Chapter 1
Advances in Flame Retardant of Different Types of Nanocomposites

State of Art New Challenges Opportunities

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Abstract The present chapter deals with a brief account on various types topics in flame retardant of polymer nanocomposites. This chapter discussed with different topics such as flame retardancy of polymer nanocomposite, recent developments in different techniques used for the flame retardancy, recent development of phosphorus flame retardants in thermoplastic blends and nanocomposites, non-halogen flame retardants in epoxy-based composites and nanocomposites, flame retardant/resistant based nanocomposites in textile, flame retardants in bitumens and nanocomposites, fire retardant for phase change material, flame retardant finishing for textiles, flame retardant of cellulosic materials and their composites.

1.1 Flame Retardancy of Polymer Nanocomposite

From the application view polymers are very flammable materials, for preventing this flammability, scientists need to improve polymer fire retardancies, and this is a major challenging. Developing the effective environmentally friendly flame retardants is challenging. Because of this materials are very hazardous; they are widely used owing to their effectiveness and low cost. Flame retardant nanocomposites with conventional fire retardants to develop more-efficient materials showing improved mechanical properties. There are numerous nanofiller/conventional-fire-retardant already prepared. From some of the work related to CNTs shows that improve the flammable properties of nanocomposites also improved the mechanical properties such as electrical, thermal properties. Nanofiller-based flame retardants show high flame-retardant efficiencies. Nanofiller can reduce the peak heat release rates (PHRRs) of polymers and thus reduce the speed at which

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flames spread throughout them. Some of the works revealed the flame-retardancy mechanism of CNTs [1–9], shows that CNTs are most well-established material, they are prepared their fire-retardancy mechanism and some of their disadvantages. CNT-containing nanocomposites absorb more radiation than polymers during fires; therefore, nanocomposite temperatures increase faster than polymer ones.

The nanotube-network layer emits radiation from the material surface and acts as a barrier against the decomposed gas supplied from the bulk polymer and against oxygen diffusing from the air into the material, which accelerates polymer decomposition. The nanotube-network layer must be smooth, crack-free, and opening-free so that it may act as an effective gas barrier. Barus et al. investigated the thermal properties of three types of CNTs and found that the dispersivity of the CNTs themselves affects the thermal degradation of nanocomposites. The CNT load is also important in determining fire retardancy, and in fact, the optimal CNT load reduces PHRR. Dittrich et al. showed that graphene were the most effective carbon-based fire retardants. Montmorillonite is the most commonly used clay because it is naturally ubiquitous, can be obtained at high purity and low cost, and exhibits very rich intercalation chemistry, meaning that it can be easily organically modified. The fire-retardancy mechanisms for clay- and carbon-based nanocomposites are almost identical. One fire-retardancy mechanism is the reduction in PHRR due to the formation of a protective surface barrier/insulation layer consisting of clay platelets accumulated with a small amount of carbonaceous char [10, 11]. The key factor determining clay- and carbon-based-nanocomposite flame retardancy is the formation of a surface network layer. The barrier/insulation effect depends on the external heat intensity.

The flame-retardancy effectiveness of clay-based nanocomposites depends on the kind of matrix [12–26]. IT of polymers such as PP, polyethylene (PE), PS, ethylene vinyl acetate (EVA), and PMMA usually decreases when nanofiller is added, because the clay itself is possibly catalytic. Most researchers have concluded that polymer/clay nanocomposites should at least exhibit PHRR reduction if nanomorphology is achieved through exfoliation and intercalation. The difference in nanomorphologies does not significantly affect polymer/clay nanocomposite flame retardancy. Nanocomposites can be obtained by organomodifying clays, and is easily achieved through melt-compounding. However, organomodified clay surfaces degrade at high temperatures, rendering organomodification problematic in melt-compounding and decreasing nanocomposite flame retardancy. Metal hydroxides are widely used in fire retardants because they are safe and inexpensive and because they reduce the amount of smoke produced in fires. However, high loads (>60 wt%) are mandatory to satisfy the V-0 classification, which is required for most fire retardants, and such high loads degrade mechanical properties, resulting in inflexible materials. The main purpose of combining nanofillers with metal hydroxides is to reduce the metal-hydroxide load without deteriorating flame retardancy. Recently reported that calcium carbonate ($CaCO_3$) nanoparticles could improve both thermal and thermo-oxidative stability [27]. Applying a flame-retardant coating is one of the most effective and economical methods of protecting substrates from fire damage. Polymer bubbling causes the nanofillers

inside materials to migrate to the surface, where they then act as a barrier against heat and mass transport and can reduce the heat intensity during combustion. It is expected that nanofiller-based coatings more efficiently reduce material flammability than materials containing nanofillers.

1.2 Recent Developments in Different Techniques Used for the Flame Retardancy

The most common approach to improve the flame retardancy performance of materials is to add flame retardants, such as halogen-based agents, phosphorous-based compounds, metal hydroxides, intumescent agents, boron and nitrogen-based flame retardants, etc. [28]. Simultaneously, smoke suppressants are developed because the majority of human deaths during fire incidents are related to the inhalation of smoke and toxic combustion gases, with carbon monoxide being particularly significant. Some approaches that were adopted to tackle this problem include the use of fillers or additives, surface treatments, and chemical or physical modification. Cone calorimeter is a modern device used to study the fire behavior of small samples of various materials in condensed phase. It is widely used in the field of fire safety engineering [29]. The cone calorimeter test has been developed for material fire evaluations, computer modeling, design purposes, and development and research to help make real world fire predictions. The test performance uses the bench-scale system to measure fire characteristics associated with heat and smoke output. The measurements can be used directly by researchers or can be used as data input into correlation or mathematical models used to predict fire development. The cone calorimeter became the premier dynamic research tool based on the principle of oxygen consumption calorimetry. The UL 94 V test is widely used both in industry and academic research centers, and is intended to meet industrial requirements as well as to hierarchically classify the polymeric materials [30].

UL 94 flame rating groups materials into categories based on their flammability. UL94 covers two types of testing: vertical burn and horizontal burn. Vertical burn test includes Vertical Testing (V-0, V-1, V-2), Vertical Testing (5VA, 5VB) and Vertical Testing of Thin Materials (VTM-0, VTM-1, VTM-2). Specimens molded from the plastic material are oriented in either a horizontal or vertical position depending on the specifications of the relevant test method, and they are subjected to a defined flame ignition source for a specified period of time [31]. Pyrolysis of polymeric materials is a complex process involving simultaneous combinations of heat, energy and mass transfer and diffusion, fluid dynamics and degradation chemistry [32]. The study on polymer combustion and fire retardancy is a complex multidisciplinary topic, encompassing physical and chemical phenomena occurring in the gas and condensed phase. Thus, aspects involved are physical chemistry of flames and thermal degradation of polymers, respectively [33]. Combustion and flammability of polymeric materials are important topics of practical interest

directly related to fire safety [34]. Polymer combustion is a complex process involving a multitude of steps and is best described in qualitative terms. In general, four major steps comprise polymer combustion: ignition, pyrolysis, combustion and feedback [35]. Depending on the flammability limit of the material, ignition is normally caused by the presence of an external heat source such as a flame or a spark or, if the temperature is high enough, occurs spontaneously.

The combustion of polymers involves a variety of processes (both physical and chemical) occurring in several phases. Thus, polymer melting and degradation, heat transfer in both solid and liquid phases and diffusion of the breakdown products through the degrading polymer into the gas phase accompany the various combustion reactions which occur. Polymers with aliphatic backbones, or those that is largely aliphatic and oxygenated, have a tendency toward low smoke generation, while polyenic polymers and those with pendant aromatic groups generally produce more smoke [36]. The relative distribution of pyrolysis products from an individual polymer is dependent on the pyrolysis temperature, the heating rate and the pyrolysis atmosphere. The amount of smoke generated in a nitrogen atmosphere passes through maxima with increasing temperature in several of the polyesters whereas from others the smoke increases steadily with temperature. The structure of a polymer influences both flammability and smoke formation [37].

1.3 Recent Development of Phosphorus Flame Retardants in Thermoplastic Blends and Nanocomposites

Use of thermoplastics and thermosetting polymers on a large scale for applications in buildings, transportation, electrical engineering and electronics, a large variety of flame retardant products have been developed over the past 40 years. Phosphorus-containing flame retardants cover a wide range of inorganic and organic compounds and include both reactive products which are chemically bound into the polymer material as well as additive products which are integrated into the material by physical mixing only. They have a broad range of applications, and a good fire safety performance. The most important phosphorus-containing flame retardants are phosphate esters, phosphonates and phosphinates. Phosphorus-based flame-retardants can be characterized by their chemical structure and how they are incorporated into the epoxy molding compounds. They are usually divided into two categories: (1) inorganic derivatives: for example, ammonium polyphosphate (APP) and red phosphorus; and (2) organic derivatives such as aromatic phosphates: for example, triphenyl phosphate; alkyl substituted triaryl phosphates such as cresyl diphenyl phosphate, isopropyl phenyldiphenyl phosphate, tert-butyl-phenyldiphenyl phosphate, tricresyl phosphate, trixylyl phosphate, and so on, and oligomeric phosphates such as resorcinol bis(diphenyl phosphate) (RDP).

Organic phosphorus compounds can be reacted directly into the polymer chain. Investigations have reported success in introducing phosphorus-containing functional groups into the backbones of epoxy. One of the advantages of organic phosphorus is that its reaction product with ambient humidity tends to be non-corrosive phosphorus compounds. This is not always the case with inorganic phosphorus. Red phosphorus has been reported to be most efficient as a flame retardant in oxygen containing polymers such as polycarbonates, polyethylene terephatalate (PET), polyamide and phenolic resins. Red phosphorus has been used as a flame retardant in polymeric material for almost 30 years [38]. Flame retardancy takes place due to formation of phosphorus-oxygen bonds that reduces the ester linkages into cross linking aromatic structures with lesser volatility. In addition the red phosphorus creates a heat shield on the polymer surface that results in flame retardant properties. Some drawbacks with the use of red phosphorus are the red color that could lead to discoloration of polymers and the formation of toxic phosphine gas during combustion and long term storage. Phosphorus flame retardants are widely used as adhesives and sealants, for building and construction, as lubricating fluids and greases, in paints and coatings as well as in thermoplastic materials. Key applications of PFR are in EPDM (ethylene propylene diene monomer) rubbers, PVC products, polystyrene, polyurethane foam, epoxy and phenolic resins.

Phosphorus-containing flame retardants (PFRs) have been used as effective flame retardants; the range of PFRs is extremely wide and diverse, since the element exists in several oxidation states. PFRs are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles [39, 40]. Phosphate esters are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol- and bisphenol A-bis-(diphenyl) phosphate). Many of the of phosphorus flame retardants are additives, and not chemically bonded to the final products, which may result in an easy release to the environment from furniture, electronic equipment, carpets, and also into the atmosphere from different sources such as buildings and vehicles [41].

The red phosphorus-based flame-retardant was coated with a primary coat of aluminum hydroxide and a secondary coat of phenol resin. The content of red phosphorus in the coated flame-retardant is preferably 60–95 % by weight. When the red phosphorus content is less than 60 % by weight, it becomes necessary to incorporate a large amount of the flame-retardant into the epoxy resin composition and the addition of a large amount of the flame-retardant decreases the moisture resistance of the encapsulant. When the content of red phosphorus exceeds 95 % by weight based on the weight of the flame-retardant, there is a problem in respect to the stability of the red phosphorus.

1.4 Non-halogen Flame Retardants in Epoxy-Based Composites and Nanocomposites

Epoxy resins are one of well-known thermosetting polymers and used for coating and adhesive applications, which can also be reinforced with fibers or additives for obtaining high strengths and good chemical resistances [28, 42–44]. It is reported that almost 65 % of glass-fiber reinforced composites have been consumed at the sectors of transport and construction. However, they are intrinsically combustible and needed flame retarded. The majority of flame retardants for epoxy resins are currently halogen-based flame retardants because their flame retardancy is very effective at gas phase and cost-effective at an industrial scale. Tetrabromobisphenol A (TBBA) is the leading halogenated flame retardant in epoxy resins system for electrical and electronic devices since it has good thermal stability and flammability as well as high Tg when it is formulated with curing agents.

In epoxy resins formulation, phosphorus-containing flame retardants can be applied as an additive, which is relatively easy to manufacturing process. However, it has some technical drawbacks, such as particle dispersion and deterioration of the physical properties of epoxy laminates when its loading is too high [45]. Thus, molecularly reactive phosphorus-containing flame retardants have been used for advanced epoxy laminates, which can give better performance on flame retardancy and material properties.

Thus, a variety of phosphorus-based flame retardants have been developed and studied for their flammability as well as rheological and mechanical properties. Recently, the two review papers extensively focused on the flame retardancy of non-halogen flame retardants for epoxy resins system [46].

Several research groups have reported that organophosphates or organophosphine oxides can be chemically pre-reacted to epoxy resins, which also imparts good flame retardancy to the cured epoxy resins [47–52]. Cheng et al. reported that di-epoxide containing phenyl phosphate [V] could be cured with DDS having 29–31 in LOI. However, the cured epoxy resin had a lower thermal stability and higher % P content needed to obtain the better flame retardancy. Moreover, the high level of the % phosphorus content may be caused to lower the glass transition temperature (Tg) of the cured epoxy resins. Thus, the % P content in a finial epoxy formulation has to be reduced while other materials properties remain as same. Ren et al. showed that the phenyl phosphine oxide with bis-phenoxyl (VI) was synthesized with the epoxy resins and then cured with DDS in which 34 of LOI and good thermal stability (~357 °C at 5 % weight loss in N_2) were obtained.

DEGBA is a good cross-linked and relatively produces higher residues because of the bisphenol groups in its backbone. It can be also synthesized with a variety of phosphorus-based flame retardants. Lin et al. reported that the amount of % P was reduced by replacing the bis-phenoxyl with bis-diphenoxyl group in the

DEGBA epoxy resin, where only 1.5 % P could be contributed to achieving above 30 in LOI, high Tg (180 °C) and higher residues remained (26 % in N_2). In the report, the advanced epoxy resins with the phosphorus-based flame retardant [VII] had the highest number of LOI obtained among the epoxy resins with other flame retardants, such as TBBA, DHBP (dihydroxybiphenyl) and PPA (phenyl phosphonic acid).

The mobility of an entangled polymer chain is frequently determined by a glass transition temperature, which is an indication of a relaxation statue of the entangled polymer chains. Unlike thermoplastic polymers, epoxy monomers can be chemically cross-liked at elevated temperatures by either itself or the aid of curing agents. Thus, a Tg of a cured epoxy resins can depend on the type of epoxy resins, curing agents and curing temperatures as well as flame retardants. It is important for epoxy laminates to obtain higher Tg at a low level of % P content, which may be a key factor to prevent a failure of the PCT (pressure cooker test) or soldering bath at electronic applications.

1.5 Flame Retardant/Resistant Based Nanocomposites in Textile

The nanomaterials strategy is one of several principles for improving the burning behavior of textiles. Textile requires effective flame retardancy properties with a minimal environmental impact, since these structures are often washed and flame retardant additives of coating can leach out into the environment [53, 54]. Flame retardant additives may have a mode of action in gas phase to extinguish the flame by radical inhibition or dilution, that leading to the decrease of the flame temperature or to reduce the availability of flammable gases and oxygen; and/or in condensed phase, in the vicinity of the flame to perturb the thermal degradation of the substrate by dehydration and char formation. Flame-retardant materials are a major business for the chemical industry and can be found practically everywhere in modern society. However, many additives have detrimental effects on the environment and human health and thus should be limited in use.

The fire behavior of a fabric largely depends on the chemical nature of the fibers that compose it. Also the same major flame retardant products for polymeric materials in general are found in textiles. Furthermore, the quantities of smoke released by fabrics from fiber blends are very difficult to predict. Indeed both polyester/wool and polyester/cotton blends release a much greater amount of smoke than the fibers alone. Finally, the presence of fire retardant in a material usually leads to a larger amount of smoke either by inhibition of the oxidation reaction generating incomplete combustion (fire retardant agent acting in the gas phase such as those based on halogen) or by reduction of the heat flux that the flaming combustion turns at time into smoldering.

1.6 Flame Retardants in Bitumens and Nanocomposites

Much attention has been paid to halogen-free flame retardants in the past two decades [55, 56]. Based on the exits problems of conventional flame retardants modified bitumen, it is of much significance to develop new types of environmentally friendly flame retardant bitumen. Some new environmental friendly flame retardants bitumen has been developed at present, such as inorganic hydroxide flame retardant bitumen, intumescent flame retardant bitumen, nanometer flame retardant bitumen and so on. Combustion processes of bitumen and bitumen/magnesium hydroxide composite are both multistage, and the volatiles are different in each temperature interval. After adding MH into bitumen, the temperature rise of bitumen matrix is inhibited due to magnesium hydroxide thermal decomposition.

Now a kind of environmental friendly flame retardant, intumescent flame retardant (IFR) is developing at a rapid pace, whose main active components are phosphorus and nitrogen. It is halogen-free, efficient and smoke-suppressive flame retardant. IFR is mainly composed of acid source, carbon source and air source, which respectively act as dehydrant, carbonific and foamer. Generally, the acid source, carbon source and air source of IFR respectively are ammonium polyphosphate (APP), pentaerythritol (PE) and melamine (MA) [57–60]. Nanocomposite technology is the newest class of flame retardant materials. As tiny particle size, nanometer has many excellent performances such as tiny size effect, surface effect, and macroscopic quantum tunnel effect.

1.7 Fire Retardant for Phase Change Material

Phase change materials (PCM) are used in a wide range of applications including latent heat thermal energy storage in buildings [61]. One of the most suited PCM are paraffin, fatty acids and their esters because it has many desirable properties such as high latent heat of fusion, varied phase change temperature, negligible super cooling, and lower vapour pressure in the melt, chemically inert and stable, self-nucleating, no phase segregation and commercially available at acceptable cost. The first type, and the most common, is known as flame quencher. Halogenated alkanes have the ability to limit or extinguish nearby flame source. In the presents of fire, oxide and hydroxide free radical are formed and reacts to fuels the propagation of fire. When halogenated alkanes are present, they react with oxide and hydroxide free radical to give an inactive halogen free radical. Halogen free radical is less reactive than oxide and hydroxide radical therefore its presence retards the spread of fire [62].

The second type is called heat absorber. Materials such as magnesium hydroxide and aluminium hydroxide, which absorb heat from the surrounding and decompose endothermically preventing nearby material from heating up and hence

minimizing its combustion. The last type is known as synergist, and is of two types, one which is not a fire retardant but can work with other types of fire retardants to improve their fire retardancy. Antimony oxide is known as a synergist for halogenated alkanes. The second type (will be refer as synergist system) is where two or more fire retardants work together to improve overall fire retardancy of a material. Montmorillonite clay (MMT) can be used as a synergist for intumescent fire retardant and heat absorber [63, 64]. MMT has two opposing effects on the composite. One is barrier effect, MMT works by forming carbonaceous-silicate charred layer at the surface which protects the underlying material from heating up. The other is catalytic effect towards the degradation of polymer matrix which decreases thermal stability. Aluminium hydroxide and magnesium hydroxide had little effect in improving fire retardancy of the composite. Addition of heat absorber reduced dripping but a very small residue was obtained after burning.

1.8 Flame Retardant Finishing for Textiles

Inorganic compounds are suitable for use as flame retardants in textiles, due to their decomposition temperatures in the range 150–400 °C. Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, mostly in endothermic reactions. Due to their properties to reduce the content of combustible products and to modify the thermal conductibility of the material, they are used alone or in combination with other flame retardants to obtain the required fire retardant properties. Aluminium trihydroxide (Al(OH)3): is the most widely used flameretardant. It is inert mineral filler, a non-toxic, white, crystalline powder and is included in the inorganic flame retardants. At about 250 °C, this compound is decomposed to form aluminium oxide and water, thus obtaining a non-flammable protection on the surface of the treated material. The most important commercial flame retardants can be classified into three categories: flame retardants based on phosphorus (condensed phase mechanism) and halogens (gas phase mechanism), synergistic systems containing flame retardant enhancers (nitrogen-phosphorus and antimony-halogens) and flame retardants with physical effects (alumina, borate). Some of these treatments have serious drawbacks: for instance the use of halogens as flame retardants is restricted because of the toxicity of their combustion gases, whereas although inorganic salts can provide excellent flame retardant properties for cellulose, they have very poor laundering durability. Polyester fibers are very easily ignitable, especially when they are blended with cotton fibers. It burns strongly and may drip, carrying flames to other surfaces. In fact, the molten material can form drops act as a second source of ignition and cause more rapid development of the fire.

1.9 Flame Retardant of Cellulosic Materials and Their Composites

Cellulosic fabrics have low fire resistance. They are composed of carbon and hydrogen (fuels) and oxygen (supporter or combustion) and burn very easily. The burning process of cellulosic materials is an oxidation process. This process may be accompanied by a flame or glow; most organic fibres undergo a glowing action after the flame has been extinguished. The glow may cause much damage as the flaming itself, since it can completely consume a textile. Flaming and glowing are distinctly different processes, taking place at different temperatures. It is useful, however to define a number of terms before going into details of fire and flame retardant finishing of textile.

This term is applied to textiles, which are essentially unaffected fire. This means that they do not support fire (flame or glow) and that there is little or no chemical or physical change when the textile is exposed to flames. Few textiles fall in this category. Carbon, asbestos, basalt and glass fibres are the one in common use today [65–67].

In the development of better flame retardants it is helpful to know what chemical reaction occur when cellulose burns and how the reaction are affected when fabrics are treated with a flame retardant. The burning characteristics of cellulose depend to a considerable extent on the chemical and thermal properties of the anhydroglucose units, on the availability of oxygen, and on the nature of noncellulosic materials that may also be present. Fibre properties such as the ignition temperature, the rate and heat of combustion products, and moisture content also affect the burning characteristic of cellulose [68, 69]. Ignition is controlled by various factors such as heat transfer from the source of ignition to cotton, thermal decomposition of cotton and reactions of decomposition products with the environmental oxygen. Thermal decomposition of cotton release a large number of combustible gases which can sustain ignition at and above certain concentration levels with oxygen of the air. A burning fabric generating more heat requires less ignition energy to continue its burning.

Most commercial treatments for cellulose are based on phosphorus, and consequently the effect of the structure of phosphorus based materials on the mechanism and efficiency of flame retardancy has been widely studied. Acidic phosphates act via phosphorylation, presumably at the C-6 hydroxyl of the anhydroglucose unit [70]. Consequently, increases of esterification are likely to be more efficient in promoting flame retardancy.

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