surface area of the nano sized particles.

Nanocomposites can be divided into three different classes depending on number of dimensions of the nanofiller that are in the nanometer range. Nanocomposites containing nanofillers that have all three dimensions in nanometer range are nanoparticles. Nanomaterials having two dimensions in nanometer range include nanotubes, nanofibers, platelets, etc. The third type of nanocomposites is composed of nanofillers that have only one dimension in nanometer range, namely; nanolayers, nanofilms and nanocoatings. Depending on the desired effect, one of these filler types are incorporated into polymer matrices. Nanoclays are in this third class with having only thickness in one to few nanometer and length of hundreds to thousands nanometer long.

Phyllosilicates are the most commonly used nanoclay minerals with crystal structure consisting of stacked layers of 1 aluminum or magnesium hydroxide octahedral sheet sandwiched between 2 tetrahedral silicate sheets, in which oxygen ions of octahedral sheet is shared by tetrahedral sheets (Figure 1.2). Isomorphic substitution within layers caused by replacement of  $Al^{+3}$  by  $Mg^{+2}$  or  $Fe^{+2}$  and  $Mg^{+2}$  by  $Li^{+1}$  generates negative charges in crystal lattice. This negative charge is counterbalanced by alkali and alkaline earth cations such as  $Fe^{+2}$ ,  $Ca^{+2}$ ,  $Na^{+}$ . These cations are not bonded to the crystal, but they form a positively charged layer between the negatively charged surfaces of the crystals.

The layer thickness is around 1 nm, and the lateral dimensions may vary from 30 nm to several microns. Stacking of the layers leads to a regular van der Waals gap between the layers called the *interlayer* or *gallery*. The sum of the single layer thickness and the interlayer is called *d-spacing* or *basal spacing*.

Nanoclays are characterized by surface charge, known as Cation Exchange Capacity (CEC) expressing the ability of clays to retain cations. Cation exchange capacity is measured in milliequivalents per 100 g of air-dried clay.



Figure 1.2 Structure of 2:1 Phyrosilicates [2]

It is an important parameter since modifications need to be done on surface of the clay layers. Nanocomposite formation cannot be achieved by just mixing polymer with nanoclays since they tend to form stacks. In order for polymers to intercalate through stacks; silicate layers that are *hydrophillic* in nature should be changed into *organophillic*. With the aim of turning silicate layers nature to more compatible with polymers, modifications are done by ion-exchange reactions. In ion-exchange reactions, the interlayer inorganic cations are ion-exchanged into organic cations such as alkylamonium or alkylphosphonium cations. Final product of this ion exchange reaction is referred as organoclays. These alkylamonium or alkylphosphonium cations between silicate layers and also expand the clay galleries depending on the surfactant chain length. Consequently, diffusion of polymer into galleries is improved resulting in larger interlayer spaces.

Two particular characteristics of nanoclays are important for nanocomposite formation. First is the ability of clay particles to exfoliate into individual layers. Second is the ability to compatibilize and modify their surfaces via ion-exchange reactions. Montmorillonite is one of the most preferred nanoclays in nanocomposite formation due to its small particle size ( $<2\mu$ m), high aspect ratios (10-2000) and high swelling capacity which eases homogeneous dispersion and facilitate polymer diffusion [3].

Different preparation methods are utilized to create the desired nanocomposites of PS with nanoclays. Solution intercalation, melt-intercalation and in-situ polymerization are considered to be most convenient methods to disperse layered silicates into nanocomposites to have exfoliated or intercalated structure.

#### (i) Solution Mixing

In solution mixing; a solvent in which polymer is soluble is used, to disperse and exfoliate nanoclays into single layers. Polymer is then added to this mixture, and adsorbs onto delaminated sheets. Upon removal of the solvent, sheets reassemble, confining polymers into clay galleries to form an ordered, multilayer structure (Figure 1.3). Even tough, it enables to obtain highly intercalated structure; this method is not preferred in industrial applications due to problems arisen by large amount of solvent usage.



Figure 1.3 Schematic Representation of the Solution Intercalation. (Reproduced from [4])

#### (ii) Melt Intercalation

In melt intercalation, nanoclays are mixed by annealing with a polymer matrix which is heated above its softening point. During annealing process, polymer chains diffuse into clay galleries if layer surfaces between clay and polymer are compatible, and form either exfoliated or intercalated structure (Figure 1.4). This method has attracted great deal of attention since it is an environmental-friendly solvent-free method, and can be operated with current industrial processes like injection or extrusion molding.



Figure 1.4 Schematic Representation of the Melt Intercalation. (Reproduced from [4])

#### (iii) In-situ Polymerization

In in-situ polymerization, nanoclay is swollen in liquid monomer or monomer solution. Polymerization initiated either by heat or a suitable initiator, occur in between the intercalated clay layers (Figure 1.5), resulting in a structure that is kinetically trapped in a well dispersed structure [5].



Figure 1.5 Schematic Representation of the In-Situ Mixing. (Reproduced.from [4])

Depending on the preparation methods used and nature of interfacial interactions between nanoclay and polymer, three main types of composites may be obtained when clay particles are incorporated into polymer matrix.

#### (a) Phase Separated (Micro) Composite

Phase separated (micro) composite is obtained when polymer chains are unable to intercalate through clay galleries, and clay remains as tactoids. Properties of phase

separated composites are similar to those traditional counterparts. Due to poor polymer and clay interaction no significant improvement is achieved in the performance of polymers.

#### (b) Intercalated Nanocomposite

Intercalated nanocomposite is obtained when one or more polymer chains diffuse between clay layers, leading to a well ordered multilayer structure of alternating polymeric and inorganic layers. Repeating distance of these layers is found to be in the range of a few nanometers. Intercalated structure causes significant improvements in the performance of polymers.

#### (c) Exfoliated Nanocomposite

In exfoliated structures, uniform and complete dispersion of individual clay layers is attained in a continuous polymer matrix. Polymer-clay interactions are maximized in exfoliated nanocomposites, leading to outstanding improvements in the performance of polymers.



Figure 1.6 Three Main Structures Obtained in Polymer/Clay Composites

#### **1.1.3** Nanocomposites with Carbon Nanotubes

Carbon nanotubes are another family of nanofiller having 2 dimensions in nanometer range. They are composed of graphene sheets (2-D hexagonal arrangement of carbon-carbon bonds) rolled into cylinders, having diameters ranging from one nanometer to tens of nanometer, with lengths up to centimeters. They attracted great attention due to their exceptional properties, since their discovery by Iijima in 1991 [6].

Nanotubes can be synthesized in two different structural forms, namely; single wall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT). MWCNTs consist of multiple layers of graphene cylinders coaxially arranged around a central hollow core (Figure 1.7). The structure of MWCNT can be described with two different models. In *Russian Doll* model, graphene sheets are arranged in concentric cylinders. In *Parchment Model*, single graphene sheets rolled around itself with interlayer separations close to distance between graphene layers. SWCNT consist of single graphene sheet rolled into a seamless cylinder. Even though SWCNT has superior mechanical, electrical and thermal properties, it is more prone to agglomerate and form ropes and bundles.



Figure 1.7 Schematic Representations of (a) Multi-Wall and (b) Single-Wall Carbon Nanotubes [7]

Additionally, atomic structure of the carbon nanotubes can be defined by orientation and magnitude of the chiral vector;  $C_h = na_1 + ma_2$ , where (n,m) are number of steps along carbon bonds of hexagonal lattice and  $(a_1, a_2)$  are unit vectors in graphene sheet. Three different morphologies are defined as *armchair* (n = m), *zigzag* (n = 0, m = 0) or *chiral* (all others); shown in Figure 1.8. Properties of carbon nanotubes are highly dependent on morphology they posses. For example, *armchair* nanotubes are considered as metallic, whereas *zigzag* and *chiral* counterparts are semiconducting in terms of electronic properties [8].

Carbon nanotubes have outstanding properties that make them excellent candidates to be used in various high-tech applications. Owing to their high aspect ratio (typically 300-1000), CNTs are able to percolate and form a network even at very low loadings and this in turn result in enhancement of mechanical, electrical, thermal and flame retardant properties. Tensile modulus and strength values of SWCNT and MWCNT were found to be in the range of 270 GPa to 1 TPa and 11 GPa to 200 GPa, respectively [9]. They are thermally stable up to 2800°C in vacuum, and they have electric current carrying capacity 1000 times higher than copper wires [10].



Figure 1.8 Schematic of Nanotube Morphologies; (a) Armchair, (b) Zig-zag, and (c) Chiral [9]

The methods of solution mixing, melt mixing and in-situ polymerization are widely applied in preparation of PS-CNT nanocomposites, as in PS-NC systems. The main focus of all fabrication methods is to improve CNT dispersion and prevent bundling occurred due to van der Waals interactions between individual tubes, since consistent dispersion leads to consistent load transfer and can result in percolation of CNTs to form a network.

#### (i) Solution Mixing

Solution mixing is the most widely used production method and it involves three major steps. First, nanotubes are dispersed in a suitable solvent in which polymer is soluble. Then, polymer is added to this mixture. High power sonication can be used to enhance formation of metastable suspensions of nanotubes or nanotube polymer mixtures in solvents. Finally, nanocomposites are recovered by precipitating or casting a film [11].

#### (ii) Melt Mixing

In melt mixing, high temperature and shear forces applied to disperse nanotubes in polymer matrix. Even though this method enables operation with current industrial processes and beneficial in terms of lack of solvent use, it is generally less effective in dispersion of nanotubes compared to solution mixing [11].

### (iii) In-situ Polymerization

In in-situ polymerization, nanotubes are dispersed in liquid monomer or monomer solution. Polymerization initiated either by heat or a suitable initiator, resulting in a well dispersed network structure. In-situ methods also can facilitate covalent bonding between functionalized nanotubes and polymer matrix, however extent of polymerization reactions are limited since viscosity increases as polymerization proceeds [11].

# **1.2 Flammability of Polymers**

When polymers are exposed to a sufficiently large heat flux radiated from a fire, they thermally decompose to yield volatile gases, solid carbonaceous char and airborne soot particles (smoke) [12]. The volatile gases arisen can either be flammable such as carbon monoxide, methane, low molecular organics, or can be non-flammable such as carbon dioxide and water. When flammable volatile gases diffuse from decomposing polymer into air, they form a gaseous mixture, reacting with oxygen or other oxidizing element leading to ignition and liberating heat. The amount of heat liberated controls the duration of combustion. In presence of sufficient heat fed back to polymer, new decomposition reactions are induced in the solid phase, more combustibles are produced, thus; process becomes self sustaining; maintaining combustion of the polymer [7].

Polymers decompose via series of chemical reaction mechanisms. First mechanism is *random-chain scission*; in which scissions occur randomly throughout the length of the chain. Second mechanism is *end-chain scission* in which individual monomer units or volatile chain fragments are removed at the chain end. *Chain stripping* is another mechanism in which atoms or groups that are not part of the main backbone (side/pendant groups) are removed. The last mechanism is *cross-linking* in which bonds are created between polymer chains, resulting in an increase in molecular weight. In most cases, polymers decompose through combination of two or more mechanisms.

Polymers that decompose via random chain scission and depolymerization are more flammable than those decompose via cross-linking and chain stripping. Cross-linking causes creation of char which lowers flammability [13]. In chain stripping, removal of the side/pendant group leads formation of double bonds which can give crosslinks. And again cross-linking result in formation of char, lowering flammability.

Polymers having aromatic or heterocyclic groups in main chain are less combustible than polymers with an aliphatic backbone [14]. Polymers having short and flexible linkages between aromatic rings tend to crosslink and char. This char formation increases thermal stability and enhance flame retardancy. On the other hand, polymers with relatively long flexible linkages between aromatic rings are relatively more combustible.

Char formation is very important in combustion process. Charring of the polymer can occur via *cross-linking*, *aromatization*, *fusion of aromatics* or *graphitization* depending on the structure of the polymer [15]. Char is formed only if the cross-linked polymer has aromatic fragments or conjugated double bonds and is prone to aromatization during thermal decomposition [13]. It works as a barrier to heat and mass flow, and stabilize carbon; preventing its conversion to combustible gases. Char effectiveness depends both on its chemical and physical structure. For an effective barrier; a rigid and crack deficient char structure must be provided to prevent the flow of volatile flammable gases into the flame and to provide sufficient thermal gradient to protect the polymer below its decomposition temperature.

Fire behavior of polymers can be divided into three stages (Figure 1.9).



Figure 1.9 Basic Stages of Polymer Combustion

(i) **Ignition:** An ignition source (flame, cigarette, glow wire, etc.) comes in contact with the volatile flammable products of the polymer combustion and flame is onset in the range of ignition temperature (300-400°C). Flammability of material is determined in this stage.

(ii) **Developing Fire:** Flaming combustion continues in this stage of fire growth, and temperature rise above the ignition temperature (400-600°C). It is characterized by an external heat flux around 20–60 kWm<sup>-2</sup>. Fire behavior is controlled by flame spread and heat release in this stage.

(iii) Fully developed fire: In this last stage of fire growth, temperatures rise above 600°C. It involves high external heat fluxes above 50 kWm<sup>-2</sup>. Fire load, fire penetration is determined in this stage.

For polystyrene, degradation to volatile products initiates around 300°C and has been explained by hydrogen loss followed by C–C bond scission to form a chain terminating carbon radical [16].

This radical can then further degrade by stepwise elimination of the styrene monomer until the polymer molecule is completely degraded, or the radical is stabilized. This is a low energy process, which is often referred to as 'unzipping', and accounts for about 50% of the volatiles formed from polystyrene pyrolysis.



Figure 1.10 Schematic Representation of Degradation for Polystyrene [17]

It can be seen in Figure 1.10 that each elimination of styrene results from the breaking of the C–C bond which is beta to the carbon bearing the radical, and produces a similar radical structure which can undergo further styrene elimination [17].

### **1.2.1 Flammability Tests**

### (i) UL-94 Vertical Burning Test

UL-94 test is developed by Underwriters Laboratory Inc. (USA), to assess the "flammability of plastic materials for parts in devices and appliances". It is a common procedure to check if a product complies necessary regulations by measuring ignitability and flame spread of polymeric materials exposed to small flame.

Specimens with a length of  $120\pm5$ mm and width of  $13\pm0.5$ mm are used to assess flammability behavior. Specimen thickness may be 3.2, 1.6 or 0.8 mm depending on the intended use of plastic. However, thinner specimens are detected to be more flammable and because of that, thickness must be stated in ratings for an effective evaluation.

As shown in Figure 1.11, bar shaped specimen is held vertically and a cotton layer is placed underneath of it, in order to detect any flammable drips that could ignite cotton.



Figure 1.11 Experimental Set Up for UL-94 V Flammability Test [7]

Flame is applied from bottom of the polymer for 10 seconds, and its afterflame time  $(t_1)$ , which is the time needed for flame to self extinguish is recorded. In the second step, flame is applied for another 10 seconds, and afterflame time  $(t_2)$  and afterglow time  $(t_3)$  which is the time needed for fire glow disappear, are recorded. Throughout the test, burning drips that can cause ignition of cotton must be observed and noted.

The test should be conducted for five specimens, and depending on the overall performance of specimens regarding duration of burning and presence of flaming drips; materials are classified into three categories. The burning characteristics required for V-0, V-1 and V-2 ratings are listed at Table 1. V-0 rating is given to materials that extinguishes in less than 10 seconds, with no combustible drips. These materials are considered to be self-extinguishing.

	<b>V-0</b>	V-1	V-2	Fail
Total afterflame time (t <sub>1</sub> + t <sub>2</sub> ) for each specimen	≤10 s	≤30 s	≤30 s	> 30 s
Total afterflame time $(t_1+t_2)$ for 5 specimens	≤50 s	≤250 s	≤250 s	
Afterflame (t <sub>2</sub> ) plus afterglow time (t <sub>3</sub> ) upon second ignition for each specimen	≤30 s	≤60 s	≤60 s	
Ignition of cotton by burning drips	No	No	Yes	
Glowing or flaming combustion of any specimen to holding clamp	No	No	No	

Table 1.1 Ratings and Their Criteria in UL-94 Vertical Burning Test

#### (ii) Limiting Oxygen Index (LOI) Tests

Limiting oxygen index test (LOI) is a small scale test, used to quantify materials flammability and resistance to ignition. LOI tests are standardized by international test standards, including ASTM D2863 and ISO 4589. LOI tests measure minimum oxygen percent that will support ignition and combustion of the material.

As shown in Figure 1.12, a bar shaped specimen is placed vertically inside a glass chimney which allows burning to be observed. During the test oxygen-nitrogen mixture with a specified oxygen concentration is supplied at the bottom of the chimney and small flame is applied at top of the specimen. If specimen does not ignite after 30 seconds of flame exposure, concentration of the oxygen is increased. Minimum percentage of oxygen for burning of sample for 3 minutes or consuming 5 cm of the sample is detected by varying the oxygen concentration through a series of tests.



Figure 1.12 Experimental Set Up for LOI Test [7]

Considering that air contains 21% oxygen; materials having LOI value lower than 21% are classified as "combustible", whereas those with LOI value higher than 26% are classified as "self-extinguishing" since their combustion cannot be sustained without any contribution of external energy source. It can be stated that, flame properties increase with increasing LOI values.
There are limitations of LOI tests, since the test does not reflect a real fire scenario. LOI is usually measured at room temperatures, whereas oxygen index values may change with higher temperature emerged at actual fire.

Although LOI test is inadequate in predicting real fire performance of materials, it is a useful test in classifying flammability and ignitability.

#### (iii) Mass Loss Cone Calorimeter (MLC)

Heat release rate measurements are accepted to be one of the most reliable techniques for investigating flame properties of combustible materials. Cone calorimeter is a bench scale instrument utilized for these measurements. The name 'cone' comes from the truncated cone shaped heater used to heat the specimen during fire testing. Generally cone calorimeters work on the basis of measuring oxygen consumption in the combustion gases of a sample subjected to a heat flux. The measurements of the oxygen consumption and gas flow are used to calculate the quantity of heat released.

However, in this study Mass Loss Cone Calorimeter (MLC) is used for flame investigations according to the standard *ISO 13927 Simple Heat Release Test Using a Conical Radiant Heater and a Thermopile Detector*.

In MLC; heat release rate is determined by use of a thermopile instead of the oxygen consumption technique. As shown in Figure 1.13 square shaped specimens with 100x100x4 mm dimensions is placed on a load cell, and conical heaters uniformly irradiate sample from above by creating a known heat flux. The combustion is, then triggered by an electric spark. Heat release rate is assessed from measurements of outputs of thermopiles located in chimney situated above burning test specimen. The outputs of thermopiles obtained in unit of millivolts (mV) are converted into heat release rate per unit area in unit of kW/m<sup>2</sup>. This conversion is executed by means of calibration graph obtained previously by burning of propane with known calorific value in the same apparatus.



Figure 1.13 Experimental Set-Up for MLC test [7]

The maximum value of heat release rate termed as **Peak Heat Release Rate** (**PHRR**), is an important parameter to evaluate fire performance of polymers. It represents maximum energy emitted from specimen during combustion and is related to flame spread in fire growth stage of burning. **Total Heat Evolved (THE)** is another parameter calculated by integration of HRR vs. time curves. It represents total heat evolved from the specimen throughout the fire. An example of *Heat Release Rate* versus *Time* and *Total Heat Evolved* versus *Time* graphs for representative neat polymer and flame retarded polymer are given in Figure 1.14. As can be seen from HRR vs. time graphs, curves are broaden and PHRR values decrease with the flame retardant addition in to the polymer. Also reductions in THE values are observed with the introduction of flame retardants.

In addition to these parameters, Mass Loss Cone Calorimeter can monitor **Time to Ignition (TTI)**, **Total Burning Time (TBT)**, **Total Mass Loss (TML)**, and **Time to Peak Heat Release Rate (TTP)**. Time to Ignition (TTI) is the time interval between sparking and ignition. It reveals ignitability of specimen. Total Burning Time (TBT) is the time between ignition and extinguishment of the flame. Time to Peak Heat Release Rate (TTP) is the time at which heat release rate reaches its maximum values.



Figure 1.14 Representative (a) Heat Release Rate and (b) Total Heat Evolved Curves

**Fire Growth Index (FGI)** and **Fire Growth Rate (FIGRA)** can be interpreted from data obtained above. Fire Growth Index (FGI) can be calculated by dividing PHRR with TTI and represents materials contribution to fire propagation. Fire Growth Rate (FIGRA) can be calculated by dividing PHRR with TTP and represents materials contribution to fire propagation rate. **THE/TML Ratio** is another important parameter to evaluate whether flame retarding action is in the gas or condensed phase. If the flame retardant added is active in gas phase, THE/TML ratio of the material changes considerably from that of the pure material.

## **1.2.2 Flame Retardancy Mechanisms**

Flame retardant systems are introduced to polymers to inhibit polymer combustion processes. Flame retardancy mechanism may act physically or chemically in condensed or gas phase. They can impede thermal degradation during heating, pyrolysis, ignition or propagation.

#### (i) Physical Action of Flame Retardants

Combustion reactions can be hindered by physical action of flame retardants in several ways. Some flame retardant additives cool the reaction medium by means of decomposing endothermically. This endothermic decomposition causes heat consumption, decreasing temperature below polymer combustion temperature.

Upon degradation some flame retardants decompose liberating inert gases such as water vapor ( $H_2O$ ) and carbon dioxide ( $CO_2$ ). Those inert gases cause dilution of combustible gas mixture, decreasing concentration of radicals in flame. Thus; ignitability decreases.

Some flame retardant can lead to formation of protective solid or gaseous layer that can act as a protective barrier. This layer inhibits the flow of heat and oxygen to the polymer and also combustible volatile gases to vapor phase. As a result polymer inside is protected and volatile gases are separated from oxygen preventing the combustion cycle to be self-sustained.

More than one flame retarding mechanism may operate simultaneously together as in the case of aluminum hydroxide  $(Al(OH)_3)$ . By endothermic decomposition of it, water vapor is released diluting radicals in the flame and cooling the reaction medium. Also a protective layer is formed by residues of alumina  $(Al_2O_3)$  acting as a barrier. However, very large amounts should be incorporated to polymer in order to be effective [18].

### (ii) Chemical Action of Flame Retardants

Chemical action of a flame retardant additive can occur either in gas phase or condensed phase.

In gas phase, flame retardant additives release radicals such as gaseous  $Cl^{\bullet}$ ,  $Br^{\bullet}$ . These radicals can react with highly energetic and reactive species (H $^{\bullet}$ ,  $OH^{\bullet}$ ) forming less energetic halogen radicals and molecules. With this alteration of the degradation pathway, radical concentration drop off, thus heat producing combustion processes decreases.

In condensed phase, flame retardants can accelerate breaking down of polymer causing melting and dripping away from the flame. Melamine cyanurate is one of the most widely used flame retardant additive causing dripping. Aliphatic bromines are also used to create same effect in foamed polystyrenes and thin films of polypropylene.

Flame retardants can also cause formation of a carbonaceous char or vitreous layer on the polymer surface. This can occur when a fire retardant removes the side chains and generates double bonds in the polymer. These double bonds give crosslinks, resulting in the formation of char. This char or vitreous layer can act as an insulating barrier in between flame zone and polymer. There are also intumescent systems in which swelling of the surface layer of polymer is sustained via blowing agents. Char produced can provide insulation and slow down heat transfer from the exposed side to the unexposed side of polymer.

## **1.2.3** Conventional Flame Retardants

Flame retardant additives are composed of compounds or mixture of compounds that are incorporated into polymers in order to decrease ignitability, or if once ignited, to manipulate its burning behavior. There are several different types of flame retardants used.

### (i) Halogen Containing Flame Retardants

When flammable volatile gases diffuse from decomposing polymer into air, they form a gaseous mixture, reacting with oxygen leading to production of highly reactive H• and OH• radicals. These radicals are very important in the chain reactions leading to the decomposition and sustained burning of polymers. Hydrogen radical (H•) is responsible for chain branching free radical reactions in the flame [5].

$$H^{\bullet} + O_2 \to OH^{\bullet} + O^{\bullet} \tag{1.1}$$

$$O\bullet + H_2 \to OH\bullet + H\bullet \tag{1.2}$$

Hydroxyl radical (OH•) is responsible for the main exothermic reaction which generates larger part of the heat in the flame [5].

$$OH \bullet + CO \rightarrow CO_2 + H \bullet$$
 (1.3)

Main flame retardancy mechanism of halogen containing flame retardants is, interrupting the gas phase reactions (1.1-1.3) that generate most of the thermal energy.

There are four types of compounds that can be used as halogenated flame retardants containing fluorine, chlorine, bromine and iodine. Fluorinated compounds are not preferred much, since they are more stable than most of the polymers and do not release its halogen in the form of fluorine radical below or at the same temperature range of decomposition temperature of the polymer. Since it releases its halogen at later stages, gas phase reactions cannot be interrupted by radical trapping process.

Iodinated compounds are again not utilized as a flame retardant, since they have very low thermal stability and this makes it difficult to be processed with commercial polymers. Apart from that, these two compounds are far more expensive than brominated and chlorinated products.

Chlorinated compounds used as flame retardants are in aliphatic and cycloaliphatic forms. Aromatic chlorine compounds are not very efficient due to their high thermal stability, thus they are not utilized in the field of flame retardancy.

Brominated flame retardants are by far, the most preferred halogenated flame retardants. Aliphatic ones are found to be more unstable than aromatic ones, due to their lower bond strength and stability that results easier dissociation at lower temperatures. They can be used only for certain polymers with low processing temperatures.

Flame retardancy mechanism of brominated flame retardants can be explained in series of reactions. An example of such reactions with an aliphatic polymer is given through Reactions 1.4 to 1.9 [5]. It begins with abstraction of halogen radical (Br•) from flame retardant (R-Br).

$$R-Br \to R^{\bullet} + Br^{\bullet} \tag{1.4}$$

Then Br• radical abstracts hydrogen from the polymer, and forms hydrogen bromide (HBr).

$$Br\bullet + CH_2-CH_2 \to CH\bullet-CH_2 + HBr$$
(1.5)

Hydrogen bromide (HBr) volatilizes and then diffuses to the combustion zone of the flame where it can react with hydrogen (H $\bullet$ ) and hydroxyl radical (OH $\bullet$ ) and regenerate bromide (Br $\bullet$ ).

(1.6)

$$HBr + H \bullet \to H_2 + Br \bullet \tag{1.7}$$

$$HBr + OH \bullet \rightarrow H_2O + Br \bullet$$
(1.8)

Bromine radicals react with the hydrocarbons, and form hydrogen bromide until all Br leaves the flame.

$$Br\bullet + RH \rightarrow HBr + R\bullet$$
(1.9)

Hydrogen bromide reduces concentration of H• and OH• radicals, which are responsible for sustaining combustion. It is found that even small additions of brominated flame retardants result in significant improvements in flame retardancy of the polymers.

In addition to chemical flame retardancy action of radical trapping, it is also believed that large heat capacity of hydrogen bromides (HBr) has profound effect on decreasing temperature of the flame. Furthermore, its dilution of the flame results in decrease of the mass concentration of the combustible gases [19].

Brominated flame retardants also have condensed phase contribution in flame retardancy by promoting charring in polymer. When bromine radicals abstract hydrogen from the polymer, this results in unsaturation (Reaction 1.5). Unsaturated polymer chain then, release a hydrogen radical and forms double bonds (Reaction 1.6) which are responsible in formation of char via cross linking or aromatization. This char can work as an insulating barrier between flame zone and polymer.

There is also another condensed phase mechanism, applicable for aliphatic bromine. It involves chain scission of polymer via bromine radicals generated at low temperatures. Breaking down of polymer chain causes melting and dripping polymer away from the flame, and extinguishes it. This mechanism functions in polypropylene and foamed polystyrene systems [20].

#### (ii) Phosphorus Containing Flame Retardants

Phosphorus containing flame retardants attract great deal of interest in recent years with increasing demand for an alternative to halogenated flame retardants. Phosphorus containing flame retardants can be in the form of elemental red phosphorus, inorganic or organic phosphorus based compounds and chloro organophosphates.

Phosphorus containing flame retardants can act in gas or condensed phase depending on the polymer it is introduced in. In polymers which does not contain oxygen or hydroxyl group, gas phase action of phosphorus is dominant. Phosphorus radicals such as; HPO<sub>2</sub>•, PO•, PO<sub>2</sub>•, and HPO•, are released into the flame at elevated temperatures. These phosphorus radicals take part in radical scavenging of highly energetic H• and OH• radicals, through series reactions (Reactions 1.10-1.14); suppressing flaming of combustion [5].

 $HPO_2 \bullet + H \bullet \to PO + H_2O \tag{1.10}$ 

$HPO_2 \bullet + H \bullet \rightarrow PO_2 + H_2$	(1.11)

- $HPO_2 \bullet + OH \bullet \to PO_2 + H_2O \tag{1.12}$
- $PO\bullet + H\bullet \to HPO \tag{1.13}$
- $PO \bullet + OH \bullet \rightarrow HPO_2$  (1.14)

A recent study [21] showed that phosphorus at the same molar concentration is, on average, five times more effective than bromine and 10 times more effective than chlorine. But in order to fully benefit from this, volatilization of the phosphorus radicals must take place below decomposition temperatures of the polymer.

Another flame retardancy mechanism of phosphorus compounds active in the gas phase is, *blanketing effect*. Phosphorus containing volatiles inhibit oxygen transfer by forming a relatively heavy phase at surface. This phase covers the surface as a blanket and prevents access of oxygen.

In polymers containing oxygen or hydroxyl group, phosphorus based flame retardants act mainly in condensed phase. In such systems, flame retardants decompose into phosphoric and polyphosphoric acids that react with hydroxyl groups of the polymer liberating water and leading to double bonds and crosslinking and finally, form significant amounts of char. This char works as an insulating barrier, protecting polymer from heat, flame and oxygen. In addition to insulating barrier formation caused by charring, release of water decrease combustible gas content, thus increase flame retardancy. The effectiveness of flame retardants for this mechanism increases with oxygen content in polymer.

Phosphorus can also promote melting of some thermoplastics by accelerating heat loss and dripping away from the flame.

#### (iii) Synergistic Additives for Flame Retardants

#### **Antimony-Halogen Synergism:**

A significant increase in fire retardancy effectiveness is observed when halogenated flame retardants are used in combination with antimony trioxide  $(Sb_2O_3)$ . It is observed that it both assist and eases delivery of halogen atom in the gas phase and extends the time which halogens exist in the flame zone, in turn more radicals can be scavenged [14].  $Sb_2O_3$  reacts with hydrogen bromide (HBr) and forms antimony tribromide (SbBr<sub>3</sub>) which is a more active radical scavenger (more volatile, boils at 288°C) than HBr.

$Sb_2O_3 + 2 HBr \rightarrow 2 SbOBr + H_2O$	(1.	15	)
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$$5 \text{ SbOBr} \rightarrow \text{Sb}_4\text{O}_5\text{Br}_2 + \text{SbBr}_3 \tag{1.16}$$

- $4 \operatorname{Sb}_4 \operatorname{O}_5 \operatorname{Br}_2 \to 5 \operatorname{Sb}_3 \operatorname{O}_4 \operatorname{Br} + \operatorname{Sb} \operatorname{Br}_3 \tag{1.17}$
- $3 \operatorname{Sb}_3\operatorname{O}_4\operatorname{Br} \to 4 \operatorname{Sb}_2\operatorname{O}_3 + \operatorname{Sb}\operatorname{Br}_3 \tag{1.18}$

In flame SbBr<sub>3</sub> is reduced through series reactions, scavenging H• and OH• radicals [5].

$SbBr_3 + H \bullet \rightarrow SbBr_2 + HBr$	(1.19)
$SbBr_2 + H \bullet \longrightarrow SbBr + HBr$	(1.20)
$SbBr + H \bullet \rightarrow Sb + HBr$	(1.21)
$Sb + OH \bullet \rightarrow SbOH$	(1.22)

#### **Phosphorus-Nitrogen Synergism:**

Melamine containing 67 wt% nitrogen in the molecule is a common flame retarding additive. Melamine can be found in the form of melamine cyanurate, melamine phosphate, melamine pyrophosphate, and melamine polyphosphate.

Flame retardancy effect of melamine is based on sublimation. Melamine sublimates at about 350°C, instead of melting. This leads to absorption of energy, resulting in decrease in surface temperature of the polymer. In a hot flame, melamine may decompose with a very endothermic process, creating cyanimid.

Melamine cyanurate is formed from a 1:1 mixture of melamine and cyanuric acid held together by two-dimensional network of hydrogen bonds. Throughout decomposition, cyanuric acid causes chain scission which enhances dripping and melting of the polymer.

Melamine is used for enhancing flame retardancy effect of phosphorus compounds. There are different mechanisms suggested for this enhancement. In one of them, this effect is based upon formation of P-N bonded intermediates, which are better char forming agents than phosphorus alone [17]. Nitrogen also helps retention of phosphorus in condensed phase. This effect is very efficient in polymers forming char, but it is not efficient for polymers forming little amounts of char in which vapor phase action is important. Nitrogen compounds also extend temperature range of polymer decomposition and decreases the evaporation rate of combustible gases [15]. Finally, nitrogen compounds enhance oxidation of phosphorus, resulting in liberation of inert gases like ammonia, thus diluting the combustible gas mixture and decreasing the concentration of radicals in flame.

## **1.2.4** Nanoadditives as Flame Retardants

Polymer nanocomposite studies on contribution of nanoclays have started in the late 1940s, with much higher clay loadings [22]. It was in 1976 that Unitka Ltd. has first stated that flame retardant properties are enhanced with introduction of layered silicates in nylon 6 (N6) polymers [23]. In 1989 Toyota research group have stated 70% increase in room temperature tensile modulus, an 87°C increase in heat distortion temperature and a significant decrease in water permeability of N6 with nanoclay addition. After that, a comprehensive study on flame retardancy properties of N6/nanoclays has been published by Gilman et al in 1997 [24]. Following to his study, flame retardancy enhancement properties of nanoclays has been investigated with different matrix polymers through various studies and similar reductions in flammability have been achieved.

In the study of Gilman et al. [25] reductions of 50-75% in peak heat release rate is achieved for nylon 6 and polystyrene nanocomposites with nanoclays. They stated that reductions in heat release rate and mass loss rate were with the general mechanism of the formation of a carbonaceous-silicate structure that builds up on the surface during combustion. This structure insulates the underlying polymer and reduces the speed of mass loss rate of combustible volatiles.

Carbonaceous-silicate structure is developed as a result of removal of polymer by pyrolysis, and leaving clay particles behind. Clay particles gained back their hydrophilic nature after degradation of organic modifier and form stacks. Clay stacks migrate to the surface creating an insulating barrier. Rising bubbles (formed by decomposition of organic modifiers and polymer) enhance accumulation of clays on surface of burning polymer. Also decreased viscosity of the polymer facilitates this migration.

In addition to barrier formation, clay particles also play an important role in char formation. Strong protonic catalythic sites are produced on nanoclay surface upon thermal decomposition of organomodifier. Those sites promote char forming reactions [26, 27]. The char promotion effect of nanoclay is observed in polymers that do not normally produce char in neat form, such as ethylene vinyl acetate (EVA) [28], polystyrene (PS) [29], acrylonitrile butadiene styrene (ABS) [30] and polypropylene (PP) [31]. Organomodifier of the nanoclay is assumed to be responsible in this char promotion. It is observed that nanoclays having larger amount of organomodifier have resulted in higher char content in the system [26].

Nanoclays can also change degradation pathway of polymers which they are introduced into. Clay layers entrap polymer chains in between and provide a super heated environment. Polymer chains find chance to go additional, alternative degradation reactions which in turn, leads to a reduction in heat release rate [27].

Carbon nanotubes were introduced as an alternative to traditional flame retardants and nanoclays by Kashiwagi et al. in 2002 [32]. Various studies confirm that CNTs improve flame retardancy of large range of polymers such as PS [33], EVA [34], PMMA [35], PP [36], PA-6 [37], LDPE [38] even at very low loading rate (<3 wt%). More than 50% reduction in PHRR was detected with incorporation of 0.5 wt% SWCNT in PMMA systems [35].

Improved flame properties are attributed to formation of a protective, structured nanotube network layer that acts as a heat shield for the polymer underneath. Network structure can also enhance barrier character, suppressing evolution of combustible volatiles and inhibiting oxygen flow. Consistent with suggested mechanism, flame retardancy is found to be improved with better CNT dispersion that results in more effective network structure [11].

Even though nanoclays and carbon nanotubes have profound contributions on flame properties of polymers, they become inadequate in lowering the total heat evolved (THE) during combustion. THE values remain almost unchanged, suggesting that all polymer burn eventually at the end of fire. Both nanoclays and carbon nanotubes also increase viscosity and inhibit dripping of polymer, which results in insufficient fire test performances like UL-94 and LOI. Time to ignition (TTI) values are also affected unfavorably with introduction of nanoclays into the system since early degradation of the organic modification increase probability of early ignition.

# **1.3 Literature Survey**

#### **1.3.1** Studies on the Flammability of Polystyrene

Polystyrene is a profoundly flammable polymer, releasing highly flammable, volatile, monomeric and oligomeric fragments in large quantities upon degradation. High flammability of PS can be healed via introduction of proper halogenated and non-halogenated flame retardant compounds into the system.

Among all non-halogenated flame retardants in use, by far the most preferable ones are phosphorus based flame retardants. Flame retardancy effect of phosphorus compounds on polystyrene is investigated through either by copolymerizing it or simply by an additive approach.

Ebdon et al. [39] copolymerized styrene with monomers containing covalently bound phosphorus. LOI values are found to be raised up to 27.4 %O<sub>2</sub> with pyrocatechol vinylphosponate copolymerization and char yield is increased to 15 wt% with diethyl-p-vinylbenzylphosphonate copolymerization. Shu et al. [40] and Allcock et al. [41] studied copolymer approach also, and found similar increases in LOI and char yield of PS values with increasing phosphorus content. Tai et al. [42] copolymerized styrene with phosphorus and nitrogen containing monomer; AEPPA (acrylox-yethyl phenoxy phosphorodiethyl amidate). They found that 10 wt% AEPPA increases thermal degradation temperatures  $T_{0.1}$  and  $T_{0.5}$  of PS by 36°C and 32°C, respectively. In their study, microscale combustion calorimeter (MCC) is utilized to determine Heat Release Capacity (HRC) by dividing maximum heat release rate by the heating rate. It is revealed that AEPPA reduced HRC of PS by 28.5%. There are also patent studies on copolymerization of phosphorus containing monomers with PS leading to V-O rated copolymer in UL-94 test [43].

Price et al. [44] investigated both additive and copolymerizing approaches with 3.5 wt% phosphorus, using triethylphosphate (TEP) and diethyl-phosphanate (DEEP) as additives. It is seen that TEP and DEEP addition to PS caused increases in LOI

values from 17.9 up to 20.7 and 22.0 %O<sub>2</sub> respectively. Copolymers on the other hand, resulted in increases up to 21.8 and 21.9 %O<sub>2</sub>. Maximum Mass Loss Rate (MLR) was 25% lower than pure PS with TEP and DEEP, while it was 40-50% with copolymers. It was concluded that phosphorus in copolymers acted as char promoter via formation of dehydrating phosphoric acid, i.e. the mechanism was condensed phase. Whereas, phosphorus in additives acted in gas phase mechanisms.

In another study by Inagaki et al. [45], tris(2,3-dibromopropyl) phosphate (TBPP) is incorporated into PS as an additive. It is stated that, with only 3 wt% addition of TBPP, PS became self-extinguishing. Furthermore, LOI values increased up to 27.9 and 31.3 %O<sub>2</sub> with introduction of 5.15 and 10.6 wt% phosphorus into PS systems, respectively.

In a recent study conducted by Beach et al. [46] various phosphorus (triphenyl phosphine oxide (TPPO), triphenyl phosphate (TPP), triphenyl phosphine sulfide (TPPS)) and bromine (hexabromocyclododecane (HBCD)) containing additives and sulfur were introduced in to PS. It was revealed that a unique flame retardant activity was obtained when 5 wt% TPP in combination with 1 wt% sulfur were added to PS, causing a significant increase in LOI to 25.5 %O<sub>2</sub>. This synergy was attributed to enhanced degradation of PS in the presence of sulfur. Sulfur degrades PS network and eases delivery of TPP, which has a high potential of gas phase activity. TPPO and TPP found to decrease OH radical concentration by 40%, indicating that their dominant mechanism was in the gas phase action.

Literature survey [46-50] proves that addition of halogenated flame retardants improve flame retardancy of PS remarkably. In the study of Beach et al. [46] 2.5 wt% addition of hexabromocyclododecane (HBCD) increased LOI of PS up to 24.0 %O<sub>2</sub>. HBCD leads to extensive HBr formation, which acts as radical scavenger and enhances PS degradation with the formation of high levels of styrene and multiple dimer and trimer species. Kaspersma et al. [47] also studied the fire retardancy effect of HBCD with and without synergist antimony trioxide in PS. They concluded that V-2 rates were attained in UL-94 tests, with the mechanisms of chain scission and flame poisoning.

Halogen containing flame retardants were also studied in other styrenic polymers, such as HIPS and ABS and expandable polystyrene. It was stated by Weil and Levchick [48] that flame retardancy properties of expandable polystyrene can be enhanced with addition of brominated flame retardant; HBCD in combination with phosphorus. In a patent study by Vo et al. [49], it was stated that decreasing the amount of HBCD as low as 2.5 wt% is possible by introduction of 0.1-4 wt% phosphorus co-additive, such as TPP. They revealed that, incorporation of decabromodiphenyl oxide (DBDPO) resulted in significant enhancement in flame retardancy of HIPS. A formulation of HIPS with 12 wt% DBDPO and 5 wt% antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) was reported to have LOI value of 25.3 %O<sub>2</sub> and V-0 rating in UL-94 test.

In the study of Mahdavian et al. [50], synergistic effect of  $Sb_2O_3$  and aluminum trihydrate (ATH) with tetrabromobisphenol-A (TBBA) was evaluated in HIPS. It was found that LOI value of HIPS increased up to 23.5 %O<sub>2</sub> with addition of 15 wt% TBBA and 4.5 wt% Sb<sub>2</sub>O<sub>3</sub>, whereas systems containing 5 wt% ATH instead of Sb<sub>2</sub>O<sub>3</sub> only resulted in 21 %O<sub>2</sub>. This indicates that Sb<sub>2</sub>O<sub>3</sub> synergism with brominated flame retardants is more effective.

## **1.3.2** Studies on the Flammability of Polystyrene Nanocomposites

#### (i) Studies on the Effects of Nanoclays

Polystyrene/nanoclay (PS/NC) nanocomposites have attracted considerable attention due to the improvements in the thermal and flammability performance of PS. It has been reported that even with nanoclay addition as little as 0.1 wt%, Peak Heat Release Rate (PHRR) is lowered by 40% and onset degradation temperature ( $T_{0.1}$ ) is increased by 40°C relative to pure PS [51].

Flame retardancy mechanism behind this reduction was explained by Gilman et al. [25], based on formation of a high-performance carbonaceous-silicate char that insulates the underlying polymer. In this study, they examined various

nanomorphologies to explore how structure effects fire behavior. It was revealed that intercalated structure shows enhanced flammability and thermal stability relative to exfoliated ones. PHRR decreased 60% relative to pure PS upon addition of 3 wt% nanoclay.

Zhu et al. [52] found similar results. In their study; nanoclays with three different modifications were used to investigate effects of modifiers. Highest reductions in PHRR of PS-NC nanocomposites were seen for intercalated systems, rather than exfoliated one. They found that PHRR is decreased 58% with the addition of 5 wt% clay, and onset degradation temperature is increased about 50°C for all nanocomposites.

In another study of Zhu et al. [53], they suggested an alternative mechanism for the flame retardancy of nanoclays which was based on paramagnetic sites. PS-NC nanocomposites were examined to determine whether paramagnetic iron could result in radical trapping. It was concluded that structural iron provides radical trapping but this mechanism is functional only at low nanoclay loadings.

In the study of Morgan et al. [54], a gasification apparatus was utilized to examine char formation of PS. They revealed that two types of nanoclay reinforced char structure containing 28% carbonaceous material might form depending on thermal conditions. Further studies conducted with gasification apparatus by Gilman et al. [55] verified these two types of carbonaceous char structure. One of them can be decomposed and volatilized by heating in nitrogen and the other can be decomposed by heating above 700°C in presence of air. They also suggested that a minimum thickness of clay-carbon char must build up for thermal barrier to be effective.

Zhang et al. [57] prepared PS nanocomposites containing oligomerically modified nanoclay, named as 'triclay' in different loadings. They found that midpoint and onset degradation temperatures ( $T_{0.5}$  and  $T_{0.1}$ ) are increased by 15°C and 7°C, respectively with the addition of 8 wt% triclay. In another study [58]  $T_{0.5}$  values were found to be increased by 23°C with addition of 3 wt% and 5 wt% 'triclay' in to PS. They also showed that PHRR values are reduced by 60% compared to neat PS.

Nazarenko et al. [56] investigated gas barrier effect of PS-NC nanocomposites and stated that oxygen barrier is formed due to tortuous diffusion pathway created by intercalated structure. Schuetz at al. [59] investigated the effect of aspect ratio and dispersion of nanoclays on fire behavior of PS. Synthetic and natural nanoclays were used to examine different aspect ratios. It was found that, synthetic nanoclays with higher aspect ratios result in 20% higher reduction in PHRR and higher thermal stability than natural counterpart.

Several studies have been cited on the kinetics of thermal degradation of PS-NC nanocomposites. Vyazovkin et al. [60] showed that introduction of nanoclay causes an increase in effective activation energy of degradation, which in turn lead to enhancement of thermal stability. Bourbigot et al. [61] revealed that thermal stability of PS is increased with the addition of nanoclays which delay chain-scission, promote charring and form protective barriers.

Jang et al. [62] observed that nanoclays cause chemical changes in degradation pathway of PS nanocomposites. By analyzing the evolved products upon degradation, it was concluded that relative abundance of styrene monomer decreases and new degradation products are originated with introduction of nanoclays. Radicals trapped in between clay layers remain in condensed phase for longer time and find more opportunity to undergo radical recombination reactions. This provides degradation to expand over a period of time and leads to large reductions in PHRR. In another study conducted by the same authors [27], it was also observed that stability of the radicals have profound effect on the alteration of degradation pathway. They showed that more stable the radicals formed upon degradation, the more opportunity they have to undergo secondary reactions. For instance, higher reductions in HRR were observed for PS which produces highly stable radicals that goes through radical recombinations and random chain scissions in the presence of nanoclays. On the other hand no reduction in HRR was observed for other polymers giving less stable radicals.

# (ii) Studies on the Effects of Nanoclays with Phosphorus Based Flame Retardants

Even though nanoclay addition provides significant improvements in fire properties of polymers; it is evident that they should be combined with conventional flame retardants to develop highly efficient synergistic systems.

For this purpose, Chigwada and Wilkie [63] prepared PS-NC nanocomposites with phosphorus containing flame retardants by bulk polymerization. Over 30 different phosphorus flame retardants were introduced in to PS-NC nanocomposites and they were evaluated via high throughput technique. This technique basically consists of screening ignition resistance of samples, upon exposure to a methane flame. Out of all samples, tricresylphosphate (TCP), trixylylphosphate (TXP) and resorcinoldiphosphate (RDP) were found to yield good results with lack of ignition. These flame retardants were further investigated to evaluate synergistic effects in combination with nanoclays. Addition of 30 wt% RDP and 5 wt% clay resulted in reduction of PHRR as high as 92%, which is normally in the range of 50-60% in presence of only nanoclays. For the same system Total Heat Evolved (THE) is decreased by 61%. It was also revealed that, 10 wt% clay addition to 30 wt% RDP and TCP containing systems resulted in V-0 ratings in UL-94 test.

In another study [64], ammonium polyphosphate (APP) was added to PS nanocomposites containing MgAl layered double hydroxide (LDH) as nanofiller. It was observed that individual addition of 5 wt% MgAl LDH and APP to PS decreases PHRR only 17% and 11%, respectively. But, 5/5 wt% combined addition of these two causes a 42% reduction in PHRR, implying synergistic interactions in between. This improvement was attributed to enhanced char promoting action of APP in presence of LDH.

In another study by Zheng and Wilkie [65] phosphates were inserted in PS-NC nanocomposites as a part of the organic treatment of nanoclay, rather than traditional addition approach. The results for all systems showed that THE values decrease by 50% upon addition of phosphate containing nanoclay into PS. It was suggested that

presence of phosphorus causes this decrease, since reduction in THE is not a typical behavior of nanoclay addition. Reductions in PHRR were found to be raised up to 70% and 80% with the addition of 5 wt% and 10 wt% phosphate containing nanoclays, respectively.

Tai et al. [66] investigated effects of phosphorus in PS nanocomposites by copolymerization approach. Phosphorus-nitrogen containing monomer AEPPA (acrylox-yethyl phenoxy phosphorodiethyl amidate) with styrene monomers were copolymerized via bulk radical polymerization in presence of  $\alpha$ -zirconium phosphate which has layered structure having properties similar to montmorillonite nanoclay. From MCC analysis, it was concluded that HRC is reduced by 29% with AEPPA copolymerization, and further reduction was observed up to 39% with 5 wt% nanofiller addition. Copolymerizing approach was also investigated in a different study, with the same phosphorus monomers with MgAl LDH as nanofiller [42] This time addition of 5 wt% nanofiller in the form of MgAl LDH reduced HRC values as high as 43%.

It seems that there is no specific research for PS investigating the possible synergism of using nanoclays and triphenylphosphate (TPP; phosphorus based flame retardant used in this study) together. On the other hand, this synergism is explored for other polymers including ABS, PP, PMMA, PC, etc. For example, Kim et al. [67] studied thermal stabilization enhancement of ABS by intercalating TPP into nanoclay galleries, developing nano-TPP. It was stated that evaporation of TPP is suppressed and thermal stability of TPP is improved with intercalation. Also, LOI values were found to be increased up to 41 %O<sub>2</sub> upon addition of 6 wt% nano TPP and 9 wt% char forming epoxy resin in ABS. He et al. [68] showed that introduction of nanoclay and TPP together in ABS result in higher improvements in flame retardancy in terms of suppressed Peak Heat Release Rate (PHRR) and decreased LOI values compared to using nanoclay alone.

Similarly, LOI and Cone Calorimeter studies of Li et al. [69] indicated that synergism of epoxy intercalated nanoclay and TPP resulted in significant improvements in flame retardancy of PP. Further TGA analyses proved that evaporation of TPP is inhibited with introduction of nanoclay due to shielding effect, named as "nanoconfinement". Kim and Wilkie [70] revealed that combined use of nanoclay and TPP enhance fire properties of PMMA further, than incorporating them individually. PMMA containing 2 wt% nanoclay and 22 wt% TPP was found to decrease PHRR value by 32% compared to pure PMMA. Feyz et al. [71] studied fire retardancy of PC/ABS blend systems and showed that use of a combination of TPP and nanoclays, result in improvements in PHRR and LOI values much higher than they expected.

#### (iii) Studies on the Effects of Nanoclays with Brominated Flame Retardants

Lu and Wilkie [72] studied fire performance of brominated flame retardants and antimonytrioxide (AO) in presence of nanoclay. Decabromodiphenyl oxide (DBDPO) and AO added to PS systems at a fixed ratio of 5/1 by weight. It was stated that introduction of nanoclay into DBDPO-AO mixture creates a synergism in char formation which acts as thermal barrier. This synergistic effect was further investigated in cone calorimeter. PHRR values were found to decrease from 1166 kW/m<sup>2</sup> to 591 kW/m<sup>2</sup> with addition of 12 wt% DBDPO-AO, whereas substitution of 2 wt% of this mixture with nanoclays causes a further decrease down to 442 kW/m<sup>2</sup>. This further reduction was attributed to combination of gas phase action and char formation effect.

In the study of Wang et al. [73] the same flame retardant DBDPO-AO mixture was introduced into another styrenic polymer ABS. It was revealed that addition of 5 wt% nanoclay in DBDPO-AO containing ABS results in decrease of PHRR by 78% relative to pure polymer. It was stated that, incorporating nanoclays into the system stabilizes the char structure; hence the time needed for the destruction of char was found to be increased from 75 to 125 s. With addition of nanoclays DBDPO-AO containing ABS systems also obtained V-0 rating in UL-94 test, whereas blends with no nanoclays failed.

Wang et al. [74] also investigated effects of bromine in PS by copolymerization approach. Dibromostyrene and styrene were bulk polymerized to obtain copolymers.

It was found that, 5 and 10 wt% of dibromostyrene/styrene copolymer nanocomposites in the presence of AO result in reductions in PHRR up to 60 and 70%, which is larger than normally seen for styrene nanocomposites. In UL-94 tests, V-0 rating was obtained for the copolymer having 10% dibromostyrene in the presence of 3 wt% nanoclay, 3 wt% AO and 0.2 wt% anti-dripping agent (PTFE). Also V-2 rate of copolymer having 40 wt% dibromostyrene was enhanced to V-0 upon addition of 3 wt% nanoclay.

In the study of Chigwada et al. [75], dibromostyrene with vinylbenzyl chloride were introduced as the modification of nanoclays. Addition of brominated nanoclays containing 3 wt% Br resulted in 36% reduction in PHRR of PS, whereas no reduction was observed in 3 wt% DBDPO containing PS. Introduction of bromine in the modification of nanoclays also brought significant reductions in THE values as much as 38%.

# (iv) Studies on the Effects of Carbon Nanotubes with Brominated Flame Retardants

Carbon nanotubes have been first used in the flame retardancy studies of polymers in 2002 by Kashiwagi et al. [32]. Effects of MWCNT on the flammability properties of PS were studied by Cipiriano et al. [33] by incorporating nanotubes with two different aspect ratios of 49 (MWCNT-49) and 150 (MWCNT-150) with mass concentrations from 0.1 to 4 wt%. Solid like net-work structures were obtained at 2 wt% of MWCNT-150 and 4 wt% of MWCNT-49, which act as a heat shield and cause decreases in PHRR values.

In the study of Costache et al. [76], influence of nanotubes on thermal degradation and fire retardancy of PS was investigated. It was seen that, addition of 5 wt% MWCNT causes reduction in PHRR up to 60% and enhances thermal stability of PS in terms of onset and mid-point degradation temperatures. However GC-MS analyses revealed that; unlike nanoclay, nanotubes have no effects on degradation products of PS. Thermal decomposition studies conducted by Antonucci et al. [77] show that degradation temperature of PS systems increases upon increase of SWCNT content due to absorption of free radicals generated during the PS decomposition by activated carbon nanotube surfaces.

In another study [78]; MWCNT was grafted with PS in an attempt to increase nanotube adhesion with PS matrix. Degradation temperature of the nanocomposite systems was found to be shifted to higher temperatures, revealing positive effect of CNTs on thermal stability.

CNTs were combined with conventional flame retardants in various studies in order to generate synergistic PS systems. In the study of Tutunea and Wilkie [79], 1.5 wt% CNT was added to RDP (resorcinoldiphosphate), ATH (aluminum trihydrate) and DECA (decabromodiphenyl oxide) flame retarded PS. TGA results showed that both onset and midpoint degradation temperatures are increased and char content is greater than expected. Moreover; 43% reduction in PHRR obtained by 10 wt% DECA containing PS, further increased up to 69% with the addition of 0.2-0.5 wt% CNT.

In another study by Lu and Wilkie [80] synergistic effects of CNT with DBDO-AO flame retarded PS was investigated. It was seen that replacement of 2 and 3 wt% of DBDO-AO by MWCNT results in 42% reduction in PHRR due to the formation of a network structure in the condensed phase during burning.

#### (v) Studies on the Effects of Nanocomposite Mixing Method

Basically three mixing methods, melt intercalation, solution intercalation and in-situ polymerization are utilized in order to obtain PS-NC nanocomposites. Type of the mixing method might influence many properties of the nanocomposites. In order to investigate effects of mixing method, Schuetz et al. [59] prepared PS-NC nanocomposites via "solution mixing" and "melt mixing". They stated that some aggregates remain in melt blending leading to poorer mechanical properties and

lower reductions in PHRR. On the other hand, solution mixing resulted in homogenously dispersed structure with higher properties.

Wang et al. [81] synthesized PS-NC nanocomposites via "in-situ polymerization" by bulk, solution, suspension and emulsion polymerization techniques. It was observed that exfoliated structure obtained via bulk polymerization exhibit better thermal and mechanical properties compared to intercalated systems. In the study of Samakande et al. [82] PS-NC nanocomposites were prepared by in-situ bulk and solution polymerization. It was stated that bulk polymerization gives exfoliated structure whereas intercalated morphologies were obtained in solution. Contrary to Wang's findings, intercalated structures were found to be most thermally stable.

In another study by Wang et al. [83], PS-NC nanocomposites were prepared via insitu free radical polymerization. It was stated that thermal stability of neat PS is increased up to 50°C. Similar results were obtained in the study of Zhong et al. [84]. They indicated that in-situ free radical bulk polymerization resulted in more than  $50^{\circ}$ C increase in the T<sub>0.5</sub> of pure PS with nanoclay loadings of 4-9 wt%.

Krishna et al. [85] investigated the effects of processing conditions and nanoclay loading on the thermal degradation of PS-NC nanocomposites. Exfoliated nanocomposites with 5% nanoclay obtained by solvent blending at 110°C gives  $T_{0.5}$ values 17°C higher than that of pure PS. In the study of Wang et al. [86], PS-clay nanocomposites were prepared via in-situ polymerization method. It was stated that nanocomposites with 4 wt% nanoclay loading gives  $T_{0.5}$  values 28°C higher than that of pure PS.

# **1.4** Aim of the Study

Polystyrene (PS) is a commodity polymer, manufactured on a very large scale. Even though it's brittle nature limits its use in high performance engineering applications; its transparency, ease of coloring and production makes it useful in applications including packaging, light covering and transparent parts of electric appliances. In many of these applications, flame retardancy is required.

Nanoclays (NC) attract great attention owing to the improvements they provide in thermal and flammability performance of many polymers. Therefore, the first aim of this study is to investigate effects of nanoclays on the flammability of PS.

It is seen that although introduction of nanoclays result in enhancement of flame properties, improvements they provide become inadequate in sustaining most fire regulations. Thus, it would be better that nanoclays should be used together with conventional flame retardants in order to develop highly efficient synergistic systems.

Therefore, the second purpose of this study is to investigate contribution of nanoclays to the flame retardancy performance of conventional phosphorus based flame retardant *triphenyl phosphate* (TPP) and its synergist *melamine cyanurate* (MCA).

As the third purpose, contribution of nanoclays to the flame retardancy performance of another conventional halogenated flame retardant *brominated epoxy polymer* (BE) and its synergist *antimony trioxide* (AO) was investigated.

In the literature, carbon nanotubes were also introduced as an alternative to nanoclays to improve flame retardancy of many polymers. Therefore, as the fourth purpose of this study, effects of carbon nanotubes (CNT) on the flame retardancy of PS with and without conventional BE-AO flame retardant system was investigated.

As an additional purpose; effects of nanocomposite mixing method on the flammability behavior was also investigated. For this purpose, PS-NC nanocomposites were prepared via *solution mixing* method and *in-situ polymerization* method for comparison.

# **CHAPTER 2**

# **EXPERIMENTAL WORK**

# 2.1 Materials Used

### (i) Matrix Materials

In this study matrix material was used in two different forms. During *solution mixing* method solid granules of polystyrene (PS) was used by dissolving in a certain solvent. However, during *in-situ polymerization* method, liquid styrene monomer was polymerized by using initiator 2,2'-azobis(isobutyronitrile) (AIBN) in the form of white powder. These matrix materials and initiator were all supplied from Aldrich Co., their chemical structure and properties are given in Table 2.1.

### (ii) Solvents

In this study, solvents were used for two main purposes. First of all, they were used for *solution mixing* method of nanocomposite production, and also for *solvent screening* procedure of carbon nanotubes. Details of these procedures are given in Section 2.2. Seven different solvents used were as follows: Toluene, Tetrahydrofuran (THF), Chloroform, Dichloromethane (DCM), N,N Dimethylformamide (DMF), Acetone and Ethanol. They are all supplied from Aldrich Co. Table 2.2 gives their chemical structure and properties.

#### (iii) Conventional Flame Retardants

In this study, two basic traditional flame retardants were used. The first one was Triphenyl Phosphate (TPP) (or *phosphoric acid triphenyl ester*) supplied from Merck Chemicals. The second one was Brominated Epoxy (BE) (or *tribromophenol end capped brominated epoxy oligomer*), product of ICL Industrial Products (Israel).

In this study, two more traditional flame retardants were used as the possible synergists with the previous basic ones. That is, Melamine Cyanurate (MCA) (the salt of melamine, a nitrogen based compound and cyanuric acid) was used together with TPP, and Antimony Trioxide (AO) (Sb<sub>2</sub>O<sub>3</sub>) was used together with BE. Chemical structure and properties of these traditional flame retardants are given in Table 2.3.

	Chemical Structure	Properties
Polystyrene (PS) $[CH_2CH(C_6H_5)]_n$	n n	Molecular Weight: 192000 g/mol Softening Point: 107°C Melt Index: 6.0-9.0/10 min (200°C/5kg)
Styrene Monomer C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	CH <sub>2</sub>	Molecular Weight: 104.15 g/mol Density: 0.906 g/mL Boiling Point: 145°C
Azobis- isobutyronitrile (AIBN) C <sub>8</sub> H <sub>12</sub> N <sub>4</sub>	$\begin{array}{c} H_{3}C  CH_{3} \\ N \equiv C  N \stackrel{^{-}N}{} N  C \equiv N \\ H_{3}C  CH_{3} \end{array}$	Molecular Weight: 164.21 g/mol Melting Point: 102-104°C

Table 2.1	Chemical	Structure	and Pr	operties	of Matrix	Materials	and Initiator
	0			op • • • • • •	01 1.10001111	1.10000110010	

	Chemical Structure	Properties
Toluene C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	CH3	Molecular Weight: 92.14 g/mol Density: 0.865 g/mL Boiling Point: 110-111°C
Tetrahydrofuran (THF) C <sub>4</sub> H <sub>8</sub> O		Molecular Weight: 72.11 g/mol Density: 0.889 g/mL Boiling Point: 67°C.
N,N Dimethylformamide (DMF) C <sub>3</sub> H <sub>7</sub> NO	H N CH <sub>3</sub> CH <sub>3</sub>	Molecular Weight: 73.09 g/mol Density: 0.948 g/mL Boiling Point: 153°C
Chloroform CHCl <sub>3</sub>	H CI <sup>C</sup> ''''CI CI	Molecular Weight: 119.38 g/mol Density: 1.48 g/mL Boiling Point: 61°C
Dichloromethane (DCM) CH <sub>2</sub> Cl <sub>2</sub>		Molecular Weight: 84.93 g/mol Density: 1.32 g/mL Boiling Point: 40°C
Acetone CH <sub>3</sub> COCH <sub>3</sub>		Molecular Weight: 58.08 g/mol Density: 0.791 g/mL Boiling Point: 56°C
Ethanol (EtOH) CH <sub>3</sub> CH <sub>2</sub> OH	H <sub>2</sub> H <sub>3</sub> COH	Molecular Weight: 46.07 g/mol Density: 0.789 g/mL Boiling Point: 78°C

 Table 2.2 Chemical Structure and Properties of Solvents

	Chemical Structure	Properties
Triphenyl Phosphate (TPP) (C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> PO		Molar Mass: 326.28 g/mol Density: 1.206 g/cm <sup>3</sup> Melting Point: 48-50°C Boiling Point: 220°C Form: White Flakes
Melamine Cyanurate (MCA) C <sub>6</sub> H <sub>9</sub> N <sub>9</sub> O <sub>3</sub>	$ \begin{array}{c c}     H \\     N \\     $	Density: 0.3-0.4 g/cm <sup>3</sup> Particle Size: 12-17 μm Form: White Powder
Brominated Epoxy (BE)	$\fbox{H_{2}-CH-CH_{2}} \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\ \bigcirc \\$	Molecular Weight: 15000 g/mol Density: 1.9 g/cm <sup>3</sup> Br Content : 52% Form: White Powder
Antimony Trioxide (AO) Sb <sub>2</sub> O <sub>3</sub>	O Sb O Sb O Sb O Sb O	Particle Size: 0.3-1.1µm Purity: 99% Form: Fine White Powder

**Table 2.3** Chemical Structure and Properties of Conventional Flame Retardants

## (iv) Nanoadditives

The main nanoadditive used to investigate effects of nanoparticles on the flame retardancy of PS was **Cloisite 10A Nanoclay** (Southern Clay, USA). It is a natural montmorillonite modified with dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium. Properties of Cloisite 10A and chemical structure of its modifier are given in Table 2.4.

Property	Value	Chemical Structure of
	, unde	Modifier
Color	Off White	
	$\%10 < 2 \ \mu m$	CH3
Dry Particle Size	$\%50 < 6 \ \mu m$	
	%90 < 13 μm	$CH_3 - N - CH_2 - \bigcirc$
Density	1.9 g/cc	HT
% Weight Loss on	39%	where HT stands for
Ignition		hydrogenated tallow; long
Modifier Concentration	125 meq/100g clay	organic molecules having
d-spacing	1.92 nm	~65% C18; ~30% C16; ~5% C14.

 Table 2.4 Properties of Cloisite 10A and Chemical Structure of its Modifier

In this study, effect of carbon nanotubes on the flame retardancy of PS was also investigated. For this purpose **multiwalled carbon nanotube Nanocyl®-7000** (Nanocyl, Belgium), was used. Their properties are given in Table 2.5.

 Table 2.5 Properties of Nanocyl 7000 Carbon Nanotubes

Property	Value
Average Diameter	9.5 nm
Average Length	1.5 μm
Carbon Purity Ignition	90 %

# **2.2 Production of the Specimens**

In this study, compounds and nanocomposites were basically produced by using "Solution Mixing" method. In order to investigate effects of production method, "In Situ Polymerization" was also used as an additional task. Details of these procedures are explained below while basic flowcharts for the Solution Mixing and In-situ Polymerization methods are given in Figures 2.1 and 2.2, respectively. After compounding, specimens for testing and analysis were shaped by "injection molding" and "compression molding". With respect to the five main purposes of this study, specimens were produced in five different groups. Designations and compositions of these specimen groups are given in Table 2.6

#### (i) Compounding by Solution Mixing

Nanoclays in certain amounts were dissolved in toluene by using magnetic stirrer with a ratio of 0.01 g/mL. After dissolving, to enhance dispersion and intercalation/exfoliation of the clays, this mixture was further held in ultrasonic stirrer for another hour. After this step, nanoclay and toluene mixture was placed on magnetic stirrer again to add PS into this mixture with ratio of 0.1 g/mL. The reason of not introducing PS into the system before this stage was using ultrasonic stirrer which might lead to chain breakage resulting in decreased molecular weight. That mixture was further stirred on magnetic stirrer for 6 hours and poured into petri dishes, then dried for solvent removal at room temperature for 5 days. For further evaporation of the residual solvents, nanocomposites obtained were grinded and kept overnight in a vacuum oven at 120°C.

Before preparation of carbon nanotube containing nanocomposites, parameters effecting the distribution were determined, such as concentration and stirring time as preliminary step. Carbon nanotubes with a ratio of 0.001 g/mL were dissolved in tetrahydrofuran (THF) with magnetic stirrer. After dissolving to enhance debundling and dispersion of CNTs, mixture was further held in ultrasonic stirrer for another hour. Then, PS was added into CNT-THF mixture with a ratio of 0.1 g/mL and ultrasonic stirring was applied for another 15 minutes. During this period, the aim

was to incorporate polymer chains within nanotube bundles as far as it is thermodynamically feasible. The rest of the procedure was the same applied for nanoclay containing compounds explained above.

Nanocomposites having traditional flame retardants were produced with the same procedure explained above. After sonication of nanoclays and carbon nanotubes in ultrasonic stirrer, traditional flame retardants were incorporated into system together with PS in certain amounts.

#### (ii) Compounding by In-situ Polymerization

As a first step, styrene monomers were distilled in order to remove inhibitors present in the system. Distilled monomers were dissolved in toluene (25 g/100mL) via magnetic stirrer and nanoclays were incorporated into the system. To enhance dispersion and monomer intercalation in between clay galleries, mixture was put in ultrasonic stirrer for 1 hour. After this step, to initiate polymerization of monomers intercalated in between clay galleries, azobis(isobutyronitrile) (AIBN) (2% of styrene) was added into the system. The resulting mixture was stirred at 90°C for 24 hours under nitrogen atmosphere in order to complete polymerization. Then the material was kept in petri dishes for drying and solvent removal at room temperature for 5 days. For further evaporation of the residual solvents, and monomers that were not participated in polymerization process; obtained nanocomposites were grinded and kept overnight in vacuum oven at 120°C.

The same procedure was followed for in-situ polymerization of nanocomposites having traditional flame retardants. These additives in certain amounts were added into the system 12 hours after initiation of polymerization.

Designations and compositions of the specimens prepared via solution mixing and in-situ polymerization are given in Table 2.6. Note that, specimens prepared by insitu polymerization are designated with the prefix "i-".



Figure 2.1 Basic Flowchart used in "Solution Mixing" Method



Figure 2.2 Basic Flowchart used in "In-situ Polymerization" Method

	I ADIC I	2.0 Designations			vio apecilien di	sdn	
Specimen	PS	NC	CNT	TPP	MCA	BE	AO
PS-NC1	66	1					
PS-NC3	97	$\mathfrak{c}$					
PS-NC5	95	5					
PS-NC7	93	L					
ddT-Sq	85			15			
<b>PS-TPP-MCA</b>	75			15	10		
<b>PS-TPP-NC</b>	80	5		15			
PS-TPP-MCA-NC	70	5		15	10		
PS-BE	80					20	
<b>PS-BE-AO</b>	77					20	ω
<b>PS-BE-NC</b>	75	5				20	
PS-BE-AO-NC	72	5				20	3
PS-CNT	66		1				
<b>PS-BE-CNT</b>	79		1			20	
PS-BE-AO-CNT	76		1			20	3
i-PS-NC	95	Ŋ				20	ю
i-PS-BE-AO-NC	72	5					
PS: Polystyrene NC: Nanoclay CNT: Carbon Nanotube	AO: Antim TPP: Triph MCA: Mela	ony Trioxide enyl Phosphat amine Cyanurate	<b>BE:</b> Brominated I <b>i-:</b> In-situ Polymer	Epoxy rization			

#### (iii) Shaping by Injection and Compression Molding

The specimens for tensile testing were shaped by injection molding using a lab-scale injection molding machine (DSM Xplore 10 cc Micro Injection Molder). During molding, barrel temperature and mold temperature were kept at 220°C and 55°C respectively, and heating time was set as 5 minutes for each cycle. Due to decreases in viscosity and thermal stability observed upon addition of TPP into system, barrel temperature was lowered to 180°C for TPP containing systems.

Specimens for flammability tests (LOI, UL-94 and MLC) were shaped by compression molding machine. Materials in the molds with 100x100x2 mm dimensions were preheated for 5 minutes at 200°C and then compressed under 100 bar pressure for 7 minutes. For LOI and UL-94 tests, plates were cut into 10x100x2 mm bars, while for MLC tests square plates of 100x100x2 mm were used directly.

# 2.3 Flammability Tests of the Specimens

Mass Loss Cone Calorimeter (MLC), Limiting Oxygen Index (LOI) and UL-94 vertical burning tests were utilized in order to investigate flammability properties of all specimens. Detailed explanations of these tests were given in Section 1.2.1, thus only the equipment and the standards used are mentioned below.

#### (i) UL-94 Vertical Burning Test

UL-94 V test measures material behavior upon removal of flame and time to selfextinguishment. UL-94 tests have been applied according to the standard *UL-94 Tests for Flammability of Plastic Materials for Parts in Devices and Appliances* developed by Underwriters Laboratories, USA.
#### (ii) Limiting Oxygen Index (LOI) Test

LOI tests measures minimum oxygen concentration in nitrogen-oxygen mixture that will sustain burning. Oxygen concentrations were determined according to procedures explained in *ISO 4589 Determination of Burning Behavior by Oxygen Index* by using an Oxygen Index apparatus (Fire Testing Technology, UK)

#### (iii) Mass Loss Cone Calorimeter (MLC) Test

MLC tests were performed according to procedures explained in *ISO 13927 Simple Heat Release Test Using a Conical Radiant Heater and a Thermopile Detector*, in order to measure heat release rates and mass loss rates of the burning specimens. Specimens were tested under a heat flux of 35 kW/m<sup>2</sup> in Fire Testing Technology (FTT) Mass Loss Cone Calorimeter with Keithley- KUSB- 3108 data accusation system

# 2.4 Other Tests and Analysis

#### (i) X-Ray Diffraction (XRD) Analysis

XRD analyses were conducted in order to characterize distribution and intercalation/exfoliation of nanoclay layers. Interlayer spacing of nanoclays were determined using Braggs' Law, n  $\lambda = 2d\sin\theta$ ; where  $\lambda$  denotes the wavelength of the X-ray radiation used, **d** denotes interlayer spacing and **\theta** is the measured diffraction angle. Injection molded specimens were analyzed via Rigaku D-Max 2200 X-Ray diffractometer under monochromatic CuK $\alpha$  radiation, for the diffraction angle 2 $\theta$ range of 1° to 10° with a scanning speed of 1°/min.

## (ii) Transmission Electron Microscopy (TEM)

TEM was used for further visual investigation of nanoclay distribution and intercalation/exfoliation level of the layers. Specimens with thickness of 100 nm

were cut by an ultra-microtome Lecia EM UC 6, with a diamond knife, operated at room temperature. Transmission electron microscopy was conducted with FEI Tecnai G2 Spirit BioTWIN at an acceleration voltage of 80 kV, and also by 100 kV JEOL JEM-2100.

#### (iii) Scanning Electron Microscopy (SEM)

SEM was used for morphological analysis of fracture surfaces of tensile testing specimens and chars of LOI specimens by using FEI Nova NanoSEM 430 and JEOL JSM-6400 microscopes.

#### (iv) Thermogravimetric Analysis (TGA)

TGA was conducted in order to investigate thermal degradation of samples. Analyses were performed via Perkin Elmer Pyris 1 thermogravimetric analyzer from room temperature to 900°C at a heating rate of 10°C/min, under nitrogen flow of 80 ml/min.

### (v) Tensile Testing

Tensile tests were performed in order to investigate effects of nanoadditives and flame retardants on mechanical performance. Dogbone shaped specimens are pulled by a 10 kN universal testing machine (Shimadzu AGS-J) with a crosshead speed of 1 mm/min, according to the standard *ISO 527 Plastics - Determination of Tensile Properties*.

# **CHAPTER 3**

# **RESULTS AND DISCUSSION**

In this study the effects of nanoclays and carbon nanotubes with and without presence of traditional flame retardants and additionally, effect of mixing method on flammability of PS nanocomposites were investigated. Detailed flammability measurements were done on samples by means of UL-94, Limiting Oxygen Index (LOI) and Mass Loss Cone Calorimetry (MLC) tests. In addition to flammability tests, samples were also characterized by XRD, SEM, TEM and mechanical tests. TGA was also conducted in order to investigate thermal stabilities of samples. Results of these studies are discussed below.

# **3.1** Effects of Nanoclays

In first part of our study, effects of nanoclay addition on the flame retardancy performance of PS were investigated. Clays of Cloisite 10A was incorporated into PS matrix from 1% to 7% in order to find nanoclay content having optimum properties in terms of flammability. Designations and compositions of the specimens produced for this purpose are given in Table 3.1.

Specimens	PS	NC
PS	100	-
PS-NC 1	99	1
PS-NC 3	97	3
PS-NC 5	95	5
PS-NC 7	93	7

Table 3.1 Designations and Compositions (wt%) of the Specimens

**PS:** Polystyrene **NC:** Nanoclay

## (i) Nanocomposite Formation

X-Ray Diffraction (XRD) patterns and Transmission Electron Microscopy (TEM) images were analyzed in order to evaluate dispersion and exfoliation/intercalation state of nanoclays in PS matrix. Figure 3.1 indicates that pristine Cloisite 10A nanoclay (NC) has a sharp peak at  $2\theta$ =4.91° corresponding to an interlayer spacing of 1.8 nm. Two main diffraction peaks are observed for all compositions of PS-NC at nearly the same 2 $\theta$  values with different intensities. The first peak (2 $\theta$ =2.84°) corresponds to interlayer spacing of 3.1 nm indicating that intercalation of PS chains through clay galleries were very well achieved.

Second diffraction peak seen at  $2\theta$ =5.26° corresponds to *d*-spacing of 1.7 nm. Second peak could be due to clay stacks forming a microcomposite structure. It is known that in order for PS chains to intercalate through all clay galleries successfully via solvent blending, a minimum critical PS concentration should be sustained in mixture [24]. The decrease observed in *d*-spacing from 1.8 nm in original Cloisite 10 (NC) to 1.7 nm in the PS-NC specimen could be due to change in conformation of alkyl chains of organic modifiers in between clay galleries. The *d*-spacing collapse of nanoclays was recently shown [87] to occur via a reversible physical process in low utilized temperatures and exposure times, as in the case of present study.

For further assessment of dispersion and exfoliation/intercalation state of PS-NC systems, TEM analysis was conducted for PS-NC5 which contains 5wt% nanoclay. TEM images of PS-NC5 given in Figure 3.2(a) confirmed that; homogeneous dispersion of nanoclays in PS matrix was achieved with almost no formation of agglomerates. Higher magnification in Figure 3.2(b) further reveals that PS was intercalated into clay galleries verifying nanocomposite formation with also certain level of exfoliation.



Figure 3.1 XRD Patterns of the Nanocomposite Specimens and Nanoclay



Figure 3.2 TEM Images of PS-NC5 Specimens Showing (a) Uniform Distribution and (b) Intercalation/Exfoliation State of the Clay Layers

## (ii) LOI and UL-94 Flammability Tests

LOI and UL-94 tests were done to samples in order to investigate effects of nanoclay addition on flammability of PS. Results of both LOI and UL-94 tests are summarized in Table 3.2. Figure 3.3 shows the appearances of the burnt specimens after LOI tests, while Figure 3.4 shows SEM micrographs of the surface char layers of LOI specimens, respectively.

Specimens	LOI (O <sub>2</sub> %) <sup>a</sup>	UL-94 Rating <sup>b</sup>
PS	$18.0 \pm 0.2$	Fail
PS-NC1	18.3 ±0.2	Fail
PS-NC3	$18.6 \pm 0.2$	Fail
PS-NC5	$19.0 \pm 0.2$	Fail
PS-NC7	19.5 ±0.2	Fail

Table 3.2 Results of LOI and UL-94 Flammability Tests

<sup>a</sup>Oxygen level required for sustained flaming combustion

<sup>b</sup> Materials flammability classifications for stringent vertical orientation; Fail (flame extinguishing t < 30 s), V-2 (flaming drips, material self-extinguishes at 10<t<30 s), V-1 (material self-extinguishes at 10<t<30 s, without dripping), V-0 (material selfextinguishes at t>10 s)

Although there was no improvement in UL-94 rating, it can be seen that LOI values increased slightly with increasing clay content. For instance, PS-NC1 nanocomposite having 1 wt% clay need 18.3% oxygen to sustain burning whereas this value increases up to 19.5 %O<sub>2</sub> for PS-NC7 having 7 wt% clay. This is attributed to the formation of carbonaceous char in non-charring PS with presence of clay. This carbonaceous-silicate char both acts as heat and mass transport barrier and inhibits flow of flammable volatile gases to combustion zone. More effective barrier was originated as clay content increases resulting in higher LOI values.

This condensed phase mechanism is apparent in the images of Figure 3.3 taken after LOI test showing char formation for PS-NC5, whereas only degradation and melting for neat PS. Further residue analysis conducted via SEM (Fig. 3.4) also reveals

contribution of clays via formation of strong char layers acting as an effective barrier for heat and mass transport.



Figure 3.3 Appearances of the Specimens after LOI Test



Figure 3.4 SEM Micrographs of the Surface Char Layers of LOI Specimens (a) PS and (b) PS-NC5

# (iii) Mass Loss Cone Calorimetry

Fire behavior of samples was analyzed with Mass Loss Cone Calorimeter. Then, (a) Heat Release Rate (HRR) vs. Time, (b) Total Heat Evolved (THE) vs Time, and (c) Mass Loss Rate (MLR) vs. Time graphs of samples subjected to an external heat flux of 35 kW/m<sup>2</sup> are given in Figure 3.5. Important parameters derived from obtained data are tabulated in Table 3.3.

Figure 3.5(a) shows that addition of nanoclay results in progressive reductions in PHRR with respect to pure PS mainly due to char formation mechanism. PHRR is reduced in parallel with clay content, since more dense and effective barrier can be obtained with increasing clay addition. This barrier inhibits flow of flammable gases to surface and protects underlying polymer and also alters degradation pathway of PS. It is observed after cone studies that residual char led to formation of a heavier and integrated barrier covering all surface upon 5 wt% and more nanoclay addition. In 5 wt% nanoclay containing PS-NC5 specimen, PHRR is reduced by 33% compared to neat PS. This also reveals that a good nanodispersion has been achieved since no reduction in PHRR was observed for microcomposites in previous studies [88,89].

Similar shapes of HRR (Figure 3.5(a)) and MLR (Figure 3.5(c)) curves also reveal that nanoclays basically work in the condensed phase flame retardancy mechanism. Evaporation of flammable volatiles was slowed down due to "nanoconfinement" via labyrinth effect of silicate layers. As a result, diffusion of combustible fire products to gas phase diminishes and time needed for peak of HRR and MLR was expanded.

It is seen from Figure 3.5(b) that THE values decrease slightly with addition of nanoclay. Drastic changes for THE values could not be observed since almost all fuel burned eventually at the end, releasing the same amount of heat.

Table 3.3 indicates that Time To Ignition (TTI) values are shortened with incorporation of nanoclay as a result of early evaporation/degradation of organic modifier from the system. Compared to neat PS, Total Burning Time (TBT) for PS-

NC systems having 5 wt% or more nanoclay are much longer owing to the barrier formed that protects the underlying polymer.

Fire Growth Index (FGI=PHRR/TTI) and Fire Growth Index Rate (FIGRA=PHRR/TTPHR) give information about flame spread and flame spread rate, respectively. Table 3.3 also shows that upon addition of 5 wt% nanoclay, FIGRA values of PS decreased from 6.9 to 4.2, showing that nanoclay is effective in suppressing flame spread rate. THE/TML ratio gives information about flame retardancy mechanism. When flame retardancy action is in gas phase, THE/TML ratio reduces significantly with respect to pure polymer. When flame retardancy action is in condensed phase, THE/TML ratio does not change much with that of pure polymer. It is seen from Table 3.3 that, THE/TML ratio of PS-NC systems is similar to pure PS, indicating that dominant flame retardancy mechanism is in the condensed phase.



Figure 3.5 (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate Curves of the Specimens







Figure 3.5 (cont'd) (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate Curves of the specimens

Specimens	THE <sup>a</sup> (MJ/m <sup>2</sup> )	PHRR <sup>b</sup> (kW/m <sup>2</sup> )	TTT <sup>c</sup> (s)	TBT <sup>d</sup> (s)	TTPHR <sup>e</sup> (s)	FGI <sup>f</sup> (kW/m <sup>2</sup> .s)	FIGRA <sup>g</sup> (kW/m <sup>2</sup> .s)	THE/TML <sup>h</sup> (MJ/m <sup>2</sup> .g)	Char <sup>i</sup> (%)
PS	59.9	672	63	279	76	10.7	6.9	3.0	0
PS-NC1	55.0	576	41	241	94	14.0	6.5	2.8	3.6
PS-NC3	49.2	472	45	276	101	10.5	4.7	2.6	6.2
PS-NC5	47.3	449	45	320	108	10.0	4.2	2.5	7.9
PS-NC7	47.0	422	37	311	104	11.4	4.1	2.5	9.3

Table 3.3 Parameters Determined from Mass Loss Cone Calorimeter

<sup>a</sup> Total Heat Evolved: Total heat released at the end of the fire scenario

<sup>b</sup> Peak Heat Release Rate: Contribution of a material to fire flashover severity

<sup>o</sup>Time To Ignition: Time interval between sparking and ignition <sup>d</sup>Total Burning Time: Time between ignition and extinguishment of the flame <sup>o</sup>Time To Peak Heat Release: Time at which heat release rate reaches its maximum values

<sup>f</sup>Fire Growth Index: Contribution of a material to fire propagation, where FGI= PHRR/TTI <sup>s</sup>Fire Growth Rate Index: Contribution of a material to fire propagation rate, where FIGRA= PHRR/TTPHR <sup>b</sup>Total Heat Evolved/Total Mass Loss: Parameter to evaluate whether flame retarding action is in the gas or condensed phase

Char Yield: Amount of solid fire residue measured at flame-out

## (iv) Thermogravimetric Analysis

Thermogravimetric analyses were conducted in order to investigate effects of nanoclays on the thermal degradation behavior of PS. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) curves of the specimens are given in Figure 3.6(a) and (b), respectively. Peak mass loss rate of differential thermogravimetry (pMLR), 5% mass loss temperature ( $T_{5\%}$ ), 50% mass loss temperature ( $T_{50\%}$ ) and % residue values determined from these curves are tabulated in Table 3.4.

Table 3.4 shows that there is 11°C decrease in onset degradation temperature ( $T_{5\%}$ ) with addition of 5 wt% nanoclay into PS. This result is in agreement with TTI values obtained in MLC, in which addition of nanoclay lowers ignition time due to early degradation of the organic modification. The mid-point degradation temperature ( $T_{50\%}$ ) is increased by 27°C in PS-NC5 specimen compared to neat PS due to char formation in the presence of nanoclay; acting as a barrier for both mass and heat transport. This barrier inhibits diffusion of volatile decomposition products and protects inner part of samples from high temperatures attained at the surface during burning.

Barrier formed in the presence of nanoclays also change degradation kinetics of PS. It is known that ~35 wt% of nanoclay (Cloisite 10A) is composed of organic modification which is not stable and decomposes at elevated temperatures. When all modification evaporates 3.25 wt% silicate present in system leads to 5 wt% char yield, proving that nanoclay alters degradation pathway of PS and enhance char formation. Contribution of nanoclays to thermal stability by the mechanism of barrier formation is further proved with reductions observed in peak Mass Loss Rate (pMLR) values in Table 3.4.







**(b)** 

Figure 3.6 (a) Thermogravimetric (TG) and (b) Differential Thermogravimetric (DTG) Curves of Specimens

Specimens	T <sub>5%</sub> <sup>a</sup> (°C)	T <sub>50%</sub> <sup>b</sup> (°C)	pMLR <sup>c</sup> (%.s <sup>-1</sup> )	Char <sup>d</sup> (wt%)
PS	379	416	0.50	0.0
PS-NC5	368	443	0.32	5.0

**Table 3.4** Thermal Degradation Parameters Obtained from TG and DTG Curves

<sup>a</sup> T<sub>5%</sub>: Thermal degradation temperature for 5 % mass loss

<sup>b</sup>  $T_{50\%}^{5\%}$ : Thermal degradation temperature for 50 % mass loss

<sup>c</sup> pMLR: peak Mass Loss Rate

<sup>d</sup>Char: % Char yield at 600 °C

# (v) Mechanical Behavior

In order to investigate effects of clay addition on the mechanical performance of PS, tensile tests were conducted. Mechanical properties obtained from these tests are tabulated in Table 3.5, while their typical stress-strain curves are given in Figure 3.7.

It is seen from Table 3.5 that Young's Modulus of PS is increased in parallel with increasing nanoclay content. Highest increase (as much as 37%) is seen for PS-NC7 systems, having 7 wt% nanoclay. This enhancement is attributed to restriction of PS chain mobility caused by high modulus inorganic clay.

As can be seen from Table 3.5 and Figure 3.7, tensile strength of PS increases with clay addition. This is attributed to strong polymer-clay interactions caused by the formation of nanocomposite structure via intercalation/exfoliation. High levels of interactions increase load bearing capacities of nanoclay layers, thus improve mechanical performance. Maximum increase in tensile strength (as much as 16%) was obtained by only 1 wt% nanoclay addition (PS-NC1). Increasing clay loading resulted in slight decreases possibly due to the difficulties in homogeneous distribution.

SEM fractographs in Figure 3.8 show that neat PS and nanocomposite (PS-NC) specimens have similar level of fracture surface roughness. Thus, nanocomposite formation leads to no significant change in the % Elongation at Break values.

Specimens	Youngs Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PS	2.21±0.34	49±0.6	2.6±0.17
PS-NC1	2.37±0.08	57±0.4	2.3±0.14
PS-NC3	2.54±0.24	55±0.9	2.8±0.19
PS-NC5	3.20±0.25	54±0.3	2.7±0.10
PS-NC7	3.02±0.15	52±0.5	2.8±0.18

Table 3.5 Tensile Mechanical Properties of the Specimens



Figure 3.7 Tensile Stress-Strain Curves of the Specimens



Figure 3.8 SEM Fractographs of the Tensile Test Specimens (a) PS and (b) PS-NC5

In this first part of the thesis, it was seen that incorporation of organomodified clays into PS lead to the formation of nanocomposite structure. XRD and TEM studies revealed that nanoclay layers were mainly intercalated with PS matrix, having certain level of exfoliation. Nanoclays improved flame retardancy of PS significantly, for instance the suppression in PHRR was as much as 37%. The dominant flame retardancy mechanism of nanoclays was *condensed phase action* via formation of strong char barrier layers inhibiting mass and heat transfer. Nanoclays also resulted in improvements in the thermal degradation temperatures and mechanical properties.

In this study, it was aimed to utilize clay benefits as much as possible without significant loss in mechanical properties. In sake of keeping the total additive amount at minimum; PS-NC5 composition which resulted in strong and integrated char barrier, was chosen to be used in combination with conventional flame retardants. Therefore, the rest of the investigation continued using only 5 wt% nanoclay in all specimen formulations.

# **3.2** Effects of Nanoclays with TPP and TPP-MCA

Although there are certain improvements in the flammability properties of PS when nanoclay was added, it becomes evident that conventional flame retardants should be introduced into the system for higher efficiency. Thus, as the second part of this thesis, nanoclays were used together with a phosphorus based conventional flame retardant system. The specific system chosen for this purpose was triphenyl phosphate (TPP) with and without its synergist melamine cyanurate (MCA). Designations and compositions of the specimens produced in this part are given in Table 3.6.

Specimens	PS	NC	TPP	MCA
PS	100	-	-	-
PS-TPP	85	-	15	-
PS-TPP-NC	80	5	15	-
PS-TPP-MCA	75	-	15	10
PS-TPP-MCA-NC	70	5	15	10
<b>PS:</b> Polystyrene	TPP: Triphen	yl Phosphate		

Table 3.6 Designations and Compositions (wt%) of the Specimens

NC: Nanoclay

**TPP:** Triphenyl Phosphate **MCA:** Melamine Cyanurate

#### (i) Nanocomposite Formation

X-Ray Diffraction (XRD) patterns (Fig. 3.9) and Transmission Electron Microscopy (TEM) images (Fig. 3.10) were analyzed in order to evaluate dispersion and exfoliation/intercalation state of nanoclays in the presence of TPP and TPP-MCA in PS matrix.

It has been shown in other studies [67, 90] that TPP has the ability to intercalate through clay galleries and support expansion of interlayer spacing. XRD patterns in Figure 3.9 shows that, the first peak of PS-TPP-NC specimen (at  $2\theta=2.66^{\circ}$ )

corresponds to interlayer spacing of 3.3 nm indicating that clay galleries were very well intercalated. Since interlayer spacing of PS-NC5 nanocomposite is 3.1 nm (Fig. 3.1), further expansion is attributed to contribution of TPP intercalation. Figure 3.9 further indicates that, introduction of MCA also lead to first diffraction peak to arise at a lower 20 value of 2.53°, indicating a further increase of interlayer spacing to 3.5 nm. Second and third diffraction peaks of PS-TPP-NC and PS-TPP-MCA-NC specimens (at 20=5.12/5.06 and 20=7.54/7.38 respectively) could be due to the second order and third order reflections corresponding to the same *d*-spacings. These reflections occur since clay layers preferentially oriented in flow directions on the surface of injection-molded samples.

TEM images (Figure 3.2 and 3.10) reveal that there is no significant difference in terms of dispersion and intercalation/exfoliation state of PS-NC5 specimens (Figure 3.2) and traditional flame retarded specimens PS-TPP-NC (Figure 3.10 (a)) and PS-TPP-MCA-NC (Figure 3.10 (b)).



Figure 3.9 XRD Patterns of the Nanoclay and Nanocomposite Specimens with TPP-MCA System (Stars (\*) designate second and third order reflections)



Figure 3.10 TEM images of the Nanocomposite Specimens (a) PS-TPP-NC and (b) PS-TPP-MCA-NC

## (ii) LOI and UL-94 Flammability Tests

LOI and UL-94 tests were done to samples in order to investigate effects of nanoclay addition in combination with TPP and TPP-MCA on the flammability of PS. Results of both LOI and UL-94 tests are summarized in Table 3.7. Figure 3.11 shows the appearances of the burnt specimens after LOI tests, whereas Figure 3.12 and 3.13 show SEM micrographs of the surface char layers of the LOI specimens.

Specimens	LOI (O <sub>2</sub> %) <sup>a</sup>	UL-94 Rating <sup>b</sup>
PS	$18.0 \pm 0.2$	Fail
PS-TPP	$22.0 \pm 0.2$	V2
PS-TPP-NC	22.4 ±0.2	Fail
PS-TPP-MCA	23.0 ±0.2	V2
PS-TPP-MCA-NC	23.3 ±0.2	Fail

Table 3.7 Results of LOI and UL-94 Flammability Tests

<sup>a</sup> Oxygen level required for sustained flaming combustion

<sup>b</sup> Materials flammability classifications for stringent vertical orientation; Fail (flame extinguishing t < 30 s), V-2 (flaming drips, material self-extinguishes at 10<t<30 s), V-1 (material self-extinguishes at 10<t<30 s, without dripping), V-0 (material selfextinguishes at t>10 s)

Triphenyl phosphate,  $(C_6H_5)_3PO$  used is a low melting flame retardant with melting point of 48-50°C and boiling point of 220°C. Depending on the degradation behavior of the polymer it is introduced into, fire retarding action may work either in condensed or gas phase. In condensed phase TPP generates phosphoric acids. Reactions between phosphoric acids result in formation of pyrophosphoric acid, which works as an insulating barrier in condensed phase.

However, dominant mechanism of TPP is suggested to be in gas phase for nonoxygenated polymers [91]. In gas phase, PO• radicals and some P•, HPO<sub>2</sub> and P<sub>2</sub> volatiles are released as a result of decomposition of TPP. These phosphorus radicals are very effective flame inhibitors and suppresses flaming combustion by scavenging H• and OH• radicals by a series of reactions given below [5]. TPP also enhances flame retardancy by decreasing viscosity of polymer which in turn causes dripping of polymer away from the flame.

$$PO\bullet + H\bullet \to HPO \tag{3.1}$$

$$PO \bullet + OH \bullet \longrightarrow HPO + O \bullet \bullet$$
 (3.2)

$$HPO + H \bullet \to H_2 + PO \bullet \tag{3.3}$$

Table 3.7 indicates that LOI values were increased from 18 % $O_2$  to 22 % $O_2$  and UL-94 V2 rating was obtained with the addition of TPP into PS matrix. This improved flame retardancy is attributed to combination of gas phase action of phosphorus radicals and decreased viscosity which promotes dripping. When TPP and MCA were used together in PS matrix, LOI values were observed to increase 1% more and reached to 23 % $O_2$ . This might be due to further dilution of combustion gases with ammonia released during break down of melamine.

Table 3.7 also shows that, LOI values were almost the same upon nanoclay incorporation into PS-TPP and PS-TPP-MCA specimens. It is known that, although nanoclays enhance flame properties via barrier formation, they could also deteriorate some of the existing flame properties. Because, in addition to gas phase action TPP also catalyzes thermal breakdown of polymer melt, reducing melt viscosity and favoring dripping of the polymer away from the combustion zone. Presence of nanoclays seems to inhibit this dripping behavior. Thus, contribution of nanoclays by barrier formation is compensated by the retardation of melt flow. This could be the main reason of having no significant increases in the LOI values of these specimens. Due to the same reasons samples containing nanoclay could not maintained UL-94 V2 ratings, either.

Appearances of the burnt specimens taken after LOI tests are shown in Figure 3.11. It is observed that addition of TPP decreased the viscosity and brought an intense dripping behavior in PS. Incorporation of MCA is found to further blow molten polymer and contributes dripping. Figure 3.11 also shows that addition of nanoclays contributes char formation.

Morphology of the chars formed on the burnt LOI test specimens were evaluated via SEM analysis. Figure 3.12 shows these microscopic SEM images of the char layers for all specimens. PS-TPP and PS-TPP-MCA specimens in Figure 3.12 (a) and (c) indicate rather smooth surfaces, with no remarkable char formation. Introduction of nanoclays to these specimens result in rather dense and strong carbonaceous char structure as displayed in Figure 3.12 (b) and (d), respectively.

Higher magnification SEM images of PS-TPP-NC and PS-TPP-MCA-NC char structures in Figure 3.13 further reveals well dispersed clay layers stacks developing a strong and tight char structure. This effective char barrier protects underlying polymer and slows down the rate of evolution of flammable gases.



Figure 3.11 Appearances of the Specimens after LOI Test



**Figure 3.12** SEM Micrographs of the Surface Char Layers of LOI Specimens (a) PS-TPP, (b) PS-TPP-NC, (c) PS-TPP-MCA and (d) PS-TPP-MCA-NC



Figure 3.13 Higher Magnification SEM Micrographs Showing Dense and Integrated Char Barrier in (a) PS-TPP-NC and (b) PS-TPP-MCA-NC specimens

# (iii) Mass Loss Cone Calorimetry

Fire behavior of samples was analyzed with Mass Loss Cone Calorimeter. Then, (a) Heat Relase Rate (HRR) vs Time, (b) Total Heat Evolved (THE) vs Time, and (c) Mass Loss Rate (MLR) vs Time graphs of samples subjected to an external heat flux of 35 kW/m<sup>2</sup> are given in Figure 3.14. Important parameters derived from obtained data are tabulated in Table 3.8.

It is seen in Figure 3.14 and Table 3.8 that addition of TPP into PS results in suppression of THE and PHRR values by 25% and 19%, respectively. Table 3.8 shows that TTI (time to ignition) and TBT (total burning time) periods of PS-TPP specimen are the shortest among all other specimens, indicating that ignition occurred easily and burning completed in a short period of time. This could be attributed to early evaporation of highly volatile TPP. Increase in FGI values with respect to neat PS also proves that TPP is not effective in reducing flame spread when used alone and should be used in combination with other synergistic compounds.

When MCA is added to PS-TPP specimen, PHRR value decreased from 547 to 494  $kW/m^2$ . The reason behind this improvement should be due to both dilution of combustion gases with ammonia and low levels of char formation promoted by the reaction took place between MCA and TPP.

Figure 3.14 and Table 3.8 also show that nanoclay addition provides significant improvements in flame retardancy of both PS-TPP and PS-TPP-MCA specimens. PHRR values of these specimens are found to decrease 38% and 54%, respectively compared to pure PS. As discussed before nanoclays promote carbonaceous char formation which act as barrier to mass and heat transport. In the presence of this barrier, evolution of flammable volatiles through combustion zone was slowed down, increasing efficiency of radical scavenging by TPP.

Figure 3.14(c) clearly shows that there are significant reductions in MLR of all specimens upon addition of nanoclays, suggesting an effective barrier formation

inhibiting diffusion. The volatilization of TPP was slowed down by intercalation through clay galleries. Thus; phosphorus radicals may find more chance to suppress flaming combustion by scavenging H• and OH• radicals and become more effective in terms of gas phase flame retardancy at higher temperatures. Decreases in THE/TML values shown in Table 3.8 further prove that nanoclay addition also amplifies gas phase action of TPP and MCA owing to stabilization/hindrance effect.

It is known that phosphorus compounds such as TPP normally does not act in condensed phase in oxygen free polymers like PS, unless they are used with a char forming synergist. On the other hand, in this study TPP induced certain levels of char formation when used together with nanoclay. Table 3.8 shows that 7.9% char residue (given in Table 3.3) obtained after NC addition increased to 11.8% when TPP and NC used together. Since no char formation was observed for the specimens containing only TPP, phosphorus entrapped in between clay galleries presumably catalyze char formation via reacting with oxygen groups or double bonds produced on the surface as the polymer burns. This was also discussed in Reference [92].

Decreases in FIGRA and FGI values (Table 3.8) also indicate that when used with nanoclay TPP and TPP-MCA flame retardants become very effective in reducing flame spread. As opposed to findings from LOI tests in which dripping has great effect upon results, assessment of MLC parameters reveal that nanoclays create synergistic effect with TPP and TPP-MCA, and provides improvement in flame retardancy action.







Figure 3.14 (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens



Figure 3.14 (cont'd) (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens

Specimens	THE <sup>a</sup> (MJ/m <sup>2</sup> )	PHRR <sup>b</sup> (kW/m <sup>2</sup> )	TTT <sup>c</sup> (s)	TBT <sup>d</sup> (s)	TTPHR <sup>e</sup> (s)	FGI <sup>f</sup> (kW/m <sup>2</sup> .s)	FIGRA <sup>g</sup> (kW/m <sup>2</sup> .s)	THE/TML <sup>h</sup> (MJ/m <sup>2</sup> .g)	Char <sup>i</sup> (wt%)
Sd	59.9	672	63	279	76	10.7	6.9	3.0	0
ddL-Sd	45.2	547	27	221	88	20.3	6.2	2.5	0
PS-TPP-NC	37.2	414	46	298	104	9.0	4.0	2.1	11.8
PS-TPP-MCA	46.1	494	32	317	86	15.4	5.7	2.4	3.5
PS-TPP-MCA-NC	37.7	309	46	333	130	6.7	2.4	1.9	9.7

Table 3.8 Parameters Determined from Mass Loss Cone Calorimeter

<sup>a</sup> Total Heat Evolved: Total heat released at the end of the fire scenario

<sup>b</sup> Peak Heat Release Rate: Contribution of a material to fire flashover severity

<sup>o</sup>Time To Ignition: Time interval between sparking and ignition <sup>d</sup>Total Burning Time: Time between ignition and extinguishment of the flame <sup>o</sup>Time To Peak Heat Release: Time at which heat release rate reaches its maximum values

<sup>f</sup>Fire Growth Index: Contribution of a material to fire propagation, where FGI= PHRR/TTI <sup>\*</sup>Fire Growth Rate Index: Contribution of a material to fire propagation rate, where FIGRA= PHRR/TTPHR

<sup>h</sup>Total Heat Evolved/Total Mass Loss: Parameter to evaluate whether flame retarding action is in the gas or condensed phase Char Yield: Amount of solid fire residue measured at flame-out

# (iv) Thermogravimetric Analysis

Thermogravimetric analyses were conducted in order to investigate effects of nanoclays together with TPP and MCA on the thermal degradation behavior of PS matrix. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) curves of the specimens are given in Figure 3.15 (a) and (b), respectively. Peak mass loss rate of differential thermogravimetry (pMLR), 5% mass loss temperature ( $T_{5\%}$ ), 50% mass loss temperature ( $T_{50\%}$ ) and % residue values determined from these curves are given in Table 3.9.

TPP used in this study is a highly volatile compound, thus its addition into PS results in a drastic decrease of  $T_{5\%}$  by 139°C due to lower thermal stability of phosphate. Unlike neat PS, decomposition occurs in two steps. Evaporation of TPP from the polymer is assumed to be responsible for early mass loss observed around 190-200 °C in DTG curve Figure 3.15 (b). No remarkable change is observed for  $T_{50\%}$  with TPP addition since phosphate is entirely removed from the system at high temperatures, hence does not alter degradation pathway of the polymer. No char residue is observed at 600°C for PS-TPP specimen, proving that TPP has no contribution in the condensed phase action.

When MCA is introduced in to PS-TPP specimen, it is found to enhance thermal stability at the beginning of heating which increases  $T_{5\%}$  by 18°C. Again two step degradation path is observed, in the first step evaporation of TPP and small amount of MCA, and in the second step decomposition of cyanuric acid and the polymer has occurred. Similar observations were discussed in References [93] and [94]. Table 3.9 also shows that MCA addition to PS-TPP specimen did not cause any change in neither  $T_{50\%}$  values nor the char yield at 600°C.

Nanoclay addition to both PS-TPP and PS-TPP-MCA specimens lead to significant increases in thermal stability. With incorporation of nanoclays,  $T_{5\%}$  and  $T_{50\%}$  temperatures increase by 24°C and 23°C in PS-TPP specimen; and by 9°C and 18°C in PS-TPP-MCA specimen. Intercalations into clay galleries delay evaporation of TPP from the system at early stages. Nanoclays provide protection and suppress

evaporation of flame retardants at high temperatures, thus increases onset and midpoint degradation temperatures.

Table 3.9 also shows that, use of nanoclays together with TPP has almost no contribution in char formation. 5% char obtained for samples containing only nanoclay (as given in Table 3.4), decreased to 4.2% and 3.5% in the presence of TPP and TPP-MCA, respectively. Contrary to MLC results, char catalyzing action of TPP was not observed in TGA. This could be due to the TGA analysis under nitrogen flow (non-oxygen containing atmosphere) leading to no possibility of required oxidizing reactions. This situation also reveals gas phase flame retardancy action of TPP and MCA in non-oxidizing environment.

Specimens	T <sub>5%</sub> <sup>a</sup> (°C)	T <sub>50%</sub> <sup>b</sup> (°C)	pMLR <sup>c</sup> (%.s <sup>-1</sup> )	Char <sup>d</sup> (wt%)
PS	379	416	0.50	0.0
PS-TPP	240	412	0.34	0.1
PS-TPP-NC	264	435	0.25	4.2
PS-TPP-MCA	258	408	0.34	0.1
PS-TPP-MCA-NC	267	425	0.21	3.5

**Table 3.9** Thermal Degradation Parameters Obtained from TG and DTG Curves

 ${}^{a}T_{5\%}$ : Thermal degradation temperature for 5% mass loss  ${}^{b}T_{50\%}$ : Thermal degradation temperature for 50% mass loss  ${}^{c}pMLR$ : peak Mass Loss Rate  ${}^{d}Char$ : % Char yield at 600 °C







**Figure 3.15** (a) Thermogravimetric (TG) and (b) Differential Thermogravimetric (DTG) curves of specimens

# (v) Mechanical Behavior

In order to investigate effects of nanoclays and conventional flame retardant system TPP-MCA on the mechanical performance of PS, tensile tests were conducted. Mechanical properties obtained from these tests are tabulated in Table 3.10, while their typical stress-strain curves and typical fracture surfaces under SEM are given in Figure 3.16 and 3.17, respectively.

Figure 3.16 and Table 3.10 show that addition of TPP and MCA results in significant decreases in tensile strength and elastic modulus values. This must be due to the very effective plasticizing action of TPP increasing the mobility of chain structure of PS. Being a low molecular weight compound TPP therefore also used as a plasticizer.

However, after addition of only 5 wt% nanoclay, strength and modulus of these specimens increased enormously. For example, the increases in tensile strength and elastic modulus of PS-TPP-NC specimen were 136% and 103%, respectively. This could be explained with the formation of nanocomposite structure. Those high aspect ratio clay layers with further level of intercalated/exfoliated structure by TPP lead to significant load transfer from the matrix to the nano additives, and very effective hindrance of the mobility of the matrix chains.

Therefore, it can be stated that decreases seen in tensile strength and elastic modulus of PS with the addition of traditional flame retardants TPP and MCA could be overcome by utilizing them in combination with nanoclays.

In this second part of the thesis, it can be simply concluded that combined use of nanoclays with conventional phosphorus based flame retardant systems (TPP-MCA) resulted in more efficient flame retardancy. XRD and TEM analyses revealed that further level of intercalation/exfoliation of silicate layers were obtained via intercalation of TPP through clay galleries. MLC flammability tests indicated that addition of conventional flame retardants TPP and TPP-MCA into PS resulted in decreases of PHRR by 19% and 26%, respectively. Incorporation of nanoclays into those systems resulted in further PHRR suppressions of 24% and 28%, respectively.

Specimens	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PS	2.21±0.34	49±0.6	2.6±0.17
PS-TPP	1.16±0.14	14±0.5	9.9±2.45
PS-TPP-NC	2.36±0.21	33±0.3	1.7±0.02
PS-TPP-MCA	1.70±0.29	18±0.6	2.1±0.19
PS-TPP-MCA-NC	2.44±0.06	26±0.8	1.3±0.06

Table 3.10 Tensile Mechanical Properties of the Specimens



Figure 3.16 Tensile Stress-Strain Curves of the Specimens



Figure 3.17 SEM Fractographs of the Tensile Test Specimens (a) PS-TPP, (b) PS-TPP-NC, (c) PS-TPP-MCA, (d) PS-TPP-MCA-NC

These additional contributions were due to the synergistic combination of "*condensed phase mechanism*" of NC and "*gas phase mechanism*" of TPP and TPP-MCA. Volatilization of TPP and evolution of radical degradation products were delayed and/or entrapped by the strong char structure with nanoclay layers, thus effectiveness of radical entrapment by TPP was increased. TGA analysis further supported that nanoclays contribute thermal stabilization of the system via suppressed volatilization of TPP by clay galleries. Tensile tests revealed that decreases in mechanical properties of PS with TPP and MCA could be overcome by the intercalated/exfoliated structure of nanoclays.

# **3.3** Effects of Nanoclays with BE and BE-AO

In the third part of this thesis, nanoclays were used together with another conventional flame retardant system to investigate their possible synergistic effects on the flame retardancy performance of PS. The conventional system chosen this time was brominated epoxy (tribromophenol end-capped epoxy oligomer) (BE) with and without its synergist antimony trioxide (AO). Designations and compositions of the specimens are given in Table 3.11.

Specimens	PS	NC	BE	AO
PS	100	-	-	-
PS-BE	80	-	20	-
<b>PS-BE-NC</b>	75	5	20	-
PS-BE-AO	77	-	20	3
PS-BE-AO-NC	72	5	20	3

 Table 3.11 Designations and Compositions (wt%) of the Specimens

**PS:** Polystyrene **NC:** Nanoclay

**BE:** Brominated Epoxy (tribromophenol end-capped epoxy oligomer) **AO:** Antimony Trioxide

# (i) Nanocomposite Formation

X-Ray Diffraction (XRD) patterns (Figure 3.18) and Transmission Electron Microscopy (TEM) images (Figure 3.19 and 3.20) were analyzed in order to evaluate dispersion and exfoliation/intercalation state of nanoclays in the presence of BE and BE-AO in PS matrix.

Regarding clay nanocomposites based on PS-BE blends, an almost fully polymer-intercalated nanomorphology was determined by analyzing multiple reflections (higher-order reflections denoted by stars in Figure 3.18) from coherent polymer-intercalated crystallites. Average *d*-spacing's were calculated as 3.1 nm  $(2\theta = 2.90^{\circ})$  for PS-BE-NC and 2.9 nm  $(2\theta = 3.08^{\circ})$  for PS-BE–AO-NC
nanocomposites. Reflections at around  $2\theta=5.62^{\circ}$  and  $2\theta=8.12^{\circ}$  for PS-BE-NC and  $2\theta=5.72^{\circ}$  and  $2\theta=8.28^{\circ}$  for PS-BE–AO-NC were indexed as higher-order (second and third) reflections. Higher-order basal reflections occur because the diffraction data are collected from the surface of injection-molded samples where a high degree of orientation of silicate crystallites is expected compared with a more random orientation of neat organoclay in powder form showing a second-order reflection with a very low intensity.



Figure 3.18 XRD Patterns of Nanoclay and Nanocomposite Specimens with BE-AO system (Stars (\*) designate second and third order reflections)

It should be clear that nanomorphology assessed by XRD transforms from a partially intercalated to almost fully polymer intercalated state with the incorporation of BE as a dispersed phase in PS. It is also important to note that intensities of basal reflections are lower for nanocomposites based on blends (Figure 3.18) than for PS-NC5 nanocomposite (Figure 3.1). It could be related with attenuation of X-rays due to significantly larger mass absorption coefficients (at 8 keV photon energy) of bromine (90.3 cm<sup>2</sup>g<sup>-1</sup>) and antimony (266.5 cm<sup>2</sup>g<sup>-1</sup>) compared with carbon (4.2

 $cm^2g^{-1}$ ) and oxygen (11.0  $cm^2g^{-1}$ ) [95]. It might also be considered as an indication of a lower amount of coherent intercalated crystallites in the blends.

TEM micrographs of PS-BE-AO-NC systems are given in Figure 3.19. The dark regions of around 0.5–1.5  $\mu$ m in Figure 3.19 are electron-dense BE showing phase separation with the continuous PS matrix. Silicate nanoparticles are dispersed at the nanoscale within the PS matrix. In order to gain more insight into silicate nanodispersion in the blend, higher-magnification images are provided in Figure 3.20. For instance, Figure 3.20 (a) reveals the presence of clay primary particles (having sizes in the range of 0.3 to 1  $\mu$ m), that is, rather coarse aggregates of polymer-intercalated crystallites with a large number of stacked clay layers.

Persistence of such primary particles in the blends, which were absent in PS-NC nanocomposite, can be attributed to higher solution viscosities encountered during sonication processing because of the presence of BE in the solution. During sonication processing of a higher-viscosity solution, some ultrasound energy will be dissipated whereas less will be transferred to nanoclay particles to delaminate and disperse crystallites at the nanoscale.

A closer view of the BE phase dispersed in PS matrix in Figure 3.20 (b) reveals some segregation of nanoclay silicate layers on PS-BE phase boundaries and also the presence of exfoliated silicate layers located inside the BE phase. The exfoliation of organoclay in BE phase could be related to favorable thermodynamic interactions of BE and clay organic modifier compared with that between polymer matrix and the organic modifier [96]. Exfoliated silicate layer segregation on PS-BE phase boundaries could be actually driven by the reduction of the surface tension of PS-BE interface.

It was demonstrated earlier that interfacial tension of a variety of blends can be reduced by nanoclay segregation on phase boundaries [97,98]. Additionally, several other mechanisms were postulated such as inhibition of coalescence/fusion of the dispersed phase by rigid silicate layers and changes in the viscosity of constituent phases among which nanoparticles are unevenly distributed [99].

Above all, in the present study, organoclay segregation on PS/BE phase boundaries favors the break-up/coalescence equilibrium of dispersed phase and hence provides a compatibilization effect between two phases, which refines the microstructure of blends. Now, the question arises on how and by what mechanism are silicate layers preferentially exfoliated in the BE phase dispersed within the PS matrix. It can be inferred from the micrograph in Figure 3.20(b) that curved phase boundaries are formed between PS and BE where silicate layers are segregated. Therefore, it could be postulated that preferential exfoliation of silicate layers within BE phase occurs through an interface-controlled mechanism rather than diffusion-controlled polymer intercalation in clay galleries.

It is thought that thermodynamically favored adsorption of BE on clay surfaces is followed by the formation of curved interfaces and subsequent penetration and exfoliation of individual silicate layers within the BE phase. Accordingly, exfoliation of silicate layers in the dispersed BE phase occurs by a completely different mechanism than that is operative in nanocomposites based on neat polymers, which involves intercalation of the macromolecule into clay galleries and subsequent delamination of silicate layers.



Figure 3.19 TEM Images of the Nanocomposite Specimens (a) PS-BE-NC and (b) PS-BE-AO-NC



**Figure 3.20** TEM Images of PS-BE-NC Specimen (**a**) Presence of Aggregated Polymer-Intercalated Crystallite in PS Matrix with BE Domains, and (**b**) Exfoliation of Nanoclay in BE Phase and Segragation of Silicate Layers on Phase Boundries between PS and BE

#### (ii) LOI and UL-94 Flammability Tests

LOI and UL-94 tests are done to samples in order to investigate effects of nanoclay addition in combination with BE and BE-AO on the flammability of PS. Results of both LOI and UL-94 tests are tabulated in Table 3.12. Figure 3.21 shows the appearances of the burnt specimens after LOI tests, whereas Figure 3.22 and 3.23 show SEM micrographs of the surface layers of the LOI specimens.

$LOI\left(O_{2}\%\right)^{a}$	UL-94 Rating <sup>b</sup>
18.0 ±0.2	Fail
$21.0 \pm 0.2$	V2
$24.0 \pm 0.2$	Fail
$24.0 \pm 0.2$	V2
25.5 ±0.2	Fail
	LOI $(O_2\%)^a$ $18.0 \pm 0.2$ $21.0 \pm 0.2$ $24.0 \pm 0.2$ $24.0 \pm 0.2$ $25.5 \pm 0.2$

 Table 3.12 Results of LOI and UL-94 Flammability Tests

<sup>a</sup> Oxygen level required for sustained flaming combustion

<sup>b</sup> Materials flammability classifications for stringent vertical orientation; Fail (flame extinguishing t < 30 s), V-2 (flaming drips, material self-extinguishes at 10 < t < 30 s), V-1 (material self-extinguishes at 10 < t < 30 s, without dripping), V-0 (material selfextinguishes at t>10 s)

BE used in this study is known to be mostly effective in gas phase. As a result of decomposition of BE, Br• radicals are released, which in turn abstracts hydrogen from polymer and results in formation of HBr. HBr is a very effective flame inhibitor and suppress flaming combustion by scavenging H• and OH• radicals by a series of reactions given below (Reactions 3.7-3.8) [5].

$R\text{-}Br \to R\bullet + Br\bullet$	(3.4)
$Br \bullet + CH_2 - CH_2 \rightarrow CH \bullet - CH_2 + HBr$	(3.5)

$CH \bullet - CH_2 \rightarrow H \bullet + CH = CH$	(3.6)

 $HBr + H \bullet \to H_2 + Br \bullet$  (3.7)

(3.8)

 $HBr + OH \bullet \rightarrow H_2O + Br \bullet$ 

Table 3.12 indicates that LOI values increased from 18% to 21%  $O_2$  with the addition of BE into PS matrix due to well known gas phase flame retardancy mechanisms. UL-94 V2 ratings were also obtained since BE alters the degradation and combustion behavior in a manner that accelerates dripping and subsequent self extinguishment of PS.

When AO (Sb<sub>2</sub>O<sub>3</sub>) is added in combination with BE, LOI values further increased to 24% O<sub>2</sub>. The synergistic flame retarding action of the BE-AO combination manifests itself by the production of SbBr<sub>3</sub>, a more effective radical scavenger then HBr via reactions between HBr and AO (Reactions 3.9-3.12) [5].

- $Sb_2O_3 + 2 HBr \rightarrow 2 SbOBr + H_2O$  (3.9)
- $5 \text{ SbOBr} \rightarrow \text{Sb}_4\text{O}_5\text{Br}_2 + \text{SbBr}_3 \tag{3.10}$
- $4 \operatorname{Sb}_4 \operatorname{O}_5 \operatorname{Br}_2 \to 5 \operatorname{Sb}_3 \operatorname{O}_4 \operatorname{Br} + \operatorname{Sb} \operatorname{Br}_3 \tag{3.11}$
- $3 \operatorname{Sb}_3\operatorname{O}_4\operatorname{Br} \to 4 \operatorname{Sb}_2\operatorname{O}_3 + \operatorname{Sb}\operatorname{Br}_3 \tag{3.12}$

In flame, SbBr<sub>3</sub> is reduced through a series of reactions, scavenging H• and OH• radicals and as a result, suppresses flaming combustion (Reactions 3.13-3.16). However, as in the case of PS-BE systems, flaming drips could not be avoided with the addition of AO, leading to a retained UL-94 V2 ratings for PS-BE-AO.

$SbBr_3 + H \bullet \rightarrow SbBr_2 + HBr$	(3.13)
$SbBr_2 + H \bullet \longrightarrow SbBr + HBr$	(3.14)
$SbBr + H \bullet \rightarrow Sb + HBr$	(3.15)
Sb+OH•→SbOH	(3.16)

Introduction of 5 wt% nanoclay into PS-BE and PS-BE-AO systems, was found to increase LOI values from 18% O<sub>2</sub> to 24% O<sub>2</sub> and 25.5% O<sub>2</sub>, respectively. These increases should be due to condensed phase flame retardancy action of clays generating a protective barrier. It is known that, BE and BE-AO alters degradation behavior of PS, speeds up the process and increases dripping. Introduction of clay inhibits this dripping behavior which deteriorates UL-94 rating from V2 to "Fail" for PS-BE-NC and PS-BE-AO-NC specimens. However, it should be noted that, LOI

values of PS-BE-NC and of PS-BE-AO specimens are the same, revealing that nanoclays are as effective as AO.

Appearances of the burnt specimens taken after LOI test are shown in Figure 3.21. Contribution of BE and BE-AO in dripping behavior of PS can be observed. This dripping is accompanied with char formation indicating that those systems have slight contribution in condensed phase flame retardancy. Figure 3.21 also shows that addition of nanoclays contributes char formation slightly.

Morphology of chars after LOI test was evaluated via SEM analysis. Figure 3.22 (a) and (c) for PS-BE and PS-BE-AO specimens show that their chars have rather plain structure. Introduction of nanoclays in these specimens results in formation of a physical barrier as can be seen from Figure 3.22 (b) and (d). Higher magnification SEM images (Figure 3.23) of these nanocomposite specimens (PS-BE-NC and PS-BE-AO-NC) also reveal that they have tortuous physical barrier layers which protects underlying polymer and slows down the rate of evolution of flammable gases.



Figure 3.21 Appearances of the Specimens after LOI Test



Figure 3.22 SEM Micrographs of the Surface Char Layers of LOI Specimens (a) PS-BE, (b) PS-BE-NC, (c) PS-BE-AO, and (d) PS-BE-AO-NC



Figure 3.23 Higher Magnification SEM Micrographs Showing Tortuous Physical Barrier Layers in (a) PS-BE-NC and (b) PS-BE-AO-NC Specimens

## (iii) Mass Loss Cone Calorimetry

Fire behavior of samples was analyzed with Mass Loss Cone Calorimeter. Then, (a) Heat Relase Rate (HRR) vs Time, (b) Total Heat Evolved (THE) vs Time, and (c) Mass Loss Rate (MLR) vs Time graphs of samples subjected to an external heat flux of 35 kW/m<sup>2</sup> are given in Figure 3.24. Important parameters derived from obtained data are tabulated in Table 3.13.

When BE was added to PS, PHRR and THE values were found to decrease 35% and 39% respectively, compared to neat PS. The mechanism behind this enhancement is the formation of HBr which is a very effective flame inhibitor and suppresses flaming combustion by scavenging hot flammable radicals. The decreases observed in THE/TML ratio from 3.0 MJm<sup>-2</sup>g<sup>-1</sup> to 1.6 MJm<sup>-2</sup>g<sup>-1</sup> with incorporation of BE also validates gas phase action of HBr. Additionally, 3.3 wt% char yield shows that BE has slight contribution in condensed phase char forming mechanism.

Combination of BE and AO yielded further reductions in PHRR and THE values as much as 64% and 63%, respectively compared to neat PS, and 44% and 39% respectively, compared to PS-BE. THE/TML ratio further decreased down to 1.0  $MJm^{-2}g^{-1}$  owing to formation of SbBr<sub>3</sub> with the reactions between HBr and Sb<sub>2</sub>O<sub>3</sub> (AO). SbBr<sub>3</sub> is a more active radical scavenger than HBr in gas phase.

Significant improvements were obtained in fire retardant properties by nanocomposite formation. Addition of nanoclay into PS-BE and PS-BE-AO specimens results in decreases of PHRR values by 42% and 27%, respectively. In terms of improvements in fire retardancy with nanocomposite formation, the following mechanisms can be postulated.







Figure 3.24 (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate Curves of the Specimen



Figure 3.24 (cont'd) (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate Curves of the Specimens

As discussed earlier by Jang and Wilkie [62], the accommodation of decomposing macroradicals within the clay interlayers, termed as "nanoconfinement," facilitates the entrapment of degradation products for a long time before they evolve into the gas phase. Besides, the tortuous pathway formed by nanodispersed high-aspect-ratio silicate layers may hinder the diffusion of volatiles within the pyrolyzing melt, and the formation of a clay-catalyzed superficial carbonaceous char which is physically reinforced and consolidated by clay layers can also be operative in shielding the underlying material by restricting heat and mass transfer across itself. As a whole, these last two effects, that is, hindered diffusion and carbonaceous char formation are termed the "barrier effects."

The extent of heat release rate reductions were almost matched to what has been observed for mass loss rates with the incorporation of organoclay into PS-BE and PS-BE-AO. Considering the above mechanisms, one can explain why such similar reduction trends were observed by nanocomposite formation. Actually, the rate at

which decomposition products evolve into the flaming zone is slowed down regardless of whether it occurs by nanoconfinement or barrier effects. Therefore, nanocomposite formation can be said to impart a predominant condensed-phase flame-retarding effect.

In fact, considering the amounts of fire residues listed in Table 3.13, no remarkable charring of PS-BE and PS-BE–AO blends can be said to have been induced by organoclays. Organoclay incorporation into PS induced the formation of around 4.4 wt% carbonaceous char. In the case of nanocomposites based on PS/BE blends, organoclay-catalyzed charring effect was reduced when around 1.4 wt% carbonaceous char was obtained. This could be related to a change in the degradation behavior of PS in the presence of halogenated flame-retardant and AO additives.

This might lead to a conclusion that the condensed phase flame retardancy of organoclays originates from nanoconfinement and hindered diffusion effects, but rather irrelevant of carbonaceous char formation. This fairly differs from the proposed mechanism for nanocomposites based on neat PS where significant charring was reported [55, 54].

As to how nanocomposite formation actually improves fire retardancy of halogenated flame-retardant PS blends, the following discussions might be useful. Although the total heat evolved is hardly changed, it is clear from Figure 3.24 (c) that flame-retardant nanocomposites unambiguously demonstrate slower mass loss during combustion in the mass loss calorimeter, which could be related to nanoconfinement and barrier effects of nanodispersed organoclays as discussed above.

These might also apply to the retardation of pyrolysis of BE to some extent; however, both effects have cumulative and predominant influence on thermal degradation of PS. Pyrolysis of PS is largely suppressed by the accommodation of macroradicals, which leads to a superheated environment where radical recombination reactions and production of higher molecular weight decomposition products are favored [62]. In light of these, it is expected that the concentration of hot radicals in the gas phase responsible for flame propagation is lower throughout

combustion of nanocomposites, which increases the efficiency of radical scavenging by halogenated species [100]. This should explain the improvement in fire-retarding effectiveness of PS-BE blend by nanocomposite formation.

Lowered rates of evolution of gaseous decomposition products into the gas phase attributed to the barrier effect operative in nanocomposites eventually apply to the evolution of HBr. The release of HBr is presumably slowed down by exfoliated clay layers preferentially residing both within the BE phase and at the PS-BE interfaces (in Figure 3.20). In this respect, it is important to note the expected increase in the time allowed for the gas–solid reaction among HBr and Sb<sub>2</sub>O<sub>3</sub>, which yields SbBr<sub>3</sub>. An increase in the yield of such a reaction will apparently enhance the gas-phase flame-retarding effectiveness of PS-BE-AO by nanocomposite formation.

It can be inferred from Table 3.13 that the fire growth rate was greatly reduced owing to significant reductions in rates of heat release by nanocomposite formation. Nanoclay incorporation reduced the fire growth rate (FIGRA) from 4.5 to 2.1 kWm<sup>-2</sup>s<sup>-1</sup> for PS-BE, which corresponds to the same performance demonstrated by PS-BE-AO (2.1 kWm<sup>-2</sup>s<sup>-1</sup>). FIGRA was further lowered from 2.1 to 1.4 kWm<sup>-2</sup>s<sup>-1</sup> for PS-BE-AO by the act of nanocomposite formation.

		<b>Table 3.13</b>	Parameters 1	Determined 1	from Mass Lo	ss Cone Calor	imeter		
Specimens	THE <sup>a</sup> (MJ/m <sup>2</sup> )	PHRR <sup>b</sup> (kW/m <sup>2</sup> )	TTI <sup>c</sup> (s)	TBT <sup>d</sup> (s)	TTPHR <sup>e</sup> (s)	FGI <sup>f</sup> (kW/m <sup>2</sup> .s)	FIGRA <sup>g</sup> (kW/m <sup>2</sup> .s)	THE/TML <sup>h</sup> (MJ/m <sup>2</sup> .g)	Char <sup>i</sup> (wt%)
Sd	59.9	672	63	279	76	10.7	6.9	3.0	0
PS-BE	36.6	436	50	198	76	8.7	4.5	1.6	3.3
PS-BE-NC	28.8	255	55	233	119	4.5	2.1	1.3	7.5
PS-BE-AO	22.3	245	64	194	119	3.8	2.1	1.0	3.7
PS-BE-AO-NC	18.4	180	49	194	124	3.7	1.4	0.8	7.9

<sup>a</sup> Total Heat Evolved: Total heat released at the end of the fire scenario

<sup>b</sup> Peak Heat Release Rate: Contribution of a material to fire flashover severity

°Time To Ignition: Time interval between sparking and ignition

<sup>d</sup>Total Burning Time: Time between ignition and extinguishment of the flame <sup>o</sup>Time To Peak Heat Release: Time at which heat release rate reaches its maximum values

<sup>f</sup>Fire Growth Index: Contribution of a material to fire propagation, where FGI= PHRR/TTI <sup>B</sup>Fire Growth Rate Index: Contribution of a material to fire propagation rate, where FIGRA= PHRR/TTPHR <sup>b</sup>Total Heat Evolved/Total Mass Loss: Parameter to evaluate whether flame retarding action is in the gas or condensed phase

Char Yield: Amount of solid fire residue measured at flame-out

## (iv) Thermogravimetric Analysis

Thermogravimetric analysis were conducted in order to investigate effects of nanoclays together with BE and AO on thermal degradation behavior of PS matrix. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) curves of specimens are given in Figure 3.25 (a) and (b), respectively. Peak mass loss rate of differential thermogravimetry (pMLR), 5% mass loss temperature ( $T_{5\%}$ ), 50% mass loss temperature ( $T_{50\%}$ ) and % residue values determined from these curves are given in Table 3.14.

Addition of BE alone did not alter thermal degradation behavior of PS much, but decreases onset degradation ( $T_{5\%}$ ) temperature by 24°C due to early polymer degradation catalyzed by HBr in the system. Char yield seen at 600°C is consistent with the results obtained from MLC tests, indicating that BE has slight contribution on the condensed phase catalyzing char formation.

Introduction of AO in to PS-BE specimens further decreases  $T_{5\%}$  by 4°C more and results in a different DTG curve. Without AO, PS-BE tends to degrade in one major step indicating that BE decomposes at similar temperatures with PS matrix. In the presence of AO, decomposition occurs in two steps. A small shoulder formed just before the major peak should be due to the formation of SbBr<sub>3</sub> and water by the interactions of AO with BE and PS. This shoulder at a lower temperature indicates that AO is responsible for the initiation of degradation process [101].

DTG curves in Figure 3.25 (b) indicates that nanocomposite formation in both systems lead to decreased mass loss rates by inhibiting diffusion of volatile products. Table 3.14 shows that pMLR decreases for PS-BE and PS-BE-AO specimens were down to 0.25 %.s<sup>-1</sup> and 0.21 %.s<sup>-1</sup>, respectively. On the other hand, due to early decomposition of the organic clay modification, T<sub>5%</sub> values were found to decrease by 16°C and 6°C compared to PS-BE and PS-BE-AO specimens. No remarkable charring was detected to be induced with clay addition (as revealed in MLC studies). The most important contribution of nanoclays in the thermal stability of flame

retarded specimens was their additional barrier effect hindering diffusion of volatiles, and decreasing mass loss rates.



Figure 3.25 (a) Thermogravimetric (TGA) and (b) Differential Thermogravimetric (DTG) curves of specimens

Specimens	T <sub>5%</sub> <sup>a</sup> (°C)	T <sub>50%</sub> <sup>b</sup> (°C)	pMLR <sup>c</sup> (%.s <sup>-1</sup> )	Char <sup>d</sup> (wt%)
PS	379	416	0.5	0.0
PS-BE	355	391	0.34	2.8
PS-BE-NC	339	387	0.25	6.6
PS-BE-AO	351	394	0.34	4.0
PS-BE-AO-NC	345	400	0.21	7.4

**Table 3.14** Thermal Degradation Parameters Obtained from TG and DTG Curves

 ${}^{a}T_{5\%}$ : Thermal degradation temperature for 5% mass loss

<sup>b</sup>T<sub>50%</sub>: Thermal degradation temperature for 50% mass loss

<sup>c</sup>pMLR: peak Mass Loss Rate

<sup>d</sup>Char: % Char yield at 600 °C

# (v) Mechanical Behavior

In order to investigate effects of nanoclays and conventional flame retardants of BE-AO on the mechanical performance of PS, tensile tests were conducted. Mechanical properties obtained from these tests are tabulated in Table 3.15, while their typical stress-strain curves and typical fracture surfaces under SEM are given in Figures 3.25 and 3.26, respectively.

Figure 3.26 and Table 3.15 simply show that addition of traditional flame retardant system BE and AO increases elastic modulus and strength while decreases ductility of PS due to basically decreased mobility of chain structure. Addition of nanoclays into these specimens increases modulus and strength values further. This should be due to the efficient load transfer and decreased chain mobility mechanisms of nanofillers as discussed in the previous sections.

Moreover, in this part there could be an additional mechanism. As shown in Figure 3.27, nanoclay addition also influences shape, size, and distribution of BE domains making them more spherical, finer, and uniformly distributed. Therefore, these morphological improvements of BE domains in PS matrix might also contribute to higher mechanical properties.

Specimens	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PS	2.21±0.34	49±0.6	2.6±0.17
PS-BE	3.20±0.07	49±2.7	1.8±0.51
PS-BE-NC	3.83±0.17	55±3.8	1.9±1.32
PS-BE-AO	3.29±0.07	52±4.3	1.5±0.07
PS-BE-AO-NC	4.03±0.13	48±5.7	1.3±0.28

**Table 3.15** Tensile Mechanical Properties of the Specimens



Figure 3.26 Tensile Stress-Strain Curves of the Specimens

If important results of this third part of the thesis were summarized, according to XRD and TEM analyses it can be said that besides intercalated/exfoliated structure of nanocomposite specimens, silicate layer segregation at the PS/BE domain boundaries and exfoliation in BE domains were also observed. MLC flammability tests indicated that addition of conventional flame retardants BE and BE-AO resulted in decreases of PHRR by 35% and 64%, respectively. These significant

improvements were obtained as a result of "gas phase" radical scavenging actions of HBr and SbBr<sub>3</sub>. Further synergistic improvements were obtained with the addition of nanoclays, for example PHRR of PS-BE and PS-BE-AO specimens were decreased by 42% and 27%, respectively. The mechanism behind this was attributed to "nanoconfinement" and tortuous pathway effects of nanoclays forming a physical barrier rather than carbonaceous char formation. TGA analysis further supported that contribution of nanoclays in thermal stability of the flame retarded specimens were the formation of physical barriers hindering diffusion of volatiles and decreasing the mass loss rates. Tensile tests revealed that addition of nanoclays increases modulus and strength values of the specimens further due to the efficient load transfer and decreased chain mobility mechanisms of the nanoadditives, and improved morphology of the BE domains by silicate layers.



Figure 3.27 SEM Fractographs of the Tensile Test Specimens (a) PS-BE, (a) PS-BE-NC, (c) PS-BE-AO and (d) PS-BE-AO-NC

# **3.4** Effects of Carbon Nanotubes with BE and BE-AO

As the fourth purpose of this study, flame retardancy effects of carbon nanotubes (CNT) when used with and without the conventional flame retardant system BE-AO were investigated. Designations and compositions of the specimens produced for this purpose are given in Table 3.16.

Specimens	PS	CNT	BE	AO
PS	100	-	-	-
PS-CNT	99	1	-	-
PS-BE	80	-	20	-
PS-BE-CNT	79	1	20	-
PS-BE-AO	77	-	20	3
PS-BE-AO-CNT	76	1	20	3

Table 3.16 Designations and Compositions (wt%) of the Specimens

**PS:** Polystyrene **CNT:** Carbon Nanotube **BE:** Brominated Epoxy (tribromophenol end-capped epoxy oligomer) **AO:** Antimony Trioxide

# (i) Preliminary Works (Solvent Screening)

In order to determine the best solvent for the highest level of CNT dispersion, "solvent screening" procedure has been applied as the preliminary step before the production of nanocomposites via solution mixing method. In this procedure, 0.1 mg CNT was incorporated into 8 different solvents of 10 mL tubes and ultrasonicated for 30 minutes. Then, these mixtures were photographed in various periodic time intervals to examine dispersability of each solvent. Solvents used were Tetrahydrofuran (THF), N,N Dimethylformamide (DMF), Toluene, Chloroform, Dichloromethane (DCM), Acetone, Ethanol, and Water. These procedures and images of each system are given in Appendix.

Dispersion of carbon nanotubes from their tightly bundled form is difficult and complicated. Un-bundling basically depends on the character of the Van der Walls forces between carbon nanotube robes and their interactions with the solvent. Due to the explosion of the micro cavities formed during sonication; forces that are equal to or higher then Van der Walls forces occur and therefore carbon nanotube bundles start to dissolve and disperse. In Table 3.17 also gives the total solubility parameters (Hildebrand Parameter) and components forming this parameter (Hansen Parameter) of each solvent used. Results of the "solvent screening" procedure are given below for each solvent.

Solvents	δd (MPa <sup>1/2</sup> )	δp (MPa <sup>1/2</sup> )	δh (MPa <sup>1/2</sup> )	δt (MPa <sup>1/2</sup> )	DISPERSION
THF	16.8	5.7	8.0	19.4	Highly Dispersed
DMF	17.4	13.7	11.3	24.8	Highly Dispersed
Chloroform	17.8	3.1	5.7	19.0	<b>Semi Dispersed</b> (High Solubility)
DCM	18.2	6.3	6.1	20.3	<b>Semi Dispersed</b> (High Solubility)
Acetone	15.5	10.4	7.0	20.0	Semi Dispersed (Low Solubility)
Ethanol (EtOH)	15.8	8.8	19.4	26.5	Semi Dispersed (Low Solubility)
Toluene	18.0	1.4	2.0	18.2	Precipitate
Water	15.6	16.0	42.3	47.8	Precipitate

 Table 3.17 Solubility Parameters and Dispersion States of the Solvents Used

 $\delta d$  = Dispersive contribution  $\delta p$  = Polar contribution

 $\delta h$  = Hydrogen bonding contribution  $\delta t$  = Total solubility parameter

The effects of solubility parameters (Hansen Components) on dispersion can be interpreted as follows. As can be seen from Figure 3.28, nanotubes dispersed homogenously with high stability as far as the dispersive Hansen parameter ( $\delta d$ ) remains at a certain interval (16–17.5 MPa<sup>1/2</sup>). Figure 3.29 shows that precipitation occurs in the systems having very high and very low polar and hydrogen bond components, and that homogenous dispersion could be achieved in systems which fall in between that interval.



Figure 3.28 Effects of Dispersive Component on Dispersion



Figure 3.29 Effects of Hydrogen Bond and Polar Component on Dispersion

When carbon nanotubes reach equilibrium after sonication with different solvents, a two phase ( $\alpha$ + $\beta$ ) structure forms (Figure 3.30). It was observed that in a very good dispersion state  $\alpha$ -phase percent is much more than  $\beta$ -phase, and CNT amount suspended in the  $\alpha$ -phase is higher. In Water-CNT solution where dispersion is very poor, it was observed that while  $\alpha$ -phase percent decreases, CNT amount in this phase also decreases remarkably. These observations are shown in the schematic phase diagram in Figure 3.30. In Figure 3.31, schematic phase stability curves were constructed according to CNT dispersability of the solvents.



Figure 3.30 Schematic Phase Diagrams for Solvent-CNT system



Figure 3.31 Schematic Phase Stabilities of Solvents 112

Results of "solvent screening" procedure indicated that the best CNT dispersion can be attained by DMF and THF. Since volatility of DMF (Tb~153°C) is very low, it could cause difficulties in the solvent removal step, thus use of THF was chosen for the production of PS-CNT nanocomposites by "solution mixing" method.

Then, in order to determine optimum CNT content for the nanocomposite production, THF solutions with three different CNT amounts were sonicated and their dispersion state examined under optical microscope. Figure 3.32 indicates that decreasing the CNT amount leads to better dispersion. Therefore, it was decided to use a low amount of CNT, that is 1 wt%, in the production of PS-CNT nanocomposites.



**(a)** 

Figure 3.32 Effect of CNT amount on the Dispersion State (a)  $10^{-3}$  gr CNT/mL, (b)  $10^{-4}$  gr CNT/mL, (c)  $10^{-5}$  gr CNT/mL



**(b)** 



(c)

Figure 3.32 (cont'd) Effect of CNT amount on the Dispersion State (a)  $10^{-3}$  gr CNT/mL, (b)  $10^{-4}$  gr CNT/mL, (c)  $10^{-5}$  gr CNT/mL

#### (ii) LOI and UL-94 Flammability Tests

LOI and UL-94 tests are done to samples in order to investigate effects of carbon nanotube addition in combination with BE and BE-AO on the flammability of PS. Results of both LOI and UL-94 tests are tabulated in Table 3.18. Figure 3.41 shows SEM micrographs of the surface char layers of the LOI specimens, whereas Figure 3.42 shows the appearances of the burnt specimens after LOI tests.

Table 3.18 indicates that LOI values were increased from 18  $\%O_2$  to 19  $\%O_2$  with the addition of 1wt% CNT into PS. However, there was no improvement when CNT was added to the specimens with traditional flame retardant system of BE and AO.

This could be due to the insufficient char barrier formation capability of CNTs. Figure 3.33 shows that dense and strong char barrier layers were not formed compared to the barriers formed by nanoclays (Figure 3.22). Since nanoclays are 2D nano-additives, they have effective barrier formation compared to the 1D geometry of carbon nanotubes. Table 3.18 also shows that UL-94 V2 rating of the specimens decreases to "Fail" rating when CNTs are incorporated. This must be especially due to the prevention of the polymer dripping by CNTs, as seen in Figure 3.34.

Specimens	LOI $(O_2\%)^a$	UL-94 Rating <sup>b</sup>
PS	18.0 ±0.2	Fail
PS-CNT	19.0±0.2	Fail
PS-BE	21.0±0.2	V2
PS-BE- CNT	21.0±0.2	Fail
PS-BE-AO	24.0±0.2	V2
PS-BE-AO-CNT	23.5±0.2	Fail

Table 3.18 Results of LOI and UL-94 Flammability Tests

<sup>a</sup> Oxygen level required for sustained flaming combustion

<sup>&</sup>lt;sup>b</sup> Materials flammability classifications for stringent vertical orientation; Fail (flame extinguishing t < 30 s), V-2 (flaming drips, material self-extinguishes at 10 < t < 30 s), V-1 (material self-extinguishes at 10 < t < 30 s, without dripping), V-0 (material selfextinguishes at t>10 s)



Figure 3.33 SEM Micrographs of the Surface Char Layers of LOI Specimens (a) PS,(b) PS-CNT, (c) PS-BE, (d) PS-BE-CNT, (e) PS-BE-AO, (f) PS-BE-AO-CNT



Figure 3.34 Appearances of the Specimens after LOI Test

### (iii) Mass Loss Cone Calorimetry

Fire behavior of samples was analyzed with Mass Loss Cone Calorimeter. Then, (a) Heat Relase Rate (HRR) vs Time, (b) Total Heat Evolved (THE) vs Time, and (c) Mass Loss Rate (MLR) vs Time graphs of samples subjected to an external heat flux of 35 kW/m<sup>2</sup> are given in Figure 3.35. Important parameters derived from obtained data are tabulated in Table 3.19.

It can be seen from Table 3.19 and Figure 3.35 that THE values decrease slightly with the addition of CNT for all specimens. PHRR decreases 13% with CNT incorporation compared to neat PS. It can be stated that this suppression was not as efficient as with the nanoclay addition leading to 33% suppression. There were no reductions in FIGRA and FGI values either, revealing that addition of CNT alone becomes inadequate in suppressing flame spread. However, when CNT was added into the specimens with BE, both PHRR and THE values decreased by 42% and 45%, respectively compared to neat PS, and by 11% and 9%, respectively compared to PS-BE. Significant decreases obtained also in FIGRA and FGI values suggest that

flame spread can be suppressed with this combination. These improvements are attributed to the combination of gas phase action of BE and physical barrier action of CNTs. It was also observed that THE/TML ratio values of PS-BE-CNT and PS-BE are the same, revealing that CNTs contribute to flame retardancy in the condensed phase but not in the gas phase action.

Incorporation of CNTs into the specimens with BE-AO further decreases PHRR and THE values by 64% and 69% respectively compared to neat PS, and by 11% and 16%, respectively compared to PS-BE-AO. Improvements observed are attributed to the gas phase synergistic action of BE and AO, and physical barrier formation of CNT. THE/TML ratio remaining unchanged compared to PS-BE-AO specimen further approves condensed phase action of CNT. Just like previous group, contribution of CNTs to the very efficient traditional BE-AO composition should be their additional barrier formation mechanism. However, these improvements are not as effective as those obtained via nanoclay addition. The reason behind this fact could be based on the geometrical difference in between CNTs and nanoclays. Nanoclays having 2D geometry could result in formation of a more effective barrier, whereas CNTs having 1D geometry become insufficient.



Figure 3.35 (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens

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Figure 3.35 Cont'd (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens

Specimens	THE <sup>a</sup> (MJ/m <sup>2</sup> )	PHRR <sup>b</sup> (kW/m <sup>2</sup> )	TTI <sup>c</sup> (s)	TBT <sup>d</sup> (s)	TTPHR <sup>¢</sup> (s)	FGI <sup>f</sup> (kW/m <sup>2</sup> .s)	FIGRA <sup>g</sup> (kW/m <sup>2</sup> .s)	THE/TML <sup>h</sup> (MJ/m <sup>2</sup> .g)	Char <sup>i</sup> (wt%)
SA	59.9	672	63	279	76	10.6	6.9	n	0
PS-CNT	56.4	584	40	304	93	14.6	6.3	2.9	4.2
PS-BE	36.6	436	50	198	76	8.7	4.5	1.6	3.3
<b>PS-BE-CNT</b>	33.2	389	47	224	87	8.3	4.5	1.7	6.3
PS-BE-AO	22.3	245	64	194	119	3.8	2.1	1	3.7
PS-BE-AO-CNT	18.8	219	42	211	88	5.2	2.5	1	6.8

Table 3.19 Parameters Determined from Mass Loss Cone Calorimeter

<sup>a</sup> Total Heat Evolved: Total heat released at the end of the fire scenario

<sup>b</sup> Peak Heat Release Rate: Contribution of a material to fire flashover severity

<sup>o</sup>Time To Ignition: Time interval between sparking and ignition <sup>d</sup>Total Burning Time: Time between ignition and extinguishment of the flame <sup>e</sup>Time To Peak Heat Release: Time at which heat release rate reaches its maximum values <sup>f</sup>Fire Growth Index: Contribution of a material to fire propagation, where FGI= PHRR/TTI

<sup>8</sup>Fire Growth Rate Index: Contribution of a material to fire propagation rate, where FIGRA= PHRR/TTPHR <sup>h</sup>Total Heat Evolved/Total Mass Loss: Parameter to evaluate whether flame retarding action is in the gas or condensed phase <sup>i</sup>Char Yield: Amount of solid fire residue measured at flame-out

## (iv) Thermogravimetric Analysis

Thermogravimetric analysis were conducted in order to investigate effects of CNT alone and together with BE and AO on the thermal degradation behavior of PS matrix. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) curves of specimens are given in Figure 3.36 (a) and (b), respectively. Peak mass loss rate of differential thermogravimetry (pMLR), 5% mass loss temperature ( $T_{5\%}$ ), 50% mass loss temperature ( $T_{50\%}$ ) and % residue values determined from these curves are given in Table 3.20.

Figure 3.36 and Table 3.20 simply show that CNTs especially contribute by decreasing the peak mass loss rates. Compared to the nanoclays, improvements in the degradation temperatures ( $T_{5\%}$  and  $T_{50\%}$ ) and char residue by CNTs are not significant. This could be due to the lower ability of physical barrier formation as discussed above.

Specimens	T <sub>5%</sub> <sup>a</sup> (°C)	T <sub>50%</sub> <sup>b</sup> (°C)	pMLR <sup>c</sup> (%.s <sup>-1</sup> )	Char <sup>d</sup> (wt%)
PS	379	416	0.5	0.0
PS-CNT	338	418	0.30	1.0
PS-BE	355	391	0.34	2.8
PS-BE-CNT	365	399	0.34	3.7
PS-BE-AO	351	394	0.34	4.0
PS-BE-AO-CNT	360	403	0.24	5.0

Table 3.20 Thermal Degradation Parameters Obtained from TG and DTG Curves

<sup>a</sup>T<sub>5%</sub>: Thermal degradation temperature for 5% mass loss

 ${}^{b}T_{50\%}$ : Thermal degradation temperature for 50% mass loss

<sup>c</sup>pMLR: peak Mass Loss Rate

<sup>d</sup>Char: % Char yield at 600 °C



**Figure 3.36 (a)** Thermogravimetric (TG) and **(b)** Differential Thermogravimetric (DTG) Curves of Specimens

# (v) Mechanical Behavior

In order to investigate effects of carbon nanotubes and conventional flame retardant system BE and AO on the mechanical performance of PS, tensile tests were conducted. Mechanical properties obtained from these tests are tabulated in Table 3.21, while their typical stress-strain curves and typical fracture surfaces under SEM are given in Figure 3.37 and 3.38, respectively.

It is seen in Figure 3.37 and Table 3.21 that elastic modulus of all specimens increase with the incorporation of CNT, which was expected as the result of very high modulus (~1TPa) nanotube structures. Consequently, % ductility of the specimens decreased with the stiffening effects of CNTs.

Unfortunately, tensile strength of all specimens decreased with the addition of CNTs. This should be basically due to the insufficient un-bundling and poor dispersion state of CNTs leading to stress concentrations and consequently lowered strength values.

Figure 3.38 also shows that unlike nanoclays, CNTs have no influences on the morphology of the BE domains, thus there was no additional contribution of BE domains as discussed in the previous section with nanoclays.

Specimens	Young's	Tensile	Elongation at
	Modulus	Strength	Break
	(GPa)	(MPa)	(%)
PS	2.21±0.34	49±0.6	2.6±0.17
PS-CNT	2.60±0.21	44±2.3	2.2±0.18
PS-BE	3.20±0.07	49±2.7	1.8±0.51
PS-BE-CNT	3.46±0.06	42±3.2	1.2±0.48
PS-BE-AO	3.29±0.07	52±4.3	1.5±0.07
PS-BE-AO-CNT	3.40±0.06	41±1.2	1.6±0.28

 Table 3.21 Tensile Mechanical Properties of the Specimens



Figure 3.37 Tensile Stress-Strain Curves of the Specimens

In this fourth part of the thesis, use of a preliminary "solvent screening" procedure indicated that THF (tetrahydrofuran) can be used as the most efficient solvent for homogenous CNT dispersion in "solution mixing" method. MLC tests revealed that addition of CNTs resulted in only 13% suppression in PHRR values. Further 11% suppressions were obtained via the use of CNTs in combination with conventional flame retardants BE and BE-AO system. However, these improvements were not as effective as those obtained via nanoclay addition. The reason behind this was attributed to the insufficient char barrier formation capability of CNTs. Since nanoclays are 2D nano-additives, they have effective barrier formation compared to the 1D geometry of carbon nanotubes. TGA analysis also revealed that contribution of CNTs in tensile tests resulted in higher elastic modulus but lower tensile strength values, which might be due to insufficient debundling and poor dispersion state of nanotubes leading to stress concentration points.


Figure 3.38 SEM Fractographs of the Tensile Test Specimens (a) PS, (b) PS-CNT, (c) PS-BE, (d) PS-BE-CNT, (e) PS-BE-AO and (f) PS-BE-AO-CNT

# 3.5 Effects of PS-Nanoclay Mixing Method

As an additional purpose, effects of PS-Nanoclay mixing method on the flame retardancy performance of PS were investigated. For this purpose, PS-NC nanocomposites were produced by "solution mixing" and "in-situ polymerization" methods for two specimens, one of them containing only NC and the other one NC with conventional flame retardant BE-AO system. Designations and compositions of these specimens are given in Table 3.22.

Specimens	PS	NC	BE	AO	Mixing Method
PS-NC	95	5	-	-	Solution
i-PS-NC	95	5	-	-	In-Situ
PS-BE-AO-NC	72	5	20	3	Solution
i-PS-BE-AO-NC	72	5	20	3	In-situ

Table 3.22 Designations and Compositions (wt%) of the Specimens

**PS:** Polystyrene **NC:** Nanoclay

**BE:** Brominated Epoxy (tribromophenol end-capped epoxy oligomer) **AO:** Antimony Trioxide

### (i) Nanocomposite Formation

Nanocomposite formation for the specimens produced by "solution mixing" method was discussed in the previous Sections 3.1 and 3.3 in detail. In this section, for the specimen produced by "in-situ polymerization" method, only XRD analysis was conducted to investigate intercalation state of the clay layers.

Figure 3.39 shows that the first sharp peak for i-PS-NC specimen occurs at  $2\theta=2.53^{\circ}$ , which corresponds to an interlayer spacing of 3.5 nm. It was 3.1 nm for PS-NC specimen prepared via solution mixing (Figure 3.1). Figure 3.39 also indicates that there is no significant change in the XRD patterns of i-PS-BE-AO-NC specimen, i.e.

*d*-spacing is again 3.5 nm, which was 2.9 nm for the PS-BE-AO-NC specimen (Figure 3.18).

Therefore, it can be concluded that compared to "solution mixing" method, use of "in-situ polymerization" method resulted in slightly higher level of intercalation.



Figure 3.39 XRD Patterns of the Nanoclay and Nanocomposite Specimens Produced by "in-situ polymerization" Method (Stars (\*) designate second and third order reflections)

### (ii) LOI and UL-94 Flammability Tests

LOI and UL-94 tests were done to samples in order to investigate effects of PS-NC mixing method on the flammability of PS based nanocomposites. Results of both LOI and UL-94 tests are summarized in Table 3.23. Figure 3.40 shows the appearances of the burnt specimens after LOI tests, whereas Figure 3.41 shows SEM micrographs of the surface char layers of the LOI specimens.

Specimens	LOI $(O_2\%)^a$	UL-94 Rating <sup>b</sup>
PS-NC	19.0 ±0.2	Fail
i-PS-NC	19.3 ±0.2	Fail
PS-BE-AO-NC	25.5 ±0.2	Fail
i-PS-BE-AO-NC	$26.0\pm0.2$	Fail

 Table 3.23 Results of LOI and UL-94 Flammability Tests

 <sup>a</sup> Oxygen level required for sustained flaming combustion
 <sup>b</sup> Materials flammability classifications for stringent vertical orientation; Fail (flame extinguishing t < 30 s), V-2</li> (flaming drips, material self-extinguishes at 10<t<30 s), V-1 (material self-extinguishes at 10<t<30 s, without dripping), V-0 (material selfextinguishes at t>10 s)

It is seen from Table 3.23 that there is no significant change in UL-94 rating and LOI values with the alteration of mixing method from "solution" to "in-situ" for both specimens.



Figure 3.40 Appearances of the Specimens after LOI Test

Figure 3.40 shows that there is no significant difference in the macro-scale char structure of each mixing method, either. However, micro-scale SEM images in Figure 3.41 indicates that "in-situ" specimens have more porous char morphology, which might be the reason of their poor MLC performance as discussed below.



Figure 3.41 SEM Micrographs of the Surface Char Layers of LOI Specimens (a) PS-NC, (b) i-PS-NC, (c) PS-BE-AO-NC and (d) i-PS-BE-AO-NC

# (iii) Mass Loss Cone Calorimetry

Fire behavior of samples was analyzed with Mass Loss Cone Calorimeter. Then, (a) Heat Relase Rate (HRR) vs Time, (b) Total Heat Evolved (THE) vs Time, and (c) Mass Loss Rate (MLR) vs Time graphs of samples subjected to an external heat flux of 35  $kW/m^2$  are given in Figure 3.42. Important parameters derived from obtained data are tabulated in Table 3.24.

Figure 3.42 and Table 3.24 reveal that compared to "solution mixing" specimens almost all MLC fire parameters are poorer for "in-situ polymerization" specimens. These deficiencies could be due to the more porous char formation and the possibility of residual monomers or oligomers left after in-situ polymerization leading to earlier degradation.

Due to the poor fire performance of the "in-situ polymerization" specimens, thermogravimetric analysis and mechanical tests were not conducted.



Figure 3.42 (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens







Figure 3.42 (cont'd) (a) Heat Release Rate, (b) Total Heat Evolved and (c) Mass Loss Rate curves of the specimens

Specimens	THE <sup>a</sup> (MJ/m <sup>2</sup> )	PHRR <sup>b</sup> (kW/m <sup>2</sup> )	TTI <sup>¢</sup> (s)	TBT <sup>d</sup> (s)	TTPHR <sup>e</sup> (s)	FGI <sup>f</sup> (kW/m <sup>2</sup> .s)	FIGRA <sup>8</sup> (kW/m <sup>2</sup> .s)	THE/TML <sup>h</sup> (MJ/m <sup>2</sup> .g)	Char <sup>i</sup> (wt%)
PS-NC	47.3	449	45	320	108	10	4.2	2.5	9.7
i-PS-NC	56.5	635	30	338	81	21.2	7.8	3.2	8.1
PS-BE-AO-NC	18.4	180	49	194	124	3.7	1.4	0.8	7.9
i-PS-BE-AO-NC	16.1	213	42	164	89	5.1	2.4	0.8	6.8

Table 3.24 Parameters Determined from Mass Loss Cone Calorimeter

<sup>a</sup> Total Heat Evolved: Total heat released at the end of the fire scenario <sup>b</sup> Peak Heat Release Rate: Contribution of a material to fire flashover severity

°Time To Ignition: Time interval between sparking and ignition

<sup>d</sup>Total Burning Time: Time between ignition and extinguishment of the flame <sup>o</sup>Time To Peak Heat Release: Time at which heat release rate reaches its maximum values

<sup>f</sup>Fire Growth Index: Contribution of a material to fire propagation, where FGI= PHRR/TTI

<sup>b</sup>Fire Growth Rate Index: Contribution of a material to fire propagation rate, where FIGRA= PHRR/TTPH <sup>b</sup>Total Heat Evolved/Total Mass Loss: Parameter to evaluate whether flame retarding action is in the gas or condensed phase

Char Yield: Amount of solid fire residue measured at flame-out

# **CHAPTER 4**

# CONCLUSIONS

Main conclusions drawn from five different parts of this thesis investigating the effects of nanoadditives and conventional flame retardants on the flammability behavior of PS are summarized below, while overall results are concluded in Table 4.1.

### (i) Effects of Nanoclays

Incorporation of organomodified clays into PS lead to the formation of nanocomposite structure. XRD and TEM studies revealed that nanoclay layers were mainly intercalated with PS matrix, having certain level of exfoliation. Nanoclays improved flame retardancy of PS significantly, for instance the suppression in PHRR was as much as 37%. The dominant flame retardancy mechanism of nanoclays was *condensed phase action* via formation of strong char barrier layers inhibiting mass and heat transfer. Nanoclays also resulted in improvements in the thermal degradation temperatures and mechanical properties.

### (ii) Effects of Nanoclays with TPP and TPP-MCA

Combined use of nanoclays with conventional phosphorus based flame retardant systems (TPP-MCA) resulted in more efficient flame retardancy. XRD and TEM analyses revealed that further level of intercalation/exfoliation of silicate layers were obtained via intercalation of TPP through clay galleries. MLC flammability tests indicated that addition of TPP and TPP-MCA into PS resulted in decreases of PHRR

by 19% and 26%, respectively. Incorporation of nanoclays into those systems resulted in further PHRR suppressions of 24% and 28%, respectively. These additional contributions were due to the synergistic combination of "*condensed phase mechanism*" of NC and "*gas phase mechanism*" of TPP and TPP-MCA. Volatilization of TPP and evolution of radical degradation products were delayed and/or entrapped by the strong char structure with nanoclay layers, thus effectiveness of radical entrapment by TPP was increased. TGA analysis further supported that nanoclays contribute thermal stabilization of the system via suppressed volatilization of TPP by clay galleries. Tensile tests revealed that decreases in mechanical properties of PS with TPP and MCA could be overcome by the intercalated/exfoliated structure of nanoclays.

### (iii) Effects of Nanoclays with BE and BE-AO

XRD and TEM analysis indicated that nanocomposites were formed with the intercalated/exfoliated structure again, but this time, silicate layer segregation at the PS/BE domain boundaries and exfoliation in BE domains were also observed. MLC flammability tests indicated that addition of conventional flame retardants BE and BE-AO resulted in decreases of PHRR by 35% and 64%, respectively. These significant improvements were obtained as a result of "gas phase" radical scavenging actions of HBr and SbBr<sub>3</sub>. Further synergistic improvements were obtained with the addition of nanoclays, for example PHRR of PS-BE and PS-BE-AO specimens were decreased by 42% and 27%, respectively. The mechanism behind this was attributed to "nanoconfinement" and tortuous pathway effects of nanoclays forming a physical barrier rather than carbonaceous char formation. TGA analysis further supported that contribution of nanoclays in thermal stability of the flame retarded specimens were the formation of physical barriers hindering diffusion of volatiles and decreasing the mass loss rates. Tensile tests revealed that addition of nanoclays increases modulus and strength values of the specimens further due to the efficient load transfer and decreased chain mobility mechanisms of the nanofillers, and improved morphology of the BE domains by silicate layers.

#### (iv) Effects of Carbon Nanotubes with BE and BE-AO

Use of a preliminary "solvent screening" procedure indicated that THF (tetrahydrofuran) can be used as the most efficient solvent for homogenous CNT dispersion in "solution mixing" method. MLC tests revealed that addition of CNTs resulted in only 13% suppression in PHRR values. Further 11% suppressions were obtained via the use of CNTs in combination with conventional flame retardants BE and BE-AO system. However; these improvements were not as effective as those obtained via nanoclay addition. The reason behind this was attributed to the insufficient char barrier formation capability of CNTs. Since nanoclays are 2D nano-additives, they have effective barrier formation compared to the 1D geometry of carbon nanotubes. TGA analysis also revealed that contribution of CNTs in tensile tests resulted in higher elastic modulus but lower tensile strength values, which might be due to insufficient debundling and poor dispersion state of nanotubes leading to stress concentration points.

### (v) Effects of PS-Nanoclay Mixing Method

XRD analysis showed that compared to the "solution mixing" method, use of "in-situ polymerization" method resulted in slightly higher level of intercalation. Significant changes were not obtained neither in UL-94 rating nor in LOI values with the alteration of mixing method from "solution" to "in-situ" for both specimens. MLC tests revealed that compared to the "solution mixing" specimens almost all MLC fire parameters are poorer for "in-situ polymerization" specimens. These deficiencies could be due to more porous char formation and the possibility of residual monomers or oligomers left after in-situ polymerization leading to earlier degradation.

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•	IOI	UL-94	THE	PHRR	ITT	FIGRA	THE/TML	Char	$T_{5\%}$	$\mathrm{T}_{50\%}$	pMLR
opecimens	$(\% O_2)$	Rating	$(MJ/m^2)$	$(kW/m^2)$	(s)	$(kW/m^2s)$	(MJ/m <sup>2</sup> g)	(%)	(O°)	(0°C)	(%.S <sup>-1</sup> )
PS	$18.0 \pm 0.2$	Fail	59.9	672	63	6.9	3.0	0	379	416	0.50
PS-NC1	$18.3 \pm 0.2$	Fail	55.0	576	41	6.5	2.8	3.6	I	ı	ı
PS-NC3	$18.6\pm0.2$	Fail	49.2	472	45	4.7	2.6	6.2	I	I	I
PS-NC5	$19.0 \pm 0.2$	Fail	47.3	449	45	4.2	2.5	7.9	368	443	0.32
PS-NC7	$19.5 \pm 0.2$	Fail	47.0	422	37	4.1	2.5	9.3	ı	ı	I
ddT-Sd	$22.0 \pm 0.2$	<b>V</b> 2	45.2	547	27	6.2	2.5	0	240	412	0.34
<b>PS-TPP-NC</b>	$22.4 \pm 0.2$	Fail	37.2	414	46	4.0	2.1	11.8	264	435	0.25
<b>PS-TPP-MCA</b>	$23.0 \pm 0.2$	<b>V</b> 2	46.1	494	32	5.7	2.4	3.5	258	408	0.34
PS-TPP-MCA-NC	$23.3 \pm 0.2$	Fail	37.7	309	46	2.4	1.9	9.7	267	425	0.21
PS-BE	<b>21.0</b> ±0.2	<b>V</b> 2	36.6	436	50	4.5	1.6	3.3	355	391	0.34
<b>PS-BE-NC</b>	$24.0 \pm 0.2$	Fail	28.8	255	55	2.1	1.3	7.5	339	387	0.25
<b>PS-BE-AO</b>	$24.0 \pm 0.2$	<b>V</b> 2	22.3	245	64	2.1	1.0	3.7	351	394	0.34
<b>PS-BE-AO-NC</b>	$25.5 \pm 0.2$	Fail	18.4	180	49	1.4	0.8	7.9	345	400	0.21
PS-CNT	19.0±0.2	Fail	56.4	584	40	6.3	2.9	4.2	338	418	0.30
<b>PS-BE-CNT</b>	$21.0 \pm 0.2$	Fail	33.2	389	47	4.5	1.7	6.3	365	399	0.34
<b>PS-BE-AO-CNT</b>	$23.5 \pm 0.2$	Fail	18.8	219	42	2.5	1	6.8	360	403	0.24
i-PS-NC	$19.3 \pm 0.2$	Fail	56.5	635	30	7.8	3.2	8.1	ı	ı	I
i-PS-BE-AO-NC	$26.0 \pm 0.2$	Fail	16.1	213	42	2.4	0.8	6.8	ı	I	ı

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# APPENDIX A SOLVENT SCREENING

### Tetrahydrofuran (THF):

It was observed that homogenous dispersion of CNTs was very well achieved in the solution of tetrahydrofuran (Figure 3.28). Images were taken at every 15 minutes in the first hour, and at every hour in the following 6 hours since no change in dispersion was observed in short time intervals. At the end of 24 hours distribution was still in the same homogeneity and it remained unchanged in the following days.



**Figure A.1** CNT Dispersion in THF 146

# N,N Dimethylformamide (DMF) :

The most homogenous dispersion was observed in the solution of DMF. Images were taken at every 15 minutes in the first hour, and at every hour in the following 6 hours (Figure 3.29). No precipitation was observed and the homogenous dispersion did not change in the following 4 days.



Figure A.2 CNT Dispersion in DMF

### **Chloroform:**

In the solution prepared with Chloroform, it was observed that some CNTs were dispersed well in the solvent but some bundles suspended at the surface (Figure 3.30). Images of these bundles were taken in every five minutes during the first hour. At the end of one hour no change was observed, and in the following days that dispersion status remained unchanged.



Figure A.3 CNT Dispersion in Chloroform

### **Dichloromethane (DCM):**

CNTs were in semi-dispersed state at the beginning but then bundling restarted and the suspended nanotube particles coalesced (Figure 3.31). Images of this rapidly changing structure were taken in every five minutes during the first hour. At the end of one hour both precipitated nanotube bundles and homogenously dispersed nanotubes were observed. That structure remained unchanged during the following days.





### Acetone:

It was observed that CNT bundles were not dispersed well in acetone; they rather precipitated (Figure 3.32). This rapid precipitation was followed up by imaging in every 5 minutes. Since no change was observed in the dispersion between 30-60 minutes, images taken in this interval are not given in the figure. In the following days, CNT bundles suspended in the solvent continued to precipitate and the solvent became more transparent.





## Ethanol (EtOH):

It was observed that CNTs were not dispersed well in ethanol either. Bundles were precipitated as was the case in acetone (Figure 3.33). In the following days suspended CNT bundles continued to precipitate and the solvent became more transparent.





### **Toluene:**

Poor dispersion was observed in the solution of CNTs with toluene. Re-bundling was detected at earlier stages (Figure 3.34). As the changes occur in short time intervals, images were taken in every 5 minutes of the first half an hour. At the end of the first hour, it was observed that CNT bundles remained suspended at the surface. At the end of 3 days it was observed that all CNTs in the solution were precipitated.



**Figure A.7** CNT Dispersion in Toluene 152

### Water:

It was observed that non-polar CNTs having hydrophobic surfaces could not disperse well in water having polar nature (Figure 3.35). Nanotubes which were temporarily dispersed in the early stages started to precipitate with time and at the end of the fourth hour no suspended nanotubes remained. In the following days, CNTs continued to precipitate and separated completely from water.



