Chapter 2
Flame Retardancy of Polymer Nanocomposite

Yoshihiko Arao

Abstract Nanofillers such as carbon nanotubes and clay are attractive materials, because addition of small amount of nanofillers can improve mechanical, thermal and electrical properties of plastics without changing processability. However, nanofillers themselves do not show excellent fire retardancy such as self-extinguish properties. Nanofillers should be combined with other fire retardants. Some combination showed positive synergy effect in fire retardancy, but some case showed negative synergy. It is important to know fire retardant mechanism of nanofiller to develop more efficient fire-retardant nanocomposites. In this chapter, we'll show the fire retardant mechanism of nanofillers. Then, effective combination of nanofiller and conventional fire retardant is introduced reviewing lots of papers.

2.1 Introduction

The use of polymers is increasing every year. The average annual increase in plastic use from 1950 to 2009 was ~9 % [1] because of their remarkable combination of properties, low weights, and ease of processing. However, plastics are highly flammable increasing their risk as fire hazards when used in practical applications. Consequently, improving polymer fire retardancies is a major challenge for extending polymer use to most applications.

The development of fire retardants is subject to regulations. Halogen-free, recyclable, environmentally friendly flame-retardant systems that do not release toxic gases have recently become preferable. For example, the waste electrical and electronic equipment (WEEE) and restriction of hazardous substances (RoHS) directives limit the use of bromine-based flame retardants. Polybrominated biphenyl

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(PBB) and polybrominated diphenyl ether (PBDE) were prohibited because, like dioxin, they are toxic to humans. Developing effective environmentally friendly flame retardants is challenging. Although bromine-based fire retardants have previously been recognized as hazardous, they are widely used owing to their effectiveness and low cost. However, bromine-based fire retardants are gradually being phased out owing to the WEEE and RoHS regulations.

It is expected to develop safe, eco-friendly fire retarded polymer nanocomposite to replace halogenated flame retardants. Nanocomposite research has progressed owing to contributions of numerous researchers, and the fire retardancy mechanisms of various nanocomposites are revealed. However, nanofillers themselves do not show excellent fire retardancy such as self-extinguish properties. Nanofillers should be combined with other fire retardants. There are infinitely many combinations of fire retardants, some of which may counteract the fire retardancy mechanisms. It is important to understand the fire retardancy mechanism of each material and choose effective combinations.

There are several excellent review papers on polymer fire retardancy. Morgan et al. show various applications and future trends for the fire retardancy of polymers [2]. Laoutid et al. and Dasari et al. summarized a vast amount of research on the fire retardancies of fundamental polymers and polymer nanocomposites [3, 4]. Morgan reviewed the flame retardancy of layered silicate nanocomposites, focusing on the effects of combining conventional polymers with nanofillers developed to 2006 [5]. A significant amount of research on combining flame retardant nanocomposites with conventional fire retardants to develop more-efficient materials showing improved mechanical properties has recently been reported. There are numerous nanofiller/conventional-fire-retardant combinations, so they should be summarized. In addition, some new technologies have been developed to improve flame retardancy. Thus, this chapter will show the flame retardancy mechanisms, especially those for nanocomposite/conventional-nanofiller combinations. Nanocoating technology (which is a versatile, cost-effective tool for improving flame retardancy) will also be introduced.

2.2 Nanocomposite-Based Fire Retardants

Polymer nanocomposites have recently attracted extensive attention in materials science because they often exhibit properties quite different from those of their counterpart polymer microcomposites whose matrices contain the same inorganic components. The surface areas of nanofillers are drastically increased so that polymer nanocomposites show macro/micro/nanointerfaces. Adding (CNTs) can improve not only the mechanical properties but also the functionalities such as electrical, thermal, and flammable properties of composites.

CNTs are one of the most typical nanomaterials used to give unique properties to polymers. Technology for the large-scale production of CNTs has recently been developed, decreasing the price of CNTs to ~$100/kg in 2013. Consequently, some

CNT-based nanocomposites have started appearing. For example, Evonik Industries is producing molding PA12 CNT-containing compounds for fuel lines [6]. The main advantage of this material is that it can avoid ignition induced by electrostatic charges. Fire risk can be substantially reduced by producing percolation networks of CNTs in polymers. Adding CNTs to polymers also modifies their flammabilities.

Nanofiller-based flame retardants show high flame-retardant efficiencies. Adding only a small amount (i.e., <5 %) of nanofiller can reduce the peak heat release rates (PHRRs) of polymers and thus reduce the speed at which flames spread throughout them. Further, the small amount of nanofiller does not reduce polymer processability and can improve the mechanical properties of polymers. However, adding only nanofiller cannot produce self-extinguishing (V-0, −1, and −2) polymers, which are required for most fire retardant products. The nanofillers should be combined with other conventional flame retardants to give a better balance of flammability/mechanical properties. The effects of combining nanofillers and flame retardants will be presented in Sect. 2.3.1. Further, the technology used to produce reliable nanocomposites requires great care and skill because nanofillers are relatively new, the technology is not yet completely understood, and polymer nanocomposite structures are unique. Thus, Sect. 2.2 summarizes the flame-retardancy mechanisms of the typical nanofillers used in carbon- and clay-based nanocomposites.

2.2.1 Fire-Retardancy Mechanism of Carbon-Based Nanocomposites

Nanocomposites can be classified into three categories according to the number of dimensions of the nanofillers (<100 nm) dispersed in polymers: (1) lamellar, (2) nanotubular, and (3) spherical polymer nanocomposites. Carbon-based nanomaterials showing such morphologies are thus named graphene, carbon nanotubes (CNTs), and carbon black (CB), respectively. Graphene is the completely exfoliated structure of graphite (single layer). The method of producing graphene was established recently, so graphene has attracted significant research interest [7–11]. CNTs are commonly used as fillers to improve the mechanical, electrical, and flame-retardancy properties of nanocomposites. Kashiwagi et al. revealed the flame-retardancy mechanism of CNTs [12–20]. Since CNTs are the most well-established material, we present mainly their fire-retardancy mechanism and some of their disadvantages here.

Figure 2.1 shows the cone-calorimetry results for single-wall nanotube and poly(methyl methacrylate) (PMMA) composites. Ignition time (IT), peak heat release rate (PHRR), and total heat release rate (THRR) are the important parameters in cone calorimetry to characterize material flammability. PHRR is the most important parameter used to describe flammability and is assumed as the driving force of the fire. Adding CNTs can reduce the PHRR; that is, the combustion heat intensity. However, it cannot change the THRR because CNTs do not act in the vapor

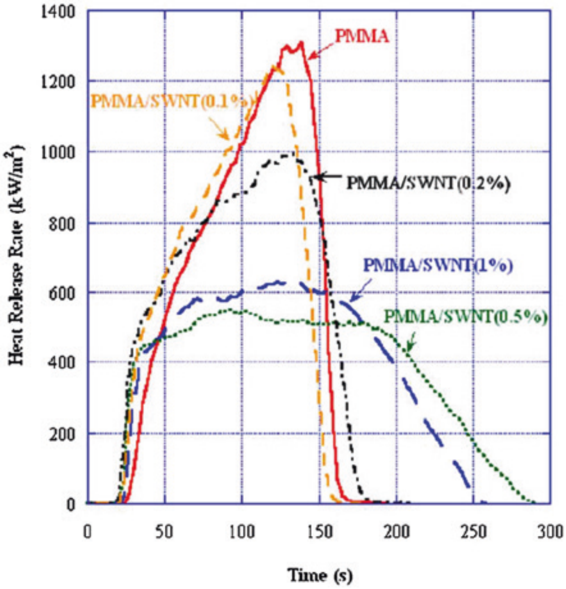


Fig. 2.1 Effects of SWNT concentration on mass loss rate of PMMA/AWNT in a nitrogen atmosphere (reprinted from [14])

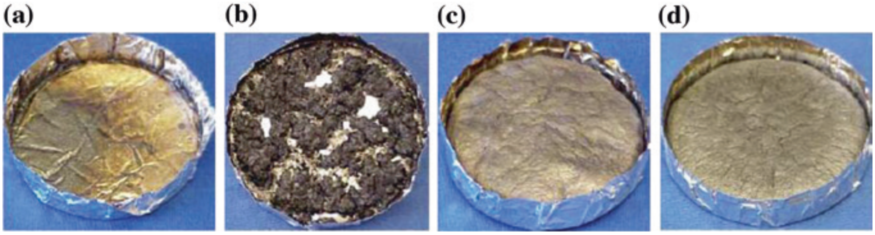
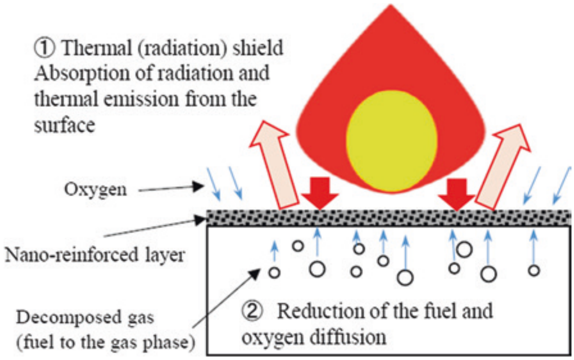


Fig. 2.2 Residues of PMMA/SWNT after the gasfication tests in a nitrogen atmosphere **a** PMMA, **b** PMMA/SWNT (0.2 %), **c** PMMA/SWNT (0.5 %), **d** PMMA/SWNT (1 %) (reprinted from [14])

phase, meaning that the amount of fuel gas required for combustion is not changed by adding CNTs. CNTs accelerate flame ignition (i.e., they reduce the IT). Most polymer/CNT composites show these tendencies. Kashiwagi et al. observed the residues (Fig. 2.2) after the cone calorimetry tests. The rate of PHRR reduction was small for the nanocomposite containing 0.2 wt% filler, as shown in Fig. 2.1. Many black discrete islands had formed during the test. In contrast, the surfaces of the nanocomposites containing >0.5 wt% CNTs were entirely covered with uniform, crack-free, opening-free CNT network layers, which significantly reduced the PHRRs. The key point of nanocomposite fire retardancy is the formation of a uniform CNT layer.

CNT-containing nanocomposites absorb more radiation than polymers during fires; therefore, nanocomposite temperatures increase faster than polymer ones. The ITs of materials decrease because the CNTs absorb large amounts

Fig. 2.3 Fire-retardant mechanism for nanoparticles

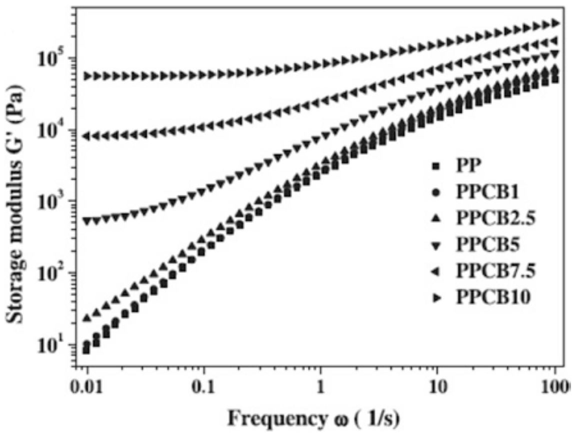


of radiation. Polymers begin to burn when they are heated to temperatures at which thermal degradation begins. The degradation products are superheated and nucleated to form bubbles. The bubbles burst at heated surfaces, evolving their contents as fuel vapor into the gas phase. There are a couple of possible mechanisms through which CNTs accumulate at material surfaces: the force of numerous rising bubbles during combustion pushes the CNTs to the material surface or the force of the polymer receding from the material surface during pyrolysis, leaving behind the CNTs.

The fire-retardancy mechanism of the CNT or char layer is depicted in Fig. 2.3. Kashiwagi et al. showed that close to 50 % of the incident flux was lost through emission from the hot nanotube surface layer and that the reminder of the flux was transferred to the nanotube-network layer and the virgin sample [14]. 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 [15]. Surface-layer cracks deteriorate nanocomposite flame retardancy during combustion.

Rheological properties appear to dominate the production of smooth CNT networks or char layers for all carbon-based nanocomposites [11, 15, 19]. Figure 2.4 shows rheological properties typical of PP/CB nanocomposites [19]. Neat PP shows typical low-frequency $G'-\omega$ scaling, where ω represents the oscillatory frequency. In contrast, the low-frequency G' scaling disappears, and G' becomes nearly constant at low frequency for the nanocomposites containing >5 wt% CB, meaning that the nanocomposite transitions from a liquid to a solid, which accompanies the formation of a mechanically stable network structure. It is well known that nanocomposites behaving like liquids cannot produce smooth CNT network layer on the material surface. The bubbles bursting at the surface disrupts the formation of an accumulation layer. Nanocomposites behaving like solids, on the other hand, contain bubbles that remain small in the high-viscosity layer and transport to the material surface, which tends not to disrupt the formation of the accumulation layer [14].

Fig. 2.4 The rheological properties of neat PP and PP/CB nanocomposites (reprinted from [19])



Uniformly dispersed nanocomposites show rheological properties similar to those of true solids. Therefore, the dispersion of carbon-based nanofillers determines the quality of the surface layer formed during combustion and thus affects the nanocomposite flame retardancy. Choosing appropriate CNTs is important. 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 [18]. The CNT load is also important in determining fire retardancy, and in fact, the optimal CNT load reduces PHRR, as shown in Fig. 2.1. Adding more CNTs once the uniform surface layer has formed deteriorates flame retardancy because it facilitates the agglomeration of CNTs and improves heat conductivity. The CNT aspect ratio affects fire retardancy, and higher aspect ratios lead to greater reductions in PHRR [16], indicating that a method of compounding thermoplastics to disperse CNTs and leave them longer is desirable.

From a practical perspective, a twin-screw extruder can be used to first compound thermoplastics, which are subsequently injection-molded in order develop a method of mass-producing thermoplastic-based goods. The relations between processing and flame-retardancy effectiveness should be discussed to apply CNTs in commercial products such as flame retardants. In fact, dispersing CNTs through a twin-screw extruder is worse than the nanocomposite produced using a closed kneader. Furthermore, injection molding orients material fibers. How these affect nanocomposite flammability should be discussed. Pötschke et al. investigated the relations between CNT dispersion and processing conditions [21–23]. They focused on the electrical conductivities of nanocomposites and conducted comprehensive experiments. Effective compounding methods are important for developing low-CNT-load fire-retardant nanocomposites.

Other carbon-based materials such as CB and graphene have also recently been investigated as flame retardants. Dittrich et al. showed that graphene were the most effective carbon-based fire retardants [11]. Interestingly, Wen et al. found new fire-retardancy mechanism for CB [19]. They showed that peroxy radicals, the chief factor affecting the thermal decomposition of polypropylene (PP), could be efficiently trapped in CB at elevated temperatures to form a gelled-ball crosslinked network. The PHRR was reduced 75 % and the LOI improved from 18 to 27.6 % by combining CB (to trap the peroxy radicals) and CNT (to create the networked layer) [20]. Surprisingly, adding CB and CNTs decreased the THRR; other nanocomposite systems do not show this tendency. The new fire-retardancy mechanism for CB has the potential to further improve the flame retardancy of carbon-based nanocomposites.

2.2.2 Fire-Retardant Mechanism for Clay-Based Nanocomposites

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 natural clay surface is hydrophilic, so the clay easily disperses in aqueous solutions but not in polymers. Natural clays are often modified using organic cations such as alkylammonium and alkylphosphonium cations, forming hydrophobic organomodified clays that can be readily dispersed in polymers. Clay-based nanocomposites are usually classified into three categories because clay properties are unique: (1) immiscible (also known as microcomposites), (2) intercalated, and (3) exfoliated (also known as delaminated). Exfoliated nanocomposites are usually desired because they show improved mechanical properties [24]. Clay-based nanocomposite loaded with <5 % clay is already used as a commercial flame retardant because of its improved mechanical properties and flame retardancy [5].

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 [25, 26]. The clay platelets accumulated because the clay remaining on the surface from polymer decomposition and clay migration was pushed by numerous rising bubbles of degradation products. The surface quality appears to determine the flame-retardant efficiency. Another mechanism suggested by Wilkie et al. is that the paramagnetic iron in the matrix traps radicals and thus enhances thermal stability. In fact, adding only 0.1 wt% iron-containing clay reduced the polystyrene (PS) PHRR by 60 % [27]. This effect was not observed for carbon-based nanocomposites because most of their iron is not on the surface and because their contact with the polymer is minimal [12].

Figure 2.5 shows HRR curves typical for polymer- and clay-based nanocomposites [25]. Adding clay can reduce the PHRR and generally reduces the IT, but it cannot vary the THRR. Carbon-based nanocomposites show the same tendencies because the fire-retardancy mechanisms for clay- and carbon-based nanocomposites; i.e., the barrier/insulation effect, are identical. Therefore, 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.

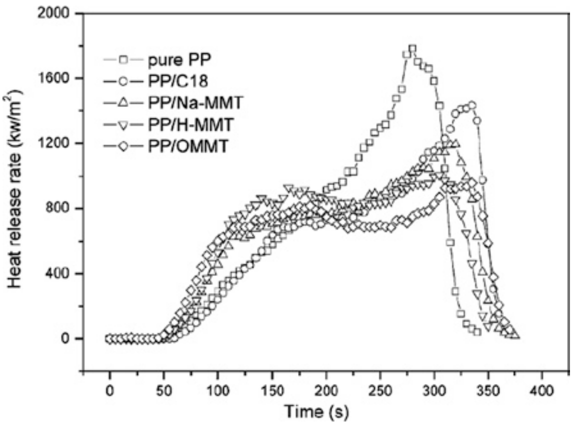


Fig. 2.5 HRR plots for pure PP, PP/C18, PP/Na-MMT, PP/H-MMT and PP/OMMT (reprinted from [25])

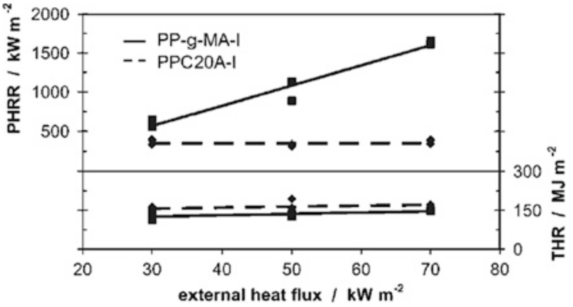


Fig. 2.6 PHRR and THR plotted against the external eat flux for PP (PP-g-MA-I) and nanocomposite (PPC20A-I) (reprinted from [28])

Schartel et al. investigated the relations between HRR and external heat flux, as shown in Fig. 2.6 [28]. THRR does not depend on external heat flux for the PP and nanocomposites. The PP PHRR, on the other hand, increases with increasing external heat flux, although the nanocomposite PHRR does not change. The fire-retardant efficiency strongly depends on irradiance such that the nanocomposite fire retardancy diminishes with decreasing irradiance. The results obtained through extrapolation to small irradiances correspond to flammability scenarios such as LOI and the UL 94 test. These results explain why adding nanofillers cannot drastically improve LOI and UL classification. In addition, they imply that adding nanofiller is effective for polymers exhibiting high HRRs.

The flame-retardancy effectiveness of clay-based nanocomposites depends on the kind of matrix [26–41]. For instance, the 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. In contrast, the IT of the PA6 nanocomposite increased when the nanoclay was added. Furthermore, rate at which PHRR decreases depends on which polymer matrix is used. PA6 and PS both decrease PHRR ~40–75 % [26, 32, 33, 37]. PMMA, on the other hand, only decreases PHRR 10–30 % [38–40]. Wilkie et al. showed that polymer nanocomposites such as PA6 and PS, which significantly reduce PHRR, exhibit significant intermolecular reactions and that the degradation pathway changes by incorporating nanoclay, whereas the PMMA did not show any change in the polymer degradation pathway or any significant HRR reduction [41]. Although adding the nanoclay to the PMMA does not significantly affect PMMA flammability, adding nanosilica to high-viscosity PMMA decreases PHRR by 50 % because silica covers the entire surface [42]. Incorporating nanoclay into PMMA is possibly effective when the nanoclay covers the entire PMMA surface. The nanoclay was less effective in improving PMMA fire retardancy possibly because the low viscosity of the PMMA prevented the nanoclay from covering the entire PMMA surface.

Modifying clay surfaces is the most important parameter for improving the fire retardancies of clay-based nanocomposites. Microcomposites are obtained instead of nanocomposites when unmodified clays are incorporated to polymers. The flammabilities of the microcomposites are usually almost identical to or sometimes worse than those of the pure polymers. Organomodifying clays produce intercalated or exfoliated nanocomposites. In addition, the char content and cone-calorimetry behavior of organomodified nanocomposites depend on the organomodifier content: increased organomodifier content leads to a more pronounced catalytic effect and more intensive char formation [29]. Figure 2.5 shows the effect of surface modification on the HRR behavior of PP. Incorporating organomodified montmorillonite (OMMT) decreased the PHRR the most owing to the nanodispersed clay and the catalytic properties of the organomodifier.

The second most important factor in improving nanocomposite fire retardancy is clay loading. Unlike CNT loading, increasing clay loading improves nanocomposite fire retardancy, and there is no optimal clay loading in the range <15 wt% [33, 34]. It is difficult to form a crack-free clay-network layer. Therefore, the main flame-retardancy mechanism is through the formation of a barrier against the heat source instead of gases. Photos of residues obtained from degraded PS/OMMT samples containing various OMMT contents are shown in Fig. 2.7. The residues from the degraded PS/OMMT samples containing 6- and 15-wt% OMMT show cracks. Thicker floccules can be obtained by adding more clay. The formation of thick floccules can significantly decrease HRR. Clay-based nanocomposite flame retardancies could be further improved if polymer-clay nanocomposites could be tuned to form more stable crack-free networks during burning.

The effect of nanomorphology on flame retardancy has previously been discussed in the literature [32, 43, 44]. 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 [37].

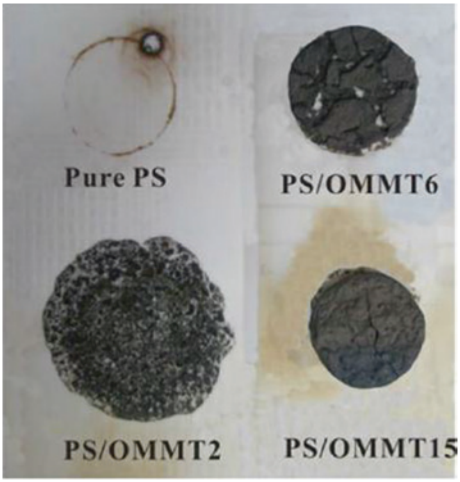


Fig. 2.7 Digital *photos* showing the residue morphology of different PS/OMMT composites after degraded at 400 ℃ for 3 h (reprinted from [33])

2.3 Polymer Nanocomposites Combined with Conventional Fire Retardants

Although the HRRs polymer-nanocomposite-only fire retardants are greatly reduced, the total amount of heat released remains unchanged so that the nanocomposites burn slowly once they ignite but do not self-extinguish. This is why nanocomposites themselves have not been used as commercial products, which must pass strict regulatory tests. It is expected that combining polymer nanocomposites with conventional fire retardants can fully exploit the fire-retardancy mechanism of nanofillers; i.e., the slow burning and the mechanical reinforcement of char layers. In fact, the material produced by combining the EVA nanocomposite with conventional aluminum hydroxide is used as a cable cover. Adding only 5 wt% organoclay can reduce the amount of aluminum hydroxide used (20 wt%) without deteriorating flame retardancy. In addition, it can improve the mechanical properties of the cable because less aluminum hydroxide is used and owing to the reinforcement of the clay. This ternary system was developed to reduce the amount of halogenated flame retardant used and to develop halogen-free fire retardants.

There are uncountable combinations of fire retardants. Some combinations synergistically improve fire retardancy but others antagonistically affect it. There is a vast amount of research available on the synergistic effects of combining nanofillers and conventional fire retardants on fire retardancy, so knowing the results and the fire-retardancy mechanisms will be useful for developing better fire retardants. Combining halogenated additives with antimony oxide (Sb_2O_3) positively affects fire retardancy. The Sb_2O_3 reacts with the hydracids generated by the halogenated additives to form antimony oxyhalides, which are much heavier than the native hydracids, thus prolonging their residence time in the flame. From this example, we can infer that clay might enhance the halogenated-additive effect because the clay can act as a barrier, delaying the burning and prolonging the residence time of hydracids. Combining polymer-clay nanocomposites with melamine cyanurate showed the antagonistic effect [45–47]. The melamine cyanurate improves LOI and UL classification by facilitating the polymer to drip away from the fire source. However, adding nanoclay increases the polymer melt viscosity; hence, the polymer in this polymer nanocomposite system will not drip away from the fire source, and this ternary system cannot pass the UL94 regulatory tests. Many previously reported combinations are discussed in the following sections.

2.3.1 Nanocomposites Combined with Halogenated Flame Retardants

Most research has been conducted on nonhalogenated flame retardants because halogenated ones have been proscribed. However, the latter are being reevaluated owing to their recyclability and highly effective flame retardancies. The European Union RoHS directive prohibited the use of PPB and PBDE. Decabromodiphenyl ethane (DB) was developed in the 1990s. The DB molecule does not contain any ether bonds and will not generate polybrominated dibenzofurans (PBDBFs) or polybrominated dibenzo-*p*-dioxin (PBDD). Further, DB is recyclable and is therefore widely used as a halogenated flame retardant.

Nanofiller distribution is the key point to obtaining synergistic effects between the nanofiller and a conventional flame retardant. Figure 2.8 shows filler distributions typical for ternary materials. The nanofiller will be incorporated into the fire retardant (structure A) if the nanofiller is more compatible with the fire retardant than with the matrix; that is, if the nanofiller shows better wettability with the fire retardant than with the matrix. The nanofiller will be dispersed into the matrix instead of the fire retardant (structure B), on the other hand, if the nanofiller shows

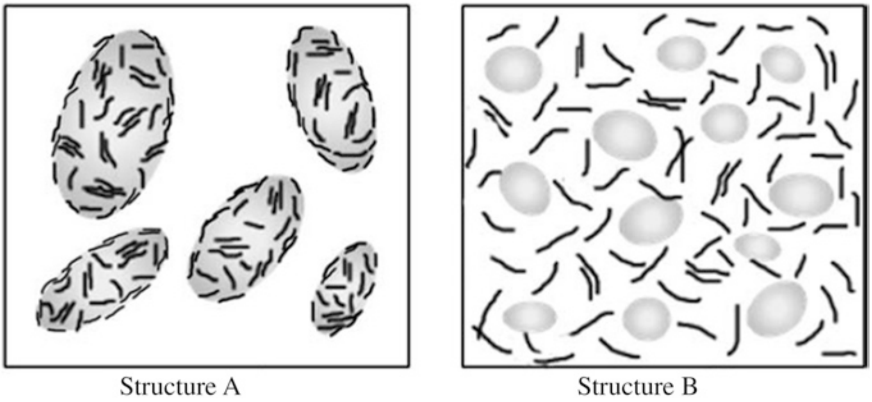


Fig. 2.8 Schemes for the two different model structures: *structure A* (nonofiller is incorporated to fire retardant) and *structure B* (nanofiller is dispersed in a matrix) (reprinted from [48])

better wettability with the matrix than with the fire retardant. For instance, the clay does not catalytically affect the matrix in structure A, and the thick, uniform char layer (which is the main fire-retardancy mechanism for clay) cannot form because the clay is poorly distributed. Therefore, structure B is preferable to structure A for enhancing ternary-composite flame retardancy. Chen et al. investigated the relation between organoclay distribution and flame retardant PP flammability for the material system consisting of PP, brominated epoxy resin/antimony oxide (BER-AO) and OMMT [48]. OMMT was incorporated into BER in the absence of polypropylene-graft-maleic anhydride (PP-g-MAH), which can increase PP polarity and aid OMMT dispersion. Adding PP-g-MAH can change the structure from A to B. Adding OMMT to the PP/BER/AO/OMMT system (structure A) worsened its flammability, and the system failed the UL-94 tests. In contrast, the PP/PP-g-MAH/BER/AO/OMMT system (structure B) showed V-0 classification. Adding OMMT significantly reduces the PHRR and THR of structure B, indicating a synergistic effect between the clay and the halogenated flame retardants. Clay distribution must be carefully considered when designing effective ternary composites.

Zanetti et al. also showed that combining nanoclay and a halogenated flame retardant produced a positive effect [49]. Adding 22 wt% DB and 6 wt% AO decreased the average HRR from 279 to 245 kWm^{-2}. They presumed that faster combustion is presumably responsible for the inability to observe synergy in the polymer, thus nullifying the retarding effects of both HBr generated by DB and the radical inhibitor $SbBr_3$ generated by DB-AO. Adding OMMT to PP/DB-OA systems, on the other hand, decreased the average HRR to 107 kWm^{-2} because of the slow burning effect achieved by adding clay. The free-radical reactions that propagate the flame were thus slow enough to enable the DB-generated HBr to slow the combustion. PP [50], PMMA [51], PS [52, 53], and PA6 [47] all showed the same synergistic effect. The clay-produced char layer can not only act as a barrier against heat and mass transport but also reinforce the halogenated-flame-retardant effect. This synergistic mechanism is not specific to these polymers; thus, it opens the possibility of formulating self-extinguishing materials from large classes of polymer nanocomposites and halogenated flame retardants [51].

Wilkie et al. combined CNTs with clay to develop a synergistic material for the PS/BER/AO system [52]. The BER and multiwalled nanotubes (MWNTs) showed better synergy than the BER and clay for improving the flame retardancy of the system possibly because the CNT-produced surface layer was compacter and denser than the clay-produced char layer. Nanofillers and halogenated fire retardants show synergistic effects as long as the surface-barrier layer is formed, and the synergistic effects depend on the nanofiller-produced-surface quality; i.e., compactness and absence of cracks.

2.3.2 *Nanocomposites Combined with Phosphorus and Intumescents*

Phosphorus-based fire retardants act in the gaseous and condensed phases, and their main fire-retardancy mechanism is through the formation of a char layer, which acts as

Table 2.1 Cone calorimetric results for PP and its composites. *Source* Reference [54]

Formulation of PP and its composites	t_{ign} (S)	t_{PHRR} (S)	PHRR ($\mathrm{kWm^{-2}}$)	THR ($\mathrm{MJm^{-2}}$)
PP(100)	37 ± 4	189 ± 12	363 ± 17	56 ± 2
PP(67)/PP-*g*-MAH(5)/IFR(28)	33 ± 3	435 ± 20	62 ± 5	24 ± 1
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/CNT(2.5)	33 ± 3	189 ± 15	145 ± 8	54 ± 1
PP(67)/PP-*g*-MAH(5)/IFR25.5)/OMMT(2.5)	31 ± 2	360 ± 18	45 ± 5	18 ± 3
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/LDH(2.5)	30 ± 2	300 ± 15	64 ± 6	20 ± 3
PP(67)/PP-*g*-MAH(5)/IFR(25.5)/POSS(2.5)	32 ± 2	375 ± 16	55 ± 5	16 ± 2

a barrier. Phosphorus-based fire retardants often contain intumescent flame retardants to improve the insulator properties of the former; hence, we categorize phosphorus and intumescents together. Phosphorus-based fire retardants and nanofillers both act as barriers during combustion; therefore, adding nanofillers to composites containing phosphorus-based fire retardants will either reinforce or deteriorate the barrier effect.

Du et al. investigated ternary systems composed of PP, intumescent flame retardant (IFR), and various nanofillers such as CNT, OMMT, layered double hydroxide (LDH), and polyhedral oligomeric silsesquioxane (POSS) [54]. They melt-blended ternary composites and showed that all the nanofillers except LDH had dispersed well throughout the matrix, not throughout the IFR. The LDH-containing composites showed intercalated and even some larger agglomerated LHD tactoids in the majority of the LDH. Their cone calorimetry results are listed in Table 2.1. Adding nanofillers to the PP/IFR composite did not vary the ignition temperature, whereas it either improved or deteriorated the PHRR and THR in cone calorimetry tests. Adding CNTs to the PP/IFR systems produced antagonistic effects; that is, adding CNTs to polymer/IFR systems increases the PHRR, indicating accelerated burning [54–56]. Istiman et al. also found that the PMMA/organophosphorus/CNT system showed the same phenomena; i.e., antagonistic effects [56]. The residue observed after the cone calorimetry test showed that adding CNTs to the PP/IFR system had generated cracks on the residue surface and that the CNTs had also inhibited intumescence. The intumescence had disrupted the formation of a uniform CNT network on the surface, while the CNTs had inhibited IFR swelling; hence, combining the CNTs with the IFR showed antagonistic effects. OMMT showed the best synergistic effect in reducing the PHRR. Substituting 2.5 % IFR for the OMMT decreased both the PHRR and the THR. Adding the OMMT reinforced the char layer, which generated the synergistic effect. Ma et al. explained that the intumescent-generated phosphoric acid had probably reacted with montmorillonite to form silicoaluminophosphate (SAPO) [57]. In addition, organomodifier decomposition produces strongly acidic catalytic sites, which may further promote oxidative dehydrogenation crosslinking charring. These phenomena enhance the efficiency of the char layer protecting against heat transfer and mass (i.e., oxygen and decomposed gas) transport.

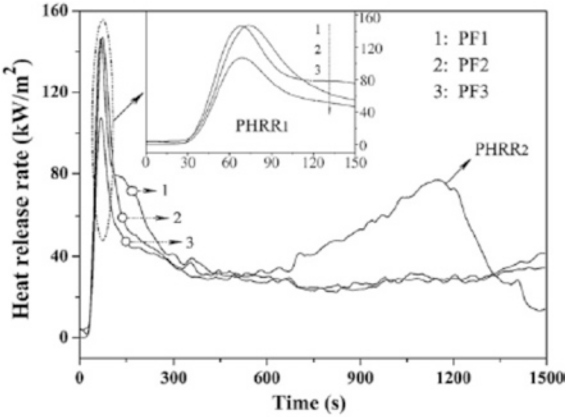


Fig. 2.9 HRR curves of PP/IFR(nitrogen-phosphorus)(PF1), and PP/IFR/OMMT(PF2, PF3). The OMMT content of PF2 and PF3 are 1.8 and 2.6 wt%, respectively (reprinted from [58])

The phosphorus and clay showed synergistic effects in improving fire retardancies of ABS [57], PP [58, 59], PE [60], and PA6 [61]. Ma et al. investigated the fire retardancy of the ABS/poly (4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB)/OMMT ternary system [57]. Adding 30 wt% PDSPB reduced the PHRR from 930 to 388 kW/m^2 during the cone calorimetry test. Interestingly, adding 18 wt% PDSPB and 2 wt% OMMT further reduced the PHRR to ~370 kW/m^2, indicating that using only 2 wt% OMMT can save the use of >10 wt% PDSPB. The mechanical properties should be improved by adding clay because it can reduce the amount of IFR used and because IFR deteriorates the mechanical properties of the materials. Du et al. examined the fire retardancy of the PP/IFR/organobentonite composite [58]. Adding 28 wt% IFR enabled the composite to achieve V-0 classification during the UL-94 test and increased the composite LOI from 18.4 to 30.7 %. Adding 2.6 wt% organobentonite increased the ternary-composite LOI to 32.8 %. Figure 2.9 shows the HRR curves for the PP/IFR and ternary composites. The HRR for the PP/IFR (PF1) shows two peaks at 33 and ~1,200 s. The intensity of the first peak attributable to HRR can be reduced by adding IFR, which forms the surface char layer. Fine cracks are gradually produced on the char layer, collapsing the char structure while the material absorbs heat. The HRR shows the second peak when the surface char layer collapses. The HRR for the PP/IFR/organobentonite system did not show the secondary peak, which is undesirable for fire retardants. The clay improves the mechanical strength of the char layer and suppresses its collapse during combustion. Huang et al. also demonstrated the synergistic effects for the PE/diphenylmethanamine spirocyclic pentaerythritol bisphosphonate (PSPD)/OMMT system [60]. The PE/PSPD(15)/OMMT(5) reduced the PHRR by ~51 % more than pure PE did, although the PHRR of the PE/PSPD(20) was reduced by only 26.8 %. Again, adding clay contributed to the formation of the high-strength char layer, reducing the intensity of the first peak attributable to the PHRR and suppressing secondary combustion.

The IFR and clay do not always show synergistic effects, and some of minor fire retardant effects were observed for PS [62], PP [63], and PMMA [56]. Chen et al. investigated the flame retardancies of PS/PDSPB/OMMT composites. Incorporating 20 wt% PDSPB into the PS reduced the PHRR from 739 to 502 kW/m^2. However, adding 4 wt% OMMT to the PS/PDSPB(20) increased the PHRR to 527 kW/m^2. The OMMT had been incorporated into and restricted in the PDSPB phase (Fig. 2.8, structure A); thus, the uniform char layer could not be obtained, and the clay and IFR did not show any synergistic effects. Szustakiewicz et al. found that the PP/APP/OMMT system did not show any synergistic effects [63] and concluded that incorporating OMMT had worsened the PP flame retardancy when intercalated or exfoliated nanomorphology was not obtained. Istiman et al. added CNTs or OMMT to try to improve the flame retardancy of the PMMA/organophosphorus (OP) system [56]. Incorporating CNTs into the PMMA/OP system deteriorated its flame retardancy through adverse effects, and incorporating OMMT into it only slightly reduced the PHRR from 63 to 66 %. The clay interacted with the PMMA less than with the other polymers; thus, the compact char layer could not form in the PMMA/OP/OMMT system. An alternative approach is thus required in order to improve PMMA flame retardancy.

Polymer/IFR/clay ternary composites show excellent fire retardancy as long as nanomorphology is formed and the clay is well distributed throughout the polymer matrix. Optimizing the clay content improves the flame retardancy of this system. Wilkie et al. surveyed thirty kinds of phosphorous that could be used to improve the fire retardancy of this system and investigated which clay and phosphorus combinations showed the best synergistic effects during the screening test [64]. Table 2.2 shows part of their results. Adding 30 wt% phosphorus fire retardant clearly reduced the PHRR by 64 % for resorcinoldiphosphate (RDP) and 38 % for trixylyphosphate (TXP). Incorporating clay further decreased the PHRR, and the optimal clay load was 5 wt% for both systems. Using the 5 wt% clay load decreased the PHRR by 92 %, which was the best PHRR reduction. Hu et al. also determined the optimal clay loads to enhance the synergistic effects between clay and various IFRs including APP and pentaerythritol (PER) [65]. The synergistic

Table 2.2 Optimal clay content for PS/resorcinoldiphosphate (RDP) and PS/trixylyphosphate (TXP). *Source* Reference [58]

Sample	t_{ign} (S)	PHRR kW/m^2 (% redution)	Total heat released (MJ/m^2)
PS	62	1419	109.7
PS/RDP 30 %	77	499 (64)	41
PS/RDP 30 %/clay 3 %	75	358 (74)	42.3
PS/RDP 30 %/clay 5 %	55	110 (92)	43.1
PS/RDP 30 %/clay 10 %	63	307 (78)	44.7
PS/TXP 30 %	57	864 (38)	53.9
PS/RDP 30 %/clay 5 %	38	313 (78)	45.5
PS/RDP 30 %/clay 10 %	59	372 (73)	49.4

effect is related to the ratio of MMT to IFR. The negative effect of adding clay is that the NH_3 is prevented from swelling the char, which is similar to the negative effect of adding the CNTs. The negative effect may outweigh the positive one (i.e., producing the char layer and reinforcing it through crosslinking) when the amount of clay added exceeds a specific value.

Other additives can be combined with polymer nanocomposites to enhance the synergistic effects in order to improve the flame retardancies of polymer/phosphate systems. Cinausero et al. improved the fire retardancy of the PMMA/APP system by adding oxide nanoparticles [66]. Alumina and silica particles, whose average diameter was 12 nm, were added to the PMMA/APP. As-prepared hydrophilic metal oxide particles were used, and some of them were surface-treated to make them hydrophobic and thus more compatible with the polymer, improving the metal-oxide dispersion throughout the polymer and the molten-metal-oxide migration. The cone calorimetry results are shown in Fig. 2.10. Alu-C8 in Fig. 2.10 indicates the surface-modified alumina particles, and Sil indicates the untreated silicate ones. Although it is difficult to improve PMMA flame retardancy, combining metal oxide with APP showed the synergistic effect, and the PHRR was reduced by more than 50 %, as shown in Fig. 2.10. The surface-treated hydrophobic silica nanoparticles showed the best flame retardancies. The PMMA/AP/Sil-C8 system had developed a smooth, crack-free residual char layer, while the other system had developed a residual char layer showing numerous cracks, meaning that adding Sil-C8 can form a compact char layer, which can improve the barrier properties. These results showed that the silica and APP had strongly interacted. Cinausero et al. mainly ascribed the flame retardancy to the

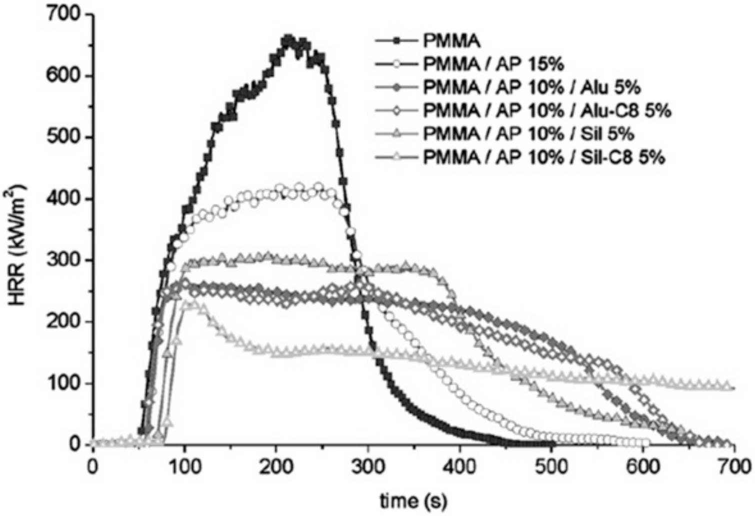


Fig. 2.10 Effect of oxide nanoparticles on fire properties of PMMA/APP composites (reprinted from [66])

crystalline silicon metaphosphate (SiP_2O_7) phase, which contributed to charring and promoted the formation of an efficient barrier. This method (i.e., combining APP with silica) can work efficiently for polymers such as PS. Their results indicate that the interaction between conventional fire retardants and other additives is important in improving fire retardancy.

Combining IFR with metal oxides such as antimony oxide (Sb_2O_3) shows synergistic effects in improving fire retardancy. For instance, adding 2 wt% Sb_2O_3 increased the LOI of the PP/IFR system from 27.8 to 36.6 % [67]. Li et al. presumed that this was because Sb_2O_3 could react with APP to form the stably crosslinked charred layers, which forms a barrier against heat transport and oxygen diffusion. Wu et al. examined nine metal oxides for their potential synergistic effects for improving the flame retardancy of the PP/IFR system [68] and found that the PP/IFR combined with Ni_2O_3 showed the best performance in their experiments.

2.3.3 Nanocomposites Combined with Metal Hydroxides

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. Clays and metal hydroxides are often combined to produce the EVA matrix, which is used for cable outer sheaths [69–72]. Unlike the polymer/phosphorus/nanofiller system, which shows an antagonistic effect, the polymer/metal hydroxide/nanofiller system has not shown an antagonistic effect to date. The nanofiller is not incorporated into the metal hydroxide as a matter of course; it is well dispersed throughout the polymer matrix.

Beyer investigated the fire retardancy of EVA/alumina trihydrate (ATH) combined with either nanoclay or CNTs [69]. The cable outer sheath is often composed of 35 wt% EVA and 65 wt% ATH. The fire-retardant composite showed a PHRR of ~200 kW/m^2 during cone calorimetry at 50 kW/m^2 heat flux. Replacing 5 wt% of the ATH with nanoclay reduced the PHRR to 100 kW/m^2. The rigid char layer that had formed for the EVA/ATH nanocomposites showed fewer cracks than that which had formed for the EVA/ATH compound, and it contributed the reduction in the PHRR during cone calorimetry. Beyer showed that ~78 wt% ATH was required for the EVA(35)/ATH/(60)/nanoclay(5) nanocomposite to achieve the same flame retardancy (*i.e.*, PHRR: 100 kW/m^2). Furthermore, the ATH content could be decreased from 65 to 45 wt% by adding only 5 wt% OMMT in order to maintain a sufficient peak heat release (200 kW/m^2). This wide range of PHRR reduction can contribute to improving material processability and mechanical properties.

Table 2.3 Optimal loading level for EVA/metal hydroxide/OMMT ternary composites. *Source* Reference [70]

Sample	LOI (%)	UL-94
EVA	19.5	–
EVA/MH(50)	27.5	V-0
EVA/MH(49)/Nanoclay(1)	33.5	V-0
EVA/MH(48)/Nanoclay(2)	34.5	V-0
EVA/MH(46)/Nanoclay(4)	31.0	V-0
EVA/MH(44)/Nanoclay(6)	30.5	V-0
EVA/ATH(50)	25.5	–
EVA/ATH(49)/Nanoclay(1)	27.0	V-0
EVA/ATH(48)/Nanoclay(2)	28.0	V-0
EVA/ATH(46)/Nanoclay(4)	26.0	–
EVA/ATH(44)/Nanoclay(6)	25.5	–

Yen et al. discussed the optimal loads for the EVA/ATH/clay and EVA/magnesium hydride (MH)/OMMT systems, as shown in Table 2.3 [60]. They used 50 wt% total filler content and replaced part of the ATH or MH with a small amount of OMMT. Replacing the metal hydroxide with OMMT increased the LOIs of both material systems; however, the LOIs stopped increasing when 2 wt% of the metal hydroxide had been replaced with OMMT because less metal hydroxide remained in the systems. Yen et al. suggested that adding OMMT reinforced the surface char layer acting as the insulation and that the formed layer had responded to the synergistic effect of flame retardancy and had suppressed the smoke from the EVA blends. Ye et al. showed that the CNT-based nanocomposite was synergistic [73]. Substituting 2 wt% MWNTs with metal hydroxide (MH) increased the EVA(50)/MH(50) LOI from 34 to 39 %. Replacing 2 wt% MWNTs with MH optimized the fire retardancy, and further replacing MWNTs decreased the LOI.

Hong et al. [74] developed fire-retardant PP-based composites to replace polyvinyl chloride (PVC), which is a cable insulator that shows excellent fire retardancy but poses health and environmental problems. Adding mineral filler to PP drastically decreases material elongation. They blended PP/poly(ethylene-co-propylene) (EPR) with mineral fillers and OMMT to retain high material elongation. The PP(36)/MDH(60)/OMMT(4) composite showed 210 % elongation at break and 27 % of the LOI. Knog et al. investigated the effects of structural iron on the fire retardancy of the PP/ATH/OMMT ternary system, as shown in Table 2.4 [75]. The iron strengthened the synergistic effect between the clay and the ATH and trapped some of the free radicals, which enhanced the thermal stability of the system and the char ratio [37, 75].

PE and high-impact polystyrene (HIP) combined with metal hydroxides and OMMT have also shown synergistic effects [76, 77]. Combining PE with 2.5 wt% inorganic clay and 20 wt% ATH reduced the PHRR 73 % more than using only pure resin [76]. This PHRR reduction is comparable to that obtained by combining PE with only 40 wt% ATH. Istman et al. solution- and melt-mixed HIP/ATH/nanoclay composites and discussed the relations between nanofiller

Table 2.4 Effect of structural iron on flammability of PP/ATH/OMMT composites. *Source* Reference [75]

Code	PP (wt%)	ATH (wt%)	Fe-OMT (wt%)	Na-OMT (wt%)	LOI	UL-94
PP0	100				17	Buringing, drip
PP1		50			23	Buringing, drip
PP2		48	2		25	V2
PP3		45	5		27	V1
PP4		43	7		29.5	V0
PP5		48		2	23	Buringing, drip
PP6		45		5	23.5	Buringing, drip
PP7		43		7	24	Buringing, drip

flame retardancies and dispersions [77]. Solution-mixing produced the nanocomposite. Melt-mixing, on the other hand, produced the microcomposite. The nanocomposite PHRR decreased twice as much as the microcomposite one during cone calorimetry. In addition, the nanocomposite mechanical properties were superior to the microcomposite ones. Incorporating 3 wt% well-dispersed nanoclay showed a similar effect on decreasing the PHRR as adding 15 wt% ATH. The LOI of the solution-mixed HIP(62)/ATH(35)/clay(3) was 22 %, indicating that more ATH was required in order to achieve V-0 classification during the UL test.

2.3.4 Other Combinations

The previous sections mainly describe combining CNT- and clay-based nanofillers with conventional fire retardants. However, many other combinations can effectively improve polymer flame retardancy. Goodariz et al. recently reported that calcium carbonate ($CaCO_3$) nanoparticles could improve both thermal and thermo-oxidative stability [78]. Table 2.5 shows the mechanical properties and fire retardancy of the composite prepared with DB, clay, and $CaCO_3$. Goodariz et al. used

Table 2.5 Remarkable improvement for fire properties by incorporating $CaCO_3$ nanoparticle. *Source* Reference [78]

Sample	LOI (%)	UL-94	PHRR reduction (%)	Young modulus (MPa)	Tensile strength (MPa)
PP	17.4	Buring	–	1,960	40
PP(85)/DB(11.25)/AO(3.75)	24.3	V-2	53	1,887	28.81
PP(95)OMMT(5)	22.7	Buring	36	3,652	43
PP(95)/$CaCO_3$(5)	23.6	V-0	59	3,721	46.32
PP(95)/OMMT(5)/$CaCO_3$(5)	29.2	V-0	76	4,365	55.21

~50 nm-diameter $CaCO_3$ nanoparticles and used a titanate coupling agent to modify the nanoparticle surfaces. Surprisingly, incorporating 5 wt% $CaCO_3$ into the nanoparticles produced self-extinguishing PP, although the $CaCO_3$ fire-retardancy mechanism is unclear. The $CaCO_3$ in PP could retard polymer oxidation [79], which might contribute to PP fire retardancy. The fire retardancy of PP combined with 5 wt% $CaCO_3$ was comparable with those of PP combined with DB and AO, and the mechanical properties of the PP/$CaCO_3$ composites were superior to those of the PP/DB/AO composites. Simultaneously incorporating $CaCO_3$ and OMMT into PP produces a synergistic effect that improves both the PP fire retardancy and mechanical properties.

Incorporating a combination of nanofillers into polymers reportedly improves polymer fire retardancy [69, 80–82]. Ma et al. incorporated clay and MWNTs into ABS resin and reduced the flammability of the nanocomposites more than incorporating either the clay or the MWNTs did. The EVA/clay/MWNT and PP/clay/MWNT ternary composites showed the same phenomenon [82]. Further, the MWNTs were linked between clays, indicating that the clay and MWNTs had strongly interacted, enabling the formation of a crack-free compact char layer. They used a one-to-one ratio of clay and MWNTs. The optimal ratio of MWNTs to clay for improving flame retardancy does exist, and further research must be conducted to determine the exact ratio.

2.4 Fire-Protective Coatings

Modifying material surfaces is an effective method of strengthening barriers against gas and heat transfer inside materials; hence, surface-modified materials are also fire retardants. 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.

Flame-retardant coatings are classified as intumescent and nonintumescent systems. Intumescent coatings are usually applied to wood and steel in order to protect the substrates from the fire. Intumescent coatings generate char and swell during combustion. The swelled char layer acts as a heat-insulation material, which can protect the substrate from the fire. There are numerous nonintumescent coatings such as halogen-based, phosphorus-based, and inorganic-additive-incorporated systems. Nonintumescent systems are significantly less efficient than the intumescent flame-retardant (IFR) coating in reducing polymer flammability. There are already comprehensive reviews on intumescent [83] and nonintumescent [84] systems, so we will briefly introduce the IFR coating and mainly highlight the nanotechnology used to produce it.

2.4.1 Intumescent Coating

Epoxy, acrylic, PVA, urethane, or silicon polymers are used as IFR binders. Some of fillers such as TiO_2 are added to increase the fire-retardant efficiency. The IFR coating is sprayed, dipped, or brushed onto the substrate to form a layer ranging from a few tens to hundreds of microns thick. The IFR coating improves the bulk-material flame retardancy without changing the mechanical properties and is aesthetically attractive. However, it is not reliable long term because the coating poorly adheres to the substrate surface, leading to delamination, which deteriorates or defeats the effectiveness of the IFR. In addition, the IFR absorbs water and ultraviolet (UV)-filtered light, further deteriorating it [85]. Therefore, an additional surface coating is required in some cases.

Many methods of coating including UV-curing, physical and chemical vapor deposition, and layer-by-layer (LBL) assembly have previously been developed. UV-curing is an attractive method because it consumes small amounts of energy and because the coatings are rapidly cured (in a few seconds). However, it is difficult to use this method in order to coat complex-shaped samples because some or part of the samples might not be exposed to UV light. Chemical vapor deposition has been used to improve the flame retardancy of textile materials and electrical devices [86].

Although LBL is a highly tailorable method of coating, it is time consuming because the substrate must be repeatedly dipped and washed until the desired number of bilayers has been deposited onto it. Therefore, this method is only used for lab-scale modeling and cannot be practically applied to large-scale production. Dipping and spraying are the simplest, most inexpensive methods; hence, they are preferable for practical large-scale production.

Bourbigot et al. and Wang et al. have dipped or sprayed substrates to develop an effective method of IFR coating [85, 87–99]. Bourbigot et al. investigated the fire retardancies of PP and PC substrates coated with either PVA-based IFR containing APP, pentaerythritol (PER), and melamine or an acrylic-resin-based formulation containing PER, silica, and phosphoric acid. Both coatings enable PP and PC to achieve V-0 classification during UL-94 tests [87]. Figure 2.11 shows the IFR-coated-PP residue after the cone calorimetry test. The varnish coating had expanded more than the PVA one, so the varnish coating is more fire-retardant efficient than the PVA one. The 200-μm-thick PP-coating PHRR was reduced to 143 and 4 kW/m^2 for the PVA

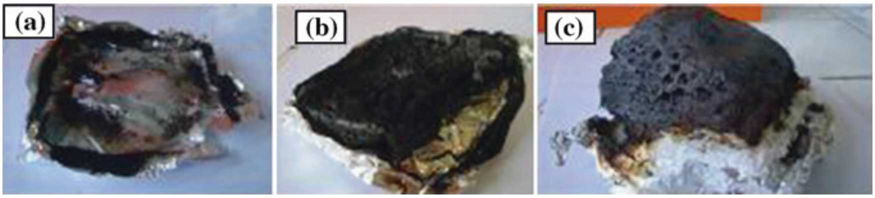


Fig. 2.11 Pictures of residues of PP (**a**), PP coated (**b**), PP varnish (**c**) (reprinted from [87])

and varnish coatings, respectively. The varnish coating can swell enough to act as an insulating barrier, completely protecting the polymer from the fire source. The 1.6-mm-thick PP and PC samples had to be coated with 158- and 42-μm-thick layers of varnish, respectively, to achieve the V-0 rating [85]. The coating worked better on the PC substrate because the PC had produced char during combustion and had interacted with the coating. The PP, on the other hand, had melted and vigorously burned without forming char. The varnished PP and PC fire retardancies slightly decreased when the varnished substrates were exposed to UV-filtered light. Bourbigot et al. attributed the decreased fire retardancies to decreased varnish adhesion rather than to chemical modification of the varnish through FTIR and TGA analyses.

2.4.2 Nanocoating

Solution casting, which is a method of producing nanocomposites with high filler contents, has recently been developed. For instance, solution-casting can be used to produce 100 % clay paper. Paper produced from CNTs is called "CNT buckypaper." Such high-nanofiller-loaded materials may be applied as coatings reduce substrate flammability. Solution-cast nanocomposites are different from bulk ones because the fillers do not migrate within the composites and because strong nanofiller networks can always be formed in nanocoatings. Preparing nanodispersed slurry is the most important step in nanocoating because nanocoating highly depends on slurry dispersion. The nanocoating can then be dipped, sprayed, or deposited layer by layer onto the substrate. Solution-casting or vacuum filtration can then be used to fabricate the nanofiller barrier film.

Platelet materials such as clay or graphene are preferable for improving gas barrier properties because they force permeating molecules to travel extended paths referred to as "tortuous pathways." The gas permeability of the thin coating layer composed of aligned platelets is some orders of magnitude lower than that of the virgin material, depending on the aspect ratio and filler content [90]. In fact, numerous researchers have used clay [90–96] and graphene [8, 97] to produce nanodispersed films showing extraordinary mechanical and gas-barrier properties. Two important fire-retardancy mechanisms involve reducing fuel-gas diffusion to the fire source and reducing oxygen diffusion inside materials. Therefore, multifunctional nanocoatings are expected to contribute flame retardancy.

The method of producing clay and polymer building blocks is depicted in Fig. 2.12. Unmodified clay is naturally hydrophilic, so a homogenizer or an ultrasonicator can be used to easily disperse it in water or aqueous solutions. Dispersed clay particles then absorb polymer onto their surface when nanodispersed slurry is poured into an aqueous solution containing a water-soluble polymer such as PVA. Polymer absorption can stabilize the clay dispersion because each polymer-coated clay particle shows steric repulsion. The polymer-coated-clay solution is then available for making paper, painting, spraying, and doctor-blading. Walther et al. produced nacre-inspired biomimetic clay films as hard segments and either PVA or chitosan as block binders [93, 94]. The biomimetic film fabricated with MMT and

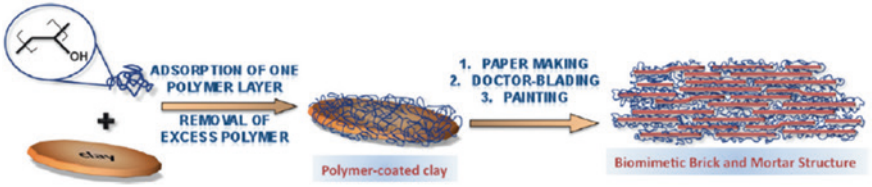


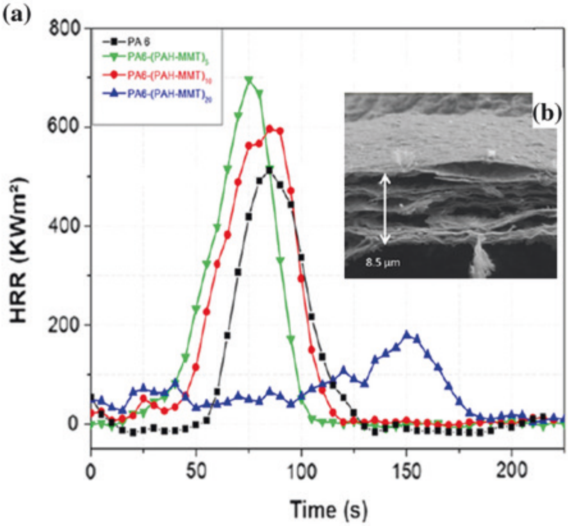
Fig. 2.12 Strategy toward the preparation of biomimetic self-assembled brick and mortar structures based on common, scalable, and simple processing method (reprinted from [93])

chitosan showed not only high mechanical stiffness (25 GPa) and tensile strength (320 MPa) but also shape-persistent fire-blocking. The film containing 40 wt% clay hardly burned while exposed to a gas-torch flame and instantly self-extinguished.

Nanocoatings have recently been used to try to reduce polymer flammability. Laauchi et al. used LBL deposition to form a nanodispersed layer composed of clay and polyallylamine hydrochloride (PAH) in order to improve substrate flame resistance [98, 99]. The thickness of the (PAH-MMT)$_n$ coating increased with the number of bilayers deposited, and reached 5 μm after 20 bilayers had been deposited. The subscript n means the number of LBL-deposited bilayers. Figure 2.13 shows HRR curves for uncoated and coated PA-6 during a cone calorimetry test. Although the PA-6-(PAH-MMT)$_5$ and PA-6-(PAH-MMT)$_{10}$ HRRs are higher than the uncoated PA-6 one, indicating that the former two combust faster than the latter, the PA-6-(PAH-MMT)$_{20}$ HRR is much lower than the uncoated PA-6 one. The PHRR was reduced by 62 % when only a 5-μm-thick nanolayer was coated onto the PA-6. A >100-μm-thick IFR coating must be coated onto the PP to reduce the PP PHRR to the same level. The nanocoated polymer obviously exhibited highly efficient flame retardancy. Although the fire-retardancy mechanisms for the nanocoating and IFR coating are completely different, both act at the condensed phase, reducing the HRR without changing the THR. IFR swells during combustion and acts as insulation, reducing the amount of heat transported into the substrate. The nanocoating, on the other hand, does not swell like IFR. Therefore, the main nanocoating fire-retardancy mechanism reduces the amounts of fuel gas and oxygen transported to the fire and into the material, respectively. The clay-platelet shape reduces the gas and oxygen diffusion rates by several orders of magnitude owing to the tortuous effect. The nanocomposite layer cannot retard the fire if it fractures during combustion, as in the case of PA-6-(PAH-MMT)$_5$ and PA-6-(PAH-MMT)$_{10}$ (Fig. 2.13). In fact, Laauchi et al. showed that the char layer cracked after the test for PA-6-(PAH-MMT)$_{10}$, and they concluded that the most important factor for producing flame retardant nanocoating is to a form uniform nanodispersed layer that does not fail during combustion. Choosing the proper clay and polymer clay binder and producing a sufficiently thick coating are all important factors in obtaining high-strength char during combustion.

Laufer et al. used LBL deposition to develop a completely green coating composed of clay and chitosan [100]. They applied the coating to a polylactic acid film and polyurethane (PU) foam to improve the oxygen barrier and fire retardancy. Notably, a <100-nm-thick clay-chitosan nanocoating reduced the oxygen

Fig. 2.13 Heat release rate curves as a function of time for coated and uncoated PA6 samples (**a**), cross-section image of 20 BL film residue after burn testing (reprinted from [99]) (**b**)



permeability of a 0.5-mm-thick PLA film by four orders of magnitude. In addition, the 30-nm-thick green nanocoating reduced the PHRR by 52 % and eliminated the secondary peak in the HRR curve. They demonstrated that environmentally benign nanocoatings can prove beneficial for application to new types of food packaging or for replacing environmentally persistent antiflammable compounds.

In addition to clay, carbon-based nanomaterials such as CNT or graphene are candidate nanocoatings to improve substrate flame-retardancies. Wu et al. tried using single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) as ~20 µm thick buckypapers to protect carbon-fiber-reinforced epoxy composites from fire [101]. Although the MWNT buckypaper was an effective flame-retardant shield, SWNT one was not. The MWNT buckypaper reduced the substrate PHRR by ~50 %; the SWNT one, on the other hand, reduced it by <10 %. The SWNT buckypaper effective air diffusivities were superior to the MWNT buckypaper ones owing to the dense SWNT network. However, unlike the MWNT buckypaper, the SWNT buckypaper could not improve the flame retardancy because SWNTs are less thermally stable than MWNTs. In fact, Wu et al. showed that the SWNT buckypaper had burned away during combustion, leaving only a red iron-catalyst residue. The MWNT buckypaper showed high thermal stability and had survived combustion. Liu et al. coated cotton fibers with CNTs and improved the fiber mechanical properties and flame retardancy [102]. They used simple dip-coating to fabricate CNT-network armors on the fiber surface and found that the CNT-coated cotton textiles exhibited enhanced mechanical properties and extraordinary flame retardancy because the CNTs had reinforced and protected the fibers.

Nanocoating technology drastically improves substrate flame retardancy. A thin nanomaterial coating can improve not only substrate fire retardancy but also substrate mechanical properties, gas permeability, and other functionalities such as UV-blocking. However, nanocoating technology must be further developed to improve long-term nanocoating reliability before applying nanocoatings to commercial products. Nanocoating flame-retardancy efficiency diminishes when nanocoatings develop cracks after long-term environment exposure because the main flame-retardancy mechanism involves nanocoatings acting as gas barriers, and cracks of nanolayer degrade the gas barrier property. However, nanocoatings can be powerful tools for improving polymer flame retardanciesy if these problems are solved.

2.5 Conclusions

This review has demonstrated polymer-nanocomposite flame retardancy toward replacing halogenated flame retardants with safe, eco-friendly polymer nanocomposite ones. Nanocomposites should be combined with proper flame retardants to achieve the same flame retardancies that halogenated compounds show. The main nanofiller flame-retardancy mechanism involves nanofillers acting as barriers against gas flow and oxygen diffusion at the condensed phase. Therefore, producing strong, dense, crack-free nanocoating surface layers during combustion is the key factor in producing effective polymer nanocomposite flame retardants. Nanofiller dispersion and distribution are important factors contributing to flame retardancy synergistic effects, which are unobtainable when nanofillers are incorporated into other flame retardants because poor nanofiller distribution scatters surface layers rendering them unable to act as barrier layers. Nanofiller/flame-retardant interactions also contribute to nanofiller flame-retardant efficiency. Dense char networks can form and the nanoreinforced char layers can act as barriers against heat propagation and gas diffusion when nanofillers interact with flame retardants. Combining flame retardants that interact during thermal degradation maximizes ternary-composite flame retardancy. Although nanocoating technology has the potential to minimize material flammabilities, it must be further developed to improve long-term nanocoating reliability before applying nanocoatings to commercial products. The enhanced nanofiller flame retardancies and improved mechanical, gas-barrier, etc. properties of polymer nanocomposite flame retardants may expedite the practical application of such nanocomposites.

References

1. http://www.plasticseurope.org/documents/document/20101006091310-final_plasticsthefacts_28092010_lr.pdf
2. Morgan, A.B., Gilman, J.W.: An overview of flame retardancy of polymeric materials: application, technology, and future directions. Fire Mater. **37**, 259–279 (2013)
3. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.M., Dubois, Ph: New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. Mater. Sci. Eng., R **63**, 100–125 (2009)

4. Dasari, A., Yu, Z.Z., Cai, G.P., Mai, Y.W.: Recent developments in the fire retardancy of polymeric materials. Prog. Polym. Sci. **38**, 1357–1387 (2013)
5. Morgan, A.B.: Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems. Polym. Adv. Technol. **17**, 206–217 (2006)
6. Evonik-industries. Safe fuel lines, http://nano.evonik.com/sites/nanotechnology/en/technology/applications/cnt/pages/default.aspx
7. Stabkovich, S., et al.: Graphene-based composite materials. Nature **442**, 282–286 (2006)
8. Dikin, D.A., et al.: Preparation and characterization of graphene oxide paper. Nature **448**, 457–460 (2007)
9. Potts, J.R., Dreyer, D.R., Bielawski, C.W., Ruoff, R.S.: Graphene-based polymer nanocomposites. Polymer **52**, 5–25 (2011)
10. Kim, H., Abdala, A.A., Macosko, C.W.: Graphene/polymer nanocomposites. Macromolecules **43**, 6515–6530 (2010)
11. Dittrich, B., Wartig, K.A., Hofmann, D., Mülhaupt, R., Schartel, B.: Flame retardancy through carbon nanomaterials; carbon black, multiwall nanotubes, expanded graphite, multi-layer grapheme and grapheme in polypropylene. Polym. Degrad. Stab. **98**, 1495–1505 (2013)
12. Kashiwagi, T., Grulke, E., Hilding, J., Groth, K., Harris, R., Butler, K., Shields, J., Kharchenko, S., Douglas, J.: Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. Polymer **45**, 4227–4239 (2004)
13. Kashiwagi, T., et al.: Nanoparticle networks reduce the flammability of polymer nanocomposites. Nat. Mater. **4**, 928–933 (2005)
14. Kashiwagi, T., Du, F., Winey, K.I., Groth, K.M., Shields, J.R., Bellayer, S.P., Kim, H., Douglas, J.F.: Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration. Polymer **46**, 471–481 (2005)
15. Kashiwagi, T., et al.: Relation between the viscoelastic and flammability properties of polymer nanocomposites. Polymer **49**, 4358–4368 (2008)
16. Cipiriano, B.H., Kashiwagi, T., Raghavan, S.R., Yang, Y., Grulke, E.A., Yamamoto, K., Shields, J.R., Douglas, J.F.: Effect of aspect ratio of MWNT on the flammability properties of polymer nanocomposites. Polymer **48**, 6086–6096 (2007)
17. Schartel, B., Pötschke, P., Knoll, U., Abdel-Goad, A.: Fire behavior of polyamide 6/multiwall carbon nanotube nanocomposites. Eur. Polymer J. **41**, 1061–1070 (2005)
18. Barus, S., Zanetti, M., Bracco, P., Musso, S., Chiodoni, A., Tagliaferro, A.: Influence of MWCNT morphology on dispersion and thermal properties of polyethylene nanocomposites. Polym. Degrad. Stab. **95**, 756–762 (2010)
19. Wen, X., Wang, Y., Gong, J., Liu, J., Tian, N., Wang, Y., Jiang, Z., Qiu, J., Tang, T.: Thermal and flammability properties of polypropylene/carbon black nanocomposites. Polym. Degrad. Stab. **97**, 793–801 (2012)
20. Wen, X., Tian, N., Gong, J., Chen, Q., Qi, Y., Liu, Z., Liu, J., Jiang, Z., Chen, X., Tang, T. Effect of nanosized carbon black on thermal stability and flame retardancy of polypropylene/carbon nanotubes nanocomposites. Polym. Adv. Technol. (2013). doi:1002/pat.3172
21. Villmow, T., Kretzschmar, B., Pötschke, P.: Influence of screw configulation, residence time, and specific mechanical energy in twin-screw extrusion of polycaprolactone/multi-walled carbon nanotube composites. Compos. Sci. Technol. **70**, 2045–2055 (2010)
22. Alig, I., Pötschke, P., Lellinger, D., Skipa, T., Pegel, S., Kasaliwal, G.R., Villmow, T.: Establishment, morphology and properties of carbon nanotube networks in polymer melts. Polymer **53**, 4–28 (2012)
23. Kasaliwal, G.R., Pegel, S., Göldel, A., Pötschke, P., Heinrich, G.: Analysis of agglomerate dispersion mechanisms of multiwalled carbon nanotubes during melt mixing in polycarbonate. Polymer **51**, 2708–2720 (2010)
24. Paul, D.R., Robeson, L.M.: Polymer nanotechnology: nanocomposites. Polymer **49**, 3187–3204 (2008)
25. Qin, H., Zhang, S., Zhao, C., Hu, G., Yang, M.: Flame retardant mechanism of polymer/clay nanocomposites based on polypropylene. Polymer **46**, 8386–8395 (2005)

26. Kashiwagi, T., Harris Jr, R.H., Zhang, X., Briber, R.M., Cipriano, B.H., Raghavan, S.R., Awad, W.H., Shields, J.R.: Flame retardant mechanism of polyamide 6-clay nanocomposites. Polymer **45**, 881–891 (2004)
27. Zhu, J., Uhl, F.M., Morgan, A.B., Wilkie, C.A.: Studies on the mechanism by which the formation of nanocomposites enhances thermal stability. Chem. Mater. **13**, 4649–4654 (2001)
28. Bartholmai, M., Schartel, B.: Layered silicate polymer nanocomposites: new approach or illusion for fire retardancy? Investigations of the potensials and the tasks using a model system. Polym. Adv. Technol. **15**, 355–364 (2004)
29. Song, R., Wang, Z., Meng, X., Zhang, B., Tang, T.: Influence of catalysis and dispersion of organically modified montmorillonite on flame retardancy of polypropylene nanocomposites. J. Appl. Polym. Sci. **106**, 3488–3494 (2007)
30. Hu, Y., Tang, Y., Song, L.: Poly(propylene)/clay nanocomposites and their application in flame retardancy. Polym. Adv. Technol. **17**, 235–245 (2006)
31. Fina, A., Cuttica, F., Camino, G.: Ignition of polypropylene/montmorillonite nanocomposites. Polym. Degrad. Stab. **97**, 2619–2626 (2012)
32. Zhang, J., Bai, M., Wang, Y., Xiao, F.: Featured structures of fire residue of high-impact polystyrene/organically modified montmorillonite nanocomposites during burning. Fire Mater. **36**, 661–670 (2012)
33. Liu, J., Fu, M., Jing, M., Li, Q.: Flame retardancy and charring behavior of polystyrene-organic montmorillonite nanocomposites. Polym. Adv. Technol. **24**, 273–281 (2013)
34. Zhao, C., Qin, H., Gong, F., Feng, M., Zhang, S., Yang, M.: Mechanical, thermal and flammability properties of polyethylene/clay nanocomposites. Polym. Degrad. Stab. **87**, 183–189 (2005)
35. Wang, S., Hu, Y., Zhongkai, Q., Wang, Z., Chen, Z., Fan, W.: Preparation and flammability properties of polyethylene/clay nanocomposites by melt intercalation method from Na+ montmorillonite. Mater. Lett. **57**, 2675–2678 (2003)
36. Zhang, J., Wilkie, C.A.: Preparation and flammability properties of polyethylene-clay nanocomposites. Polym. Degrad. Stab. **80**, 163–169 (2003)
37. Gilman, J.W., Jackson, C.L., Morgan, A.B., Harris Jr, R.H.: Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. Chem. Mater. **12**, 1866–1873 (2000)
38. Zhu, J., Start, P., Mauritz, K.A., Wilkie, C.A.: Thermal stability and flame retardancy of poly(methyl methacrylate)-clay nanocomposites. Polym. Degrad. Stab. **77**, 253–258 (2002)
39. Jash, P., Wilkie, C.A.: Effects of surfactants on the thermal and fire properties of poly(methyl methacrylate)/clay nanocomposites. Polym. Degrad. Stab. **88**, 401–406 (2005)
40. Sahoo, P.K., Samal, R.: Fire retardancy and biodegradability of poly(methyl methacrylate)/montmorillonite nanocomposite. Polym. Degrad. Stab. **92**, 1700–1707 (2007)
41. Jang, B.N., Costache, M., Wilkie, C.A.: The relationship between thermal degradation behavior of polymer and the fire retardancy of polymer/clay nanocomposites. Polymer **46**, 10678–10687 (2005)
42. Kashiwagi, T., Shields, J.R., Harris Jr, R.H., Davis, R.D.: Flame-retardant mechanism of silica: effects of resin molecular weight. J. Appl. Polym. Sci. **87**, 1541–1553 (2003)
43. Samyn, F., Bourbigot, S., Jama, C., Bellayer, S.: Fire retardancy of polymer clay nanocomposites: is there an influence of the nanomorphology? Polym. Degrad. Stab. **93**, 2019–2024 (2008)
44. Szustakiewicz, K., Kiersnowski, A., Gazińska, M., Bujnowicz, K., Pigłowski, J.: Flammability, structure and mechanical properties of PP/OMMT nanocomposites. Polym. Degrad. Stab. **96**, 291–294 (2011)
45. Zhang, J., Lewin, M.: Pearce Eli, Zammarano M, Gliman JW. Flame retarding polyamide 6 with melamine cyanurate and layered silicates. Polym. Adv. Technol. **19**, 928–936 (2008)
46. Kiliaris, P., Papaspyrides, C.D., Pfaendner, R.: Polyamide 6 filled with melamine cyanurate and layered silicates: Evaluation of flame retardancy and physical properties. Macromol. Mater. Eng. **293**, 740–751 (2008)
47. Hu, Y., Wang, S., Ling, Z., Zhuang, Y., Chen, Z., Fan, W.: Preparation and combustion properties of flame retardant nylon 6/montmorillonite nanocomposite. Macromol. Mater. Eng. **288**, 272–276 (2003)

48. Chen, Y., Guo, Z., Fang, Z.: Relationship between the distribution of organo-montmorillonite and the flammability of flame retardant polypropylene. Polym. Eng. Sci. **52**, 390–398 (2012)
49. Zanetti, M., Camino, G., Canavese, D., Morgan, A.B., Lamelas, F.J., Wilkie, C.A.: Fire retardant halogen-antimony-clay synergism in polypropylene layered silicate nanocomposites. Chem. Mater. **14**, 189–193 (2002)
50. Chen, X., Yu, Z., Zhang, S.: Synergistic effect of decarbomodiphenyl ethane and montmorillonite on flame retardancy of polypropylene. Polym. Degrad. Stab. **94**, 1520–1525 (2009)
51. Si, M., Zaitsev, V., Goldman, M., Frenkel, A., Peiffer, D.G., Weil, E., Sokolov, J.C., Rafailovich, M.H.: Self-extinguishing polymer/organoclay nanocomposites. Polym. Degrad. Stab. **92**, 86–93 (2007)
52. Lu, H., Wilkie, C.A.: Synergistic effect of carbon nanotubes and decabromodiphenyl oxide/ Sb_2O_3 in improving the flame retardancy of polystyrene. Polym. Degrad. Stab. **95**, 564–571 (2010)
53. Chigwada, G., Jash, P., Jiang, D.D., Wilkie, C.A.: Synergy between nanocomposite formation and low levels of bromine on fire retardancy in polystyrenes. Polym. Degrad. Stab. **88**, 382–393 (2005)
54. Du, B., Ma, H., Fang, Z.: How nano-fillers affect thermal stability and flame retardancy of intumescent flame retarded polypropylene. Polym. Adv. Technol. **22**, 1139–1146 (2011)
55. Du, B., Fang, Z.: Effects of carbon nanotubes on the thermal stability and flame retardancy of intumescent flame-retarded polypropylene. Polym. Degrad. Stab. **96**, 1725–1731 (2011)
56. Isitman, N.A., Kaynak, C.: Nanoclay and carbon nanotubes as potential synergists of an organophosphorus flame-retardant in poly(methyl methacrylate). Polym. Degrad. Stab. **95**, 1523–1532 (2010)
57. Ma, H., Tong, L., Xu, Z., Fang, Z.: Intumescent flame retardant-montmorillonite synergism in ABS nanocomposites. Appl. Clay Sci. **42**, 238–245 (2008)
58. Du, B., Guo, Z., Song, P., Liu, H., Fang, Z., Wu, Y.: Flame retardant mechanism of organo-bentonite in polypropylene. Appl. Clay Sci. **45**, 178–184 (2009)
59. Du, B., Guo, Z., Fang, Z.: Effects of organo-clay and sodium dodecyl sulfonate intercalated layered double hydroxide on thermal and flame behavior of intumescent flame retarded polypropylene. Polym. Degrad. Stab. **94**, 1979–1985 (2009)
60. Huang, G., Zhu, B., Shi, H.: Combination effect of organics-modified montmorillonite with intumescent flame retardants on thermal stability and fire behavior of polyethylene nanocomposites. J. Appl. Clay Sci. **121**, 1285–1291 (2011)
61. Isitman, N.A., Gunduz, H.O., Kaynak, C.: Nanoclay synergy in flame retarded/glass fibre reinforced polyamide 6. Polym. Degrad. Stab. **94**, 2241–2250 (2009)
62. Chen, Y., Fang, Z., Yang, C., Wang, Y., Guo, Z., Zhang, Y.: Effect of clay dispersion on the synergism between clay and intumescent flame retardants in polystyrene. J. Appl. Polym. Sci. **115**, 777–783 (2010)
63. Szustakiewicz, K., Kiersnowski, A., Grazuńska, M., Bujnowicz, K., Pigłowski, J.: Flammability, structure and mechanical properties of PP/OMMT nanocomposites. Polym. Degrad. Stab. **96**, 291–294 (2011)
64. Chigwada, G., Wilkie, C.A.: Synergy between conventional phosphorus fire retardants and organically-modified clays can lead to fire retardancy of styrenics. Polym. Degrad. Stab. **80**, 551–557 (2003)
65. Hu, Y., Tang, Y., Song, L.: Poly(propylene)/clay nanocomposites and their application in flame retardancy. Polym. Adv. Technol. **17**, 235–245 (2006)
66. Cinausero, N., Azema, N., Lopez-Cuesta, J.M., Cochez, M., Ferriol, M.: Synergistic effect between hydrophobic oxide nanoparticles and ammonium polyphosphate on fire properties of poly(methyl methacrylate) and polystyrene. Polym. Degrad. Stab. **96**, 1445–1454 (2011)
67. Li, N., Mao, Z., Wang, L., Guan, Y., Zheng, A.: Influence of antimony oxide on flammability of polypropylene/intumescent flame retardant system. Polym. Degrad. Stab. **97**, 1737–1744 (2012)
68. Wu, N., Yang, R.: Effects of metal oxides on intumescent flame retardant polypropylene. Polym. Adv. Technol. **22**, 495–501 (2011)

69. Beyer, G.: Flame retardancy of nanocomposites based on organoclays and carbon nanotubes with aluminium trihydrate. Polym. Adv. Technol. **17**, 218–225 (2006)
70. Yen, Y.Y., Wang, H.T., Guo, W.J.: Synergistic flame retardant effect of metal hydroxide and nanoclay in EVA composites. Polym. Degrad. Stab. **97**, 863–869 (2012)
71. Laoutid, F., Gaudon, P., Taulemesse, J.M., Lopez-Cuesta, J.M., Velasco, J.L., Piechaczyk, A.: Study of hydromagnesite and magunesium hydroxide based fire retardant systems for ethylene-vinyl acetate containing organo-modified montmorillonite. Polym. Degrad. Stab. **91**, 3074–3082 (2006)
72. Witkowski, A., Stec, A.A., Hull, R.: The influence of metal hydroxide fire retardants and nanoclay on the thermal decomposition of EVA. Polym. Degrad. Stab. **97**, 2231–2240 (2012)
73. Ye, L., Wu, Q., Qu, B.: Synergistic effects and mechanism of multiwalled carbon nanotubes with magnesium hydroxide in halogen-free flame retardant EVA/MH/MWNT nanocomposite. Polym. Degrad. Stab. **94**, 751–756 (2009)
74. Hong, C.H., Lee, Y.B., Bae, J.W., Jho, J.Y., Nam, B.U., Nam, G.J., Lee, K.J.: Tensile and flammability properties of polypropylene-based RTPO/clay nanocomposites for cable insulating materials. J. Appl. Polym. Sci. **97**, 2375–2381 (2005)
75. Kong, Q., Hu, Y., Song, L., Yi, C.: Synergistic flammability and thermal stability of polypropylene/aluminum trihydroxide/Fe-montmorillonite nanocomposites. Polym. Adv. Technol. **20**, 404–409 (2009)
76. Zhang, J., Wilkie, C.A.: Fire retardancy of polyethylene-alumina trihydrate containing clay as a synergist. Polym. Adv. Technol. **16**, 549–553 (2005)
77. Isitman, N.A., Kaynak, C.: Tailored flame retardancy via nanofiller dispertion state: Synergistic action between a conventional flame-retardant and nanoclay in high-impact polystyrene. Polym. Degrad. Stab. **95**, 1759–1768 (2010)
78. Goodarzi, V., Monemian, S.A., Angaji, M.T., Motahari, S.: Improvement of thermal and fire properties of polypropylene. J. Appl. Polym. Sci. **110**, 2971–2979 (2008)
79. Zaharescu, T., Jipa, S., Kappel, W., Supaphol, P.: The control of thermal and radiation stability of polypropylene containing calcium carbonate nanoparticles. Macromol. Symp. **242**, 234–319 (2006)
80. Ma, H., Tong, L., Xu, Z., Fang, Z.: Synergistic effect of carbon nanotube and clay for improving the flame retardancy of ABS resin. Nanotechnology **18**, 375602 (2007)
81. Peeterbroeck, S., Dubois, Ph, et al.: Polymer-layered silicate-carbon nanotube nanocomposites: unique nanofiller synergistic effect. Compos. Sci. Technol. **64**, 2317–2323 (2004)
82. Hapuarachchi, T.D., Peijs, T., Bilotti, E.: Thermal degradation and flammability behavior of polypropylene/clay/carbon nanotube composite systems. Polym. Adv. Technol. **24**, 331–338 (2013)
83. Weil, E.D.: Fire-protective and flame-retardant coatings-a state-of-the-art review. J. Fire Sci. **29**, 259–296 (2011)
84. Liang, S., Neisius, N.M., Gaan, S.: Recent development in flame retardant polymeric coatings. Prog. Org. Coat. **76**, 1642–1655 (2013)
85. Duquesne, S., Jimenez, M., Bourbigot, S. Aging of the flame-retardant properties of polycarbonate and polypropylene protected by an intumescent coating. J. Appl. Polym. Sci. (2013). doi:10.1002/app.39566
86. Vargas, J.R., Gracia, T., Goto, T.: Thermal barrier coatings produced by chemical vapor deposition. Sci. Technol. Adv. Mater. **4**, 397–402 (2003)
87. Jimenez, M., Duquesne, S., Bourbigot, S.: Fire protection of polypropylene and polycarbonate by intumescent coatings. Polym. Adv. Technol. **23**, 130–135 (2012)
88. Wang, X.Y., Han, E.H., Liu, F.C., Ke, W.: Fire and corrosion resistances of intumescent nano-coating containing nano-SiO_2 in salt spray condition. J. Mater. Sci. Technol. **26**, 75–81 (2010)
89. Wang, X.Y., Han, E.H., Ke, W.: Fire-resistant effect of nanoclay on intumescent nanocomposite coating. J. Appl. Polym. Sci. **103**, 1681–1689 (2007)
90. Gusev, A.A., Lusti, R.: Rational design of nanocomposite for barrier applications. Adv. Mater. **13**, 1641–1643 (2001)

91. Ebina, T., Mizukami, F.: Flexible transparent clay film with heat-resistant and high gas-barrier properties. Adv. Mater. **19**, 2450–2453 (2007)
92. Priolo, M.A., Gamboa, D., Holder, K.M., Grunlan, J.C.: Super gas barrier of transparent polymer-clay multilayer ultrathin films. Nano Lett. **10**, 4970–4974 (2010)
93. Walther, A., Bjurhager, I., Malho, J.M., Pere, J., Ruokolainen, J., Berglund, L.A., Ikkala, O.: Large-area, lightweight and thick biomimetic composites with superior material properties via fast, economic, and green pathways. Nano Lett. **10**, 2742–2748 (2010)
94. Das, P., Schipmann, S., Malho, J.M., Zhu, B., Klemradt, U., Walther, A.: Facile access to large-scale, self-assembled, narcre-inspired, high-performance materials with tunable nanoscale periodicities. ACS Appl. Mater. Interfaces **5**, 3738–3747 (2013)
95. Liu, A., Walther, A., Ikkala, O., Belova, L., Berglund, L.A.: Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions. Biomacromolecules **12**, 633–641 (2011)
96. Podsiadlo, P., et al.: Ultrastrong and stiff layered polymer nanocomposites. Science **318**, 80–83 (2007)
97. Putz, K.W., Compton, O.C., Palmeri, M.J., Nguyen, S.T., Brinson, L.C.: High-nanofiller-content grapheme oxide-polymer nanocomposites via vacuum-assisted self-assembly. Adv. Funct. Mater. **20**, 3322–3329 (2010)
98. Laachachi, A., Ball, V., Apaydin, K., Toniazzo, V., Ruch, D.: Diffusion of polyphosphates into (poly(allylamine)-montmorillonite) multilayer films: Flame retardant-intumescent films with improved oxygen barrier. Langmuir **27**, 13879–13887 (2011)
99. Apaydin, K., Laauchachi, A., Ball, V., Jimenez, M., Bourbigot, S., Toniazzo, V., Ruch, D.: Polyallylamine-montmorillonite as super flame retardant coating assemblies by layer-by layer deposition on polyamide. Polym. Degrad. Stab. **98**, 627–634 (2013)
100. Laufer, D., Kirkland, C., Cain, A.A., Grunlan, J.C.: Clay-chitosan nanobrick walls: Completely renewable gas barrier and flame-retardant nanocoatings. ACS Appl. Mater. Interfaces **4**, 1643–1649 (2012)
101. Wu, Q., Zhu, W., Liang, Z., Wang, B.: Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites. Carbon **48**, 1799–1806 (2010)
102. Liu, Y., Wang, X., Qi, K., Xin, J.H.: Functionalization of cotton with carbon nanotubes. J. Mater. Chem. **18**, 3454–3460 (2008)