

Chapter 12

Polymer–Clay Nanocomposites: A Novel Way to Enhance Flame Retardation of Plastics and Applications in Wire and Cable Industry

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12.1 Introduction

Polymer nanocomposites are a new class of materials that have demonstrated unique performance properties which conventional composites cannot offer. These properties can be achieved with minimum addition of the nanodimensional fillers/additives. Polymer nanocomposites are commonly defined as the combination of a polymer matrix and fillers that have at least one dimension in the 100-nanometer or smaller-size range. Polymers with nano-sized inorganic fillers are the most widely researched materials in the last 15–20 years. Flame retardation is one of the most significant performance properties of polymer nanocomposite materials along with other enhanced properties such as mechanical reinforcement, barrier properties, and dimensional stability.

Polymer–clay nanocomposites are the most studied materials up to date. Montmorillonite is the widely used clay particle as filler/additives to make polymer–clay nanocomposite. Addition of a few percentage of organic-modified montmorillonite can effectively reduce the peak heat release rate (HRR) of the polymer in a standard cone calorimeter testing. The reduced HRR indicates the reduction of the flammability of the plastic and allows formulators to form new flame-retardant plastics in combination with the reduced amount of the traditional flame retardants. The formation of polymer–clay nanocomposite in low-smoke halogen-free (LSOH) compounds also reduces the heat generated in the cable burning test. This allows cables to pass newly approved EU's Construction Product Regulation.

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12.2 Bentonite Clay Surface Chemistry

Montmorillonite clays can be extracted or purified from mined bentonite ores. The best purification method is disclosed in AMCOL's patent US Patent 6,050,509 [1]. Purified montmorillonite has more than 98 % purity with defined cation exchange capacity for the subsequent clay surface modification. Montmorillonite has layered structure (Fig. 12.1), with each platelet consisting of octahedral alumina sheets sandwiched between two tetrahedral silica sheets. The alumina sheet has partial replacement of aluminum cations (Al^{3+}) by magnesium (Mg^{2+}) which provides a net negative charge to the platelet. The negative charge is balanced by inorganic cations like Na^+ or Ca^{2+} , and these cations are typically hydrated and the clay inner surface is hydrophilic. Ion exchange reaction is the easiest way to modify the montmorillonite clay to hydrophobic. Hydrophobic montmorillonite clays are also commonly called as organoclay. Various alkyl ammonium cations are used to modify the montmorillonite clay to allow inner layer compatibility with various polymer resins. The organic modification is the key modifying montmorillonite from hydrophilic to hydrophobic. Figure 12.2 shows the schematic ion exchange diagram. The exchange reaction is carried out in a media like water or mixture of water and some organic solvents.

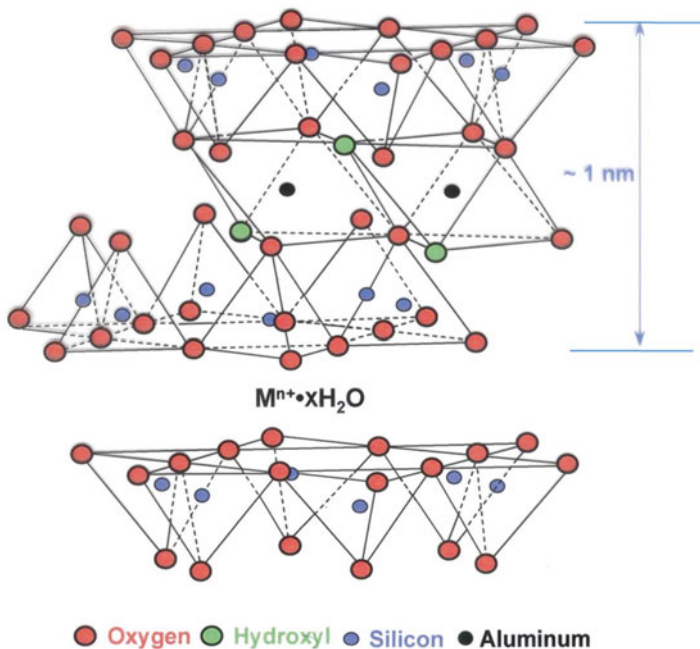


Fig. 12.1 Structure of 2:1 layered silicate like montmorillonite clay

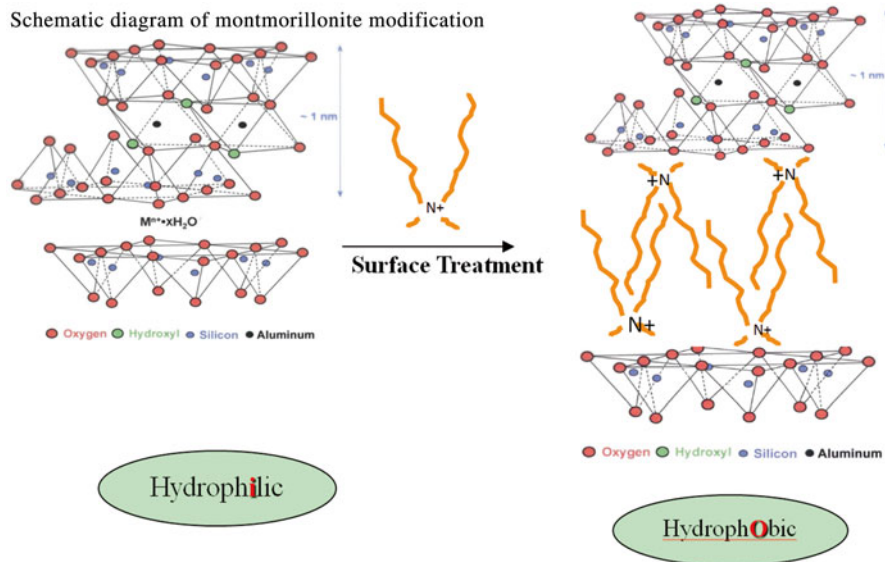


Fig. 12.2 Schematic of the formation of organoclay via ion exchange reaction

Quaternary ammonium, dimethyl dihydrogenated tallow ammonium chloride (DMDHT), is one of the most commonly used surface modifications. The ionic bonding of DMDHT to the clay negatively charged surface is quite strong. NaCl, as the ion exchange reaction by-product will be washed out from the clay. After surface modification, the inner layer region of the clay is hydrophobic. After ion exchange with organic treatment, montmorillonite clays are supplied in an agglomerate form. There are a few commercial products based on DMDHT treatment chemistry, like Nanomer[®] I.44P, Cloisite[®] 15A, and 20A. Other quaternary ammoniums like trimethyl hydrogenated tallow ammonium (TMHT), dimethyl benzyl hydrogenated tallow (DMBHT), and methyl benzyl di-hydrogenated tallow (MBDHT) are also used to make organoclay products. Although alkyl quaternary ammonium is suitable for most of the organoclay modification, however, the nature of the chemical also creates a limitation. The most significant limitation is the heat stability. Traditional organoclays with quaternary ammonium like DMDHT as exchange cations were considered with a heat stability only up to 200 °C [2]. Even with special selection of chemical and refined processing, the heat stability can only be improved to 240 °C. This is mainly due the Hoffman elimination reaction associated to the quaternary ammonium. Attempt to increase the heat stability has been a hot topic with emphasis on the use of quaternary phosphonium chemistry (Fig. 12.3).

We selected primary amine (octadecyl amine, ODA) to improve the heat stability of our organoclay due to the fact that primary amine does not undergo Hoffman elimination reaction upon heating. Octadecyl amine was protonated by HCl and dissolved in water for the cation exchange reaction. Octadecyl amine-modified

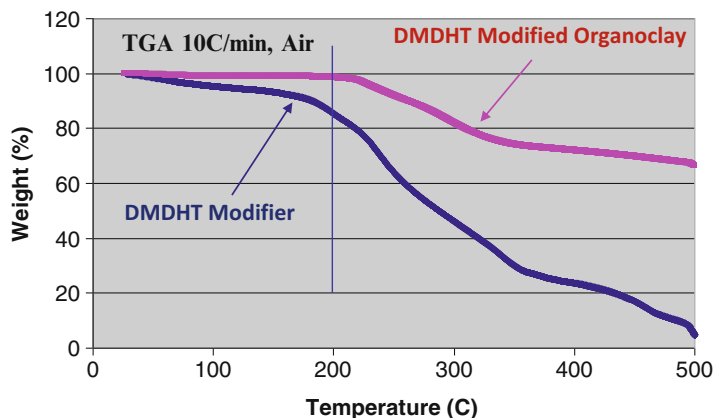


Fig. 12.3 TGA of dimethyl dihydrogenated tallow (DMDHT) ammonium chloride and DMDHT-modified organoclay, 10C/min, in air

organoclay has good hydrophobic properties like other organoclays to allow polymer to invade its interlayer resin to form nanocomposite materials.

Isothermal TGA was used to study the heat stability of the organoclay. In this method, we heat the sample rapidly at 50 °C/min to 250 °C or 300 °C and then hold the temperature to record the weight loss of the organoclay at these temperatures. This testing is similar to the heat experience of an organoclay experienced in a polymer extrusion process. In Fig. 12.4a, b, we report the weight losses of the traditional DMDHT-modified organoclay and the weight loss of ODA-modified montmorillonite clay. The ODA-modified organoclay has much better improved heat stability. Table 12.1 summarizes the heat stability results of DMDHT- and ODA-modified organoclays. For ODA-modified clay, the weight loss at 250 °C isotherm is only 0.8 % at 5 min compared to 8 % weight loss of DMDHT-modified organoclay. At 300 °C isotherm, ODA-modified organoclay has 5 % weight loss versus 15 % weight loss of DMDHT-modified organoclay. Considering 5 min as residence time of a typical plastic processing, the organoclay with ODA can be used for processing up to 280 °C, whereas organoclay with DMDHT can only be used at 220 °C. Organoclay with ODA may be suitable to use in engineering thermal plastics like polyamides and polyester to create new flame-retardant compounds.

After ion exchange reaction, the organoclay was dewatered and dried and milled. The final process should yield final product in a fine powder form. Air classification is recommended to remove the large particle in these milled products. The mean particle size is normally in the range of 15–20 µm. Given that particle size is a distribution of particles, the top size (99 % of the clay particle sizes) should be less than 60 µm.

Coordination chemistry has been used to modify the bentonite clay inner surface with dipole–dipole interaction [3]. Combination of flame-retardant like resorcinol diphenyl phosphate oligomer with pristine Na-montmorillonite shows potential use as resin compatibilizer and flame-retardant additives [4]. The reaction is carried out in semisolid environment. Phosphate ester was mixed with montmorillonite with addition of water. The mixture was processed in a continuous mixer or

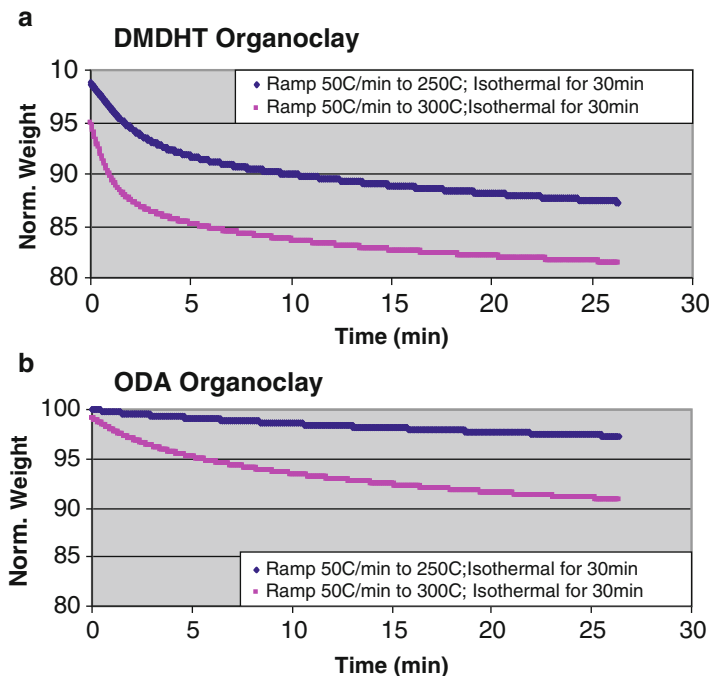


Fig. 12.4 (a, b) Isothermal TGA of DMDHT- and ODA-modified montmorillonite clays

Table 12.1 Weight loss of DMDHT and ODA organoclays

Samples (TGA, 50C/min to ISO temperature)	Weight loss at 250 °C	Weight loss at 300 °C	Max. compounding temp (°C)
	5 min	5 min	
DMDHT organoclay	8.0 %	15 %	220
ODA organoclay	0.8 %	5 %	280

extruder. Finished products were obtained with subsequent drying and milling. Figure 12.5 shows the phosphate ester Phosflex[®] 418-modified montmorillonite (Charex 418515). The d_{001} was increased to 26 Å from 12 Å of the original clay. TGA of Phosflex[®] 418-modified montmorillonite is shown in Fig. 12.6. The decomposition profile is quite similar to the phosphate ester decomposition. SEM image (Fig. 12.7) reveals the morphological nature of the modified clay.

12.3 Nanocomposite Formation and Structure

Preparation of polymer–clay nanocomposite has been a hot topic for polymer chemist and polymer-processing engineers in the two decades. Generally speaking, the process involves de-agglomerate micron-size organoclay and introduces nanoscale

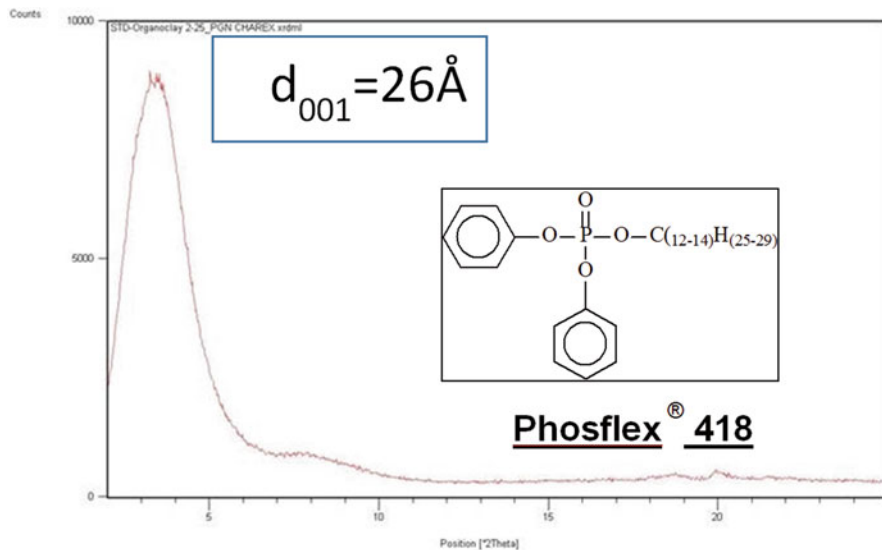


Fig. 12.5 XRD of dialkyl phosphate ester (Phosflex 418)-modified montmorillonite clay

Sample: PGN-418 5-2 SO050212B
 Size: 19.5780 mg
 Method: Cetco Hi-res 100C/min-1000C

TGA

File: C:\...\Scott\PNG-418 5-2 SO0212b.001
 Operator: SO
 Run Date: 07-May-2010 09:18
 Instrument: TGA Q5000 V3.15 Build 263

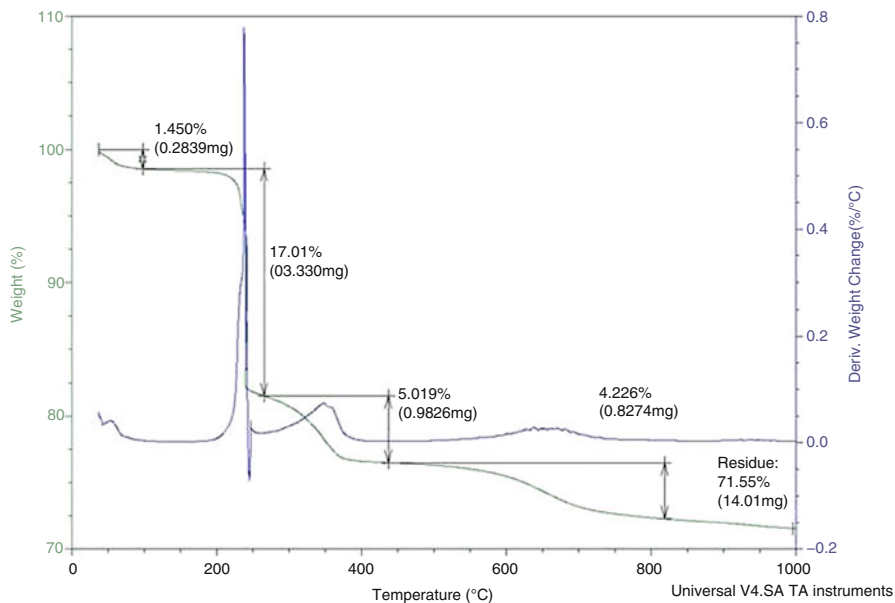


Fig. 12.6 TGA of dialkyl phosphate ester (Phosflex 418)-modified montmorillonite clay

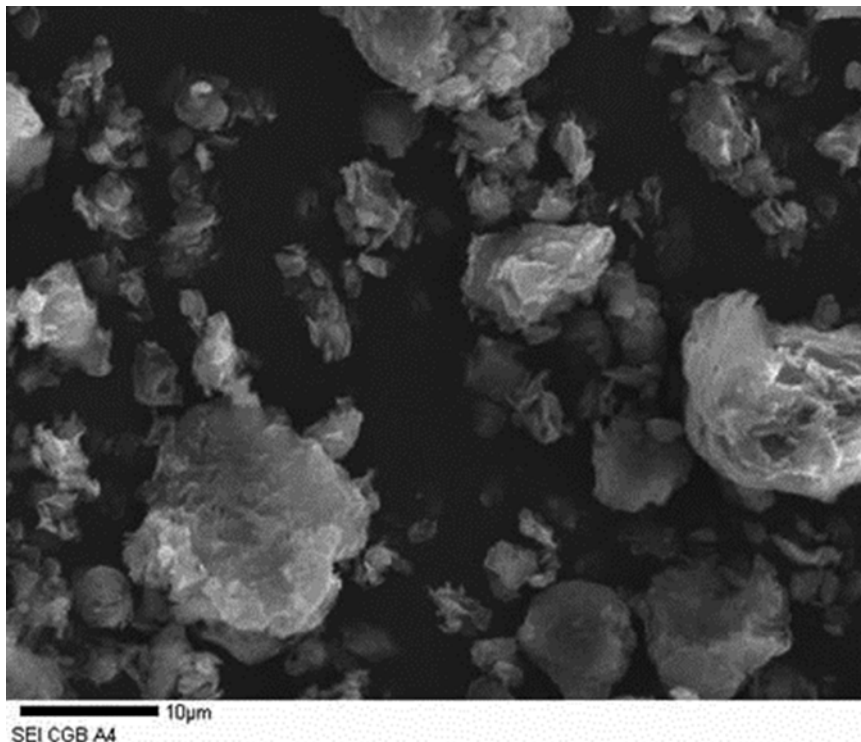


Fig. 12.7 SEM of dialkyl phosphate ester (Phosflex 418)-modified montmorillonite clay

interaction between polymer matrix and organoclay. The nanoscale interaction is caused by the insertion or intercalation of melt polymers into the hydrophobic region of the inner layer space of the organoclays. Monomer or oligomer can be used as starting materials to achieve the interaction followed by polymerization induced by heat or other means. This process is called in situ polymerization process. The first commercial polymer–clay nanocomposite technology developed by Toyota researchers was to use monomer in situ polymerization in organoclay [5]. It has been proven that the polyamide 6 monomer, caprolactam molecules, can enter the inner gallery resins before the polymerization. In the polymerization process, due the presence of polymer catalyst in the clay gallery, continuous migration of monomers into the gallery resin will expand the organoclay gallery further to a degree of delamination or exfoliation. The clay silicate clay stacking was disturbed by the presence of the polymers formed in the inner layer gallery region. Several attempts to use in situ polymerization of polymer–clay nanocomposites have been reported for both thermoset and thermoplastic resins.

Polymer–clay nanocomposite can also be formed with preformed polymer interaction with organoclays. The hydrophobicity of the organoclay provides an organic moiety to allow nanoscale interaction of resin molecules with silicate layers of the

organoclay. The inner layer spacing expands to a certain degree to accommodate the intercalated polymer. However, most of the case, the silicate layer stacking is still regular. The regular stacking can be measured by standard powder X-ray diffraction technique. The polymer melt interaction into the organoclay is illustrated in Fig. 12.8. The X-ray basal spacing (d_{001}) will increase to d'_{001} . Similarly to d_{001} , which is determined by the clay charge density and chain length of the alkyl ammonium in the bentonite clay treatment, d'_{001} is governed by the chain length of the alkyl chain in the surface treatment. In addition, it is also determined by the shear force in the melt extrusion. The X-ray diffraction peak may become broad under high-shear processing condition, indicating less stacking order of the silicate layer in the composite. For flame retardation, the intercalation is more important than exfoliation. The intercalation enables the polymer to form smaller domain size in the composite. It is unlikely the polymers existing in separated intercalated clay layer regions to have a chance to recombine to form bulk polymer. Therefore, the presence of the silicate clay layers reduces the tendency of the dripping when the composite is exposed to fire or other heat sources. In addition, the polymer also has different decompose mechanisms once they are intercalated into the clay inner layer region. The restricted space enables free radicals to reform stable molecules. This process will eventually allow the polymer to form large amount of char deposited on the clay layer surfaces. Figure 12.9 shows the surface morphology of burned EVA–clay nanocomposite. The EVA–clay nanocomposite was lighted by a burner in ambient condition and allows it to burn to the end naturally. The residual sample is char-like. The char is about two to three times as the loading level of the organoclay in the sample. For instance, the remaining weight is 10–15 wt% of original sample weight with 5 wt% organoclay loading. Clearly, not all EVA was burned into H_2O and CO_2 in burning process. The presence of the clay enables char formation of the EVA in the burning process. The reduced burning fuel and burning intensity allows regular flame retardant to perform better to stop extinguish the fire.

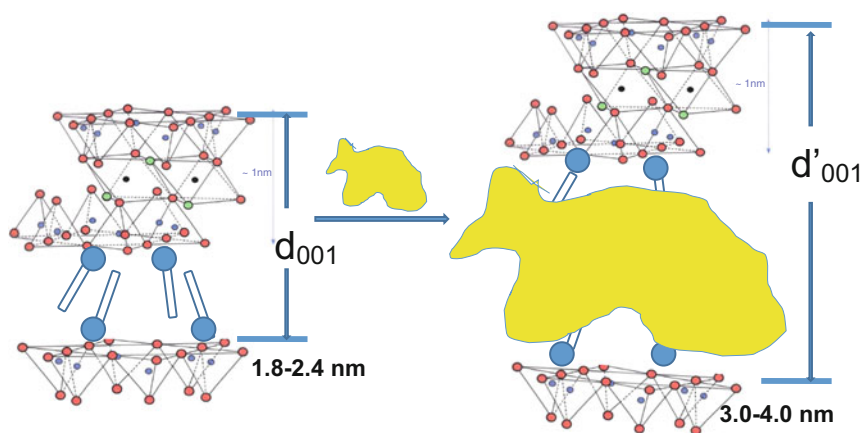


Fig. 12.8 Schematic of the polymer interaction into organoclay and nanocomposite formation process

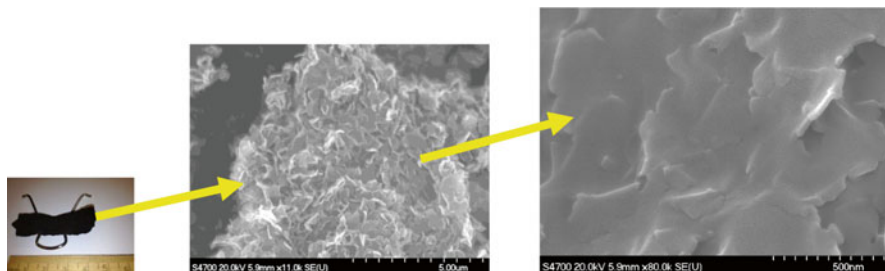


Fig. 12.9 Morphology of burned EVA–clay nanocomposite

Polar polymers like EVA (ethylene vinyl acetate) or EBA (ethylene butyl acrylate) are very easy to form nanocomposite under regular melt-compounding process. Low-polarity polymers like polyethylene and polypropylene have difficulty to enter the organoclay inner gallery region until assisted by modified polyethylene and polypropylene. Maleic-anhydride grafted PE or PP resins are commonly used as compatibilizer to facilitate organoclay dispersion and polymer insertion to the inner gallery region. The selection of PP-g-MA and processing conditions has significant impact in the performance of final PP nanocomposites [6]. Masterbatch process has been developed to minimize and eliminate these concerns [7]. A typical nanoclay masterbatch product contains 30–50 % of organoclay. These organoclay masterbatch products can be used with ease in commercial processing equipment. For flame retardation compounds, these master batches can be used as regular additive masterbatch at the compounding and injection molding process in combination with other additives and fillers.

12.4 Flame Retardation of Polymer–Clay Nanocomposites

The first flame retardation of polymer–clay nanocomposite material was reported by Dr. Jeff Gilman and others at NIST publication [8] “Interactions of Polymers with Fillers and Nanocomposites, NIST, June 18-19, 1998: A Workshop Report.” In their report, they disclosed that both exfoliated and intercalated nanocomposites reduce the flammability of polymer-layered silicate (clay) nanocomposites. In studying the flame-retardant effect of the nano-dispersed clays, XRD and TEM analysis identified a nano-reinforced protective silicate/carbon-like high-performance char from the combustion residue that provides a physical mechanism of flammability control. The report also disclosed that “the nanocomposite structure of the char appears to enhance the performance of the char layer. This char layer may also act as an “insulation and mass transport barrier slowing the escape of the volatile products generated as the polymer decomposes.” Cone calorimetry was used to study the flame retardation. The HRR (heat release rate) of thermoplastic and thermoset polymer-layered silicate nanocomposites are reduced by 40–60 % in

delaminated or intercalated nanocomposites containing a very low silicate mass fraction of only 2–6 wt%. Based on their expertise and experience in the plastic flammability, they concluded that the polymer–clay nanocomposite is a very promising new method for flame retarding polymers. In addition, they predict that the addition of organoclay into plastics has little or no drawbacks associated with other additives. That is, the physical properties are not degraded by the additive (silicate); instead, they are improved. Regarding to the mechanism of flame retardation of organoclay, they concluded that the nanocomposite structure of the char appears to enhance the performance of the char layer. This layer may act as an insulator and a mass transport barrier showing the escape of the volatile products generated as the polymer decomposes.

Nanocomposites based on EVA are the most widely studied system for flame retardation due to easy processing and wide use in low smoke halogen-free compound (LSOH) [9]. Flame retardation of EVA–clay nanocomposite was reported from Cone calorimetry study (Fig. 12.10) with a heat flux of 35 kW/m^2 . Under such conditions, the flame-retardant effect of the organoclay was already observed for 3 % organoclay loading level. With increased amount of the organoclay to 5 %, a significant decrease by 47 % of the PHRR compared to the neat EVA was achieved. In addition, the time to reach the PHRR was also delayed. Further increasing the organoclay content from 5 to 10 % did not significantly improve the reduction of the PHRR. However, the higher clay loading level prolongs the onset of the second burning level peak. Most of the case, the second burning peak is related to the fracture of the char to allow new flame to develop. This also quantitatively confirms the char forming and char reinforcement by the formation of the nanocomposite. As a decrease in

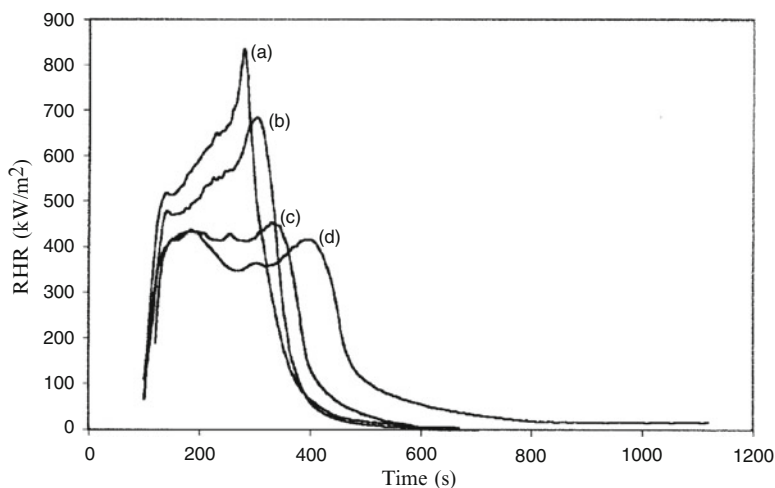


Fig. 12.10 Rate of heat release rate at heat flux = 35 kW/m^2 for various EVA (Escorene UL 00328 with 28 % vinyl acetate content)-based materials. (a) Neat EVA; (b) EVA + 3 % organoclay; (c) EVA + 5 % organoclay; (d) EVA + 10 % organoclay (From Ref. [9]; John Wiley & Sons Limited. Reproduced with permission)

PHRR indicates a reduction of burnable volatiles generated by the degradation of the polymer matrix, such a decrease clearly showed the flame-retardant effect due to the presence of the organoclays and their “molecular” distribution throughout the matrix. Furthermore, the flame-retardant properties were improved by the fact that the PHRR was spread over a much longer period. The flame-retardant properties were due to the formation of a char layer during the nanocomposite combustion. This char acted as an insulating and non-burning material and reduced the emission of volatile products (fuel) into the flame area. The silicate layers of the organoclay played an active role in the formation of the char but also strengthened it and made it more resistant to ablation.

The degradation of EVA and EVA nanocomposites was investigated by solid phase cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectroscopy (CP-MAS- ^{13}C -NMR). Bourbigot [10] described the measurement method in detail. EVA (Exxon’s EVA Escorene UL 00112 with 12 wt% vinyl acetate content) and a nanocomposite based on the same EVA with 5 wt% of the organoclay were degraded by irradiation in a cone calorimeter with a heat flux of 50 kW/m^2 . Chemical shifts of $-\text{CH}_2-$, $-\text{CH}_3$, and $-\text{C}=\text{O}$ were used as evidence of the existence of EVA during the burning process. Neat EVA samples lost the presence of EVA functional groups after irradiation of 150 s, whereas the EVA nanocomposite remains good signal of EVA even after 200 s irradiation. Clearly, formation of EVA nanocomposite has prolonged the surviving time of the EVA in fire. The char formation reduced the heat transfer to the sample and slowed down the diffusion of degraded combustible matters from the bulk phase to the surface. The recombination of radicals in the nanoclay inner gallery may also contribute the slow burning process.

Camino et al. [11] described the synthesis and thermal behavior of layered EVA nanocomposites; the nanofiller was an organoclay based on fluorohectorite, which is a synthetic layered silicate, and protection against thermal oxidation and mass loss was observed in air. The modified silicates accelerated the deacetylation of the polymer but reduced the thermal degradation of the deacetylated polymer due to the formation of a barrier at the surface of the polymer. Zanetti et al. [12] mixed modified fluorohectorite with EVA in an internal mixer and indicated that the accumulation of the filler on the surface of a burning specimen created a protective barrier to heat and mass loss during combustion. In the vertical combustion test, their nanocomposites had much reduced dripping of burning droplets and reduced the hazard of flame spread to surrounding materials. Melt intercalated and additionally gamma-irradiated PE/EVA nanocomposites were prepared by Hu et al. [13, 14] based on a modified montmorillonite; increasing the clay content from 2 to 10 % was beneficial for the improvement of flammability properties. Thermogravimetric analysis (TGA) data showed that nano-dispersion of the modified montmorillonite within the polymer inhibited the irradiation degradation of the PE/EVA blend, which led to nanocomposites with better irradiation-resistant properties than those of the standard polymer blend. Concerning the reaction mechanism of degradation and FR behavior of EVA nanocomposites, Wilkie et al. [15] found that in the early EVA degradation, the loss of acetic acid seemed to be catalyzed by the hydroxyl groups which were

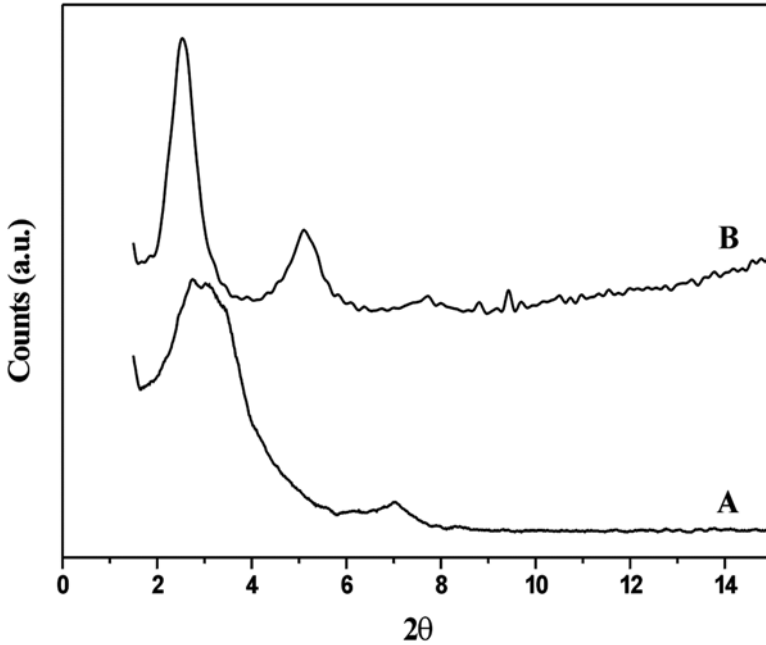


Fig. 12.11 X-ray diffraction of starting organoclay (DMDHT type) *Curve A* and TPU nanocomposite (5 %), *Curve B* (From Ref. [17]; SAGE. Reproduced with permission)

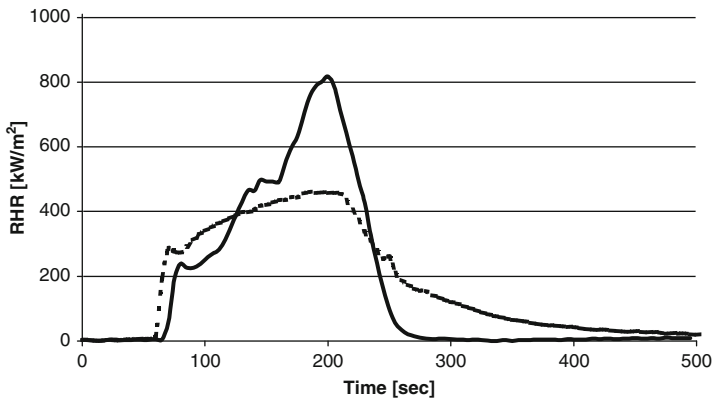


Fig. 12.12 Rate of heat release at heat flux: 35 kW/m^2 for various TPU and TPU nanocomposite (5 % organoclay) based materials: — : Neat TPU. - - - : TPU nanocomposite (5 % organoclay) (From Ref. [17]; SAGE. Reproduced with permission)

present on the edges of the montmorillonite. The thermal degradation of EVA in the presence and in the absence of the organoclay showed that the formation of reaction products differed in quantity and identity. The products were formed as a result of radical recombination reactions that could occur because the degrading polymer was contained within the layers for a long enough time to permit the reactions. The formation of these new products explained the variation of heat release rates. In cases with multiple degradation pathways, the presence of the modified montmorillonite could promote one of these at the expense of another and thus led to different products and hence a different rate of volatilization.

TPU (thermoplastic polyurethane) is a polymer offering a good balance of mechanical properties such as tensile strength, flexibility, and abrasion resistance. One of the TPU applications is for cables used in industrial control automation and medical devices. Despite the possible adjustment property portfolio by combination of polymer segments, TPUs have only moderate thermal stability and low flame retardance. The first of TPU organoclay nanocomposites was reported by Mc Laughlin [16]. Due to the polar nature of the TPU resins, the dispersion of traditional DMDHT-treated organoclay into a TPU (polyether or polyether based) is relatively easy. The formation of intercalated TPU clay-based nanocomposites was investigated by Beyer [17]. X-ray diffraction patterns of the (Fig. 12.11) starting organoclay and TPU nanocomposite indicate very similar structure like the EVA–clay nanocomposite we discussed early in this chapter. The organoclay in the nanocomposite has an intercalated structure. The d_{001} spacing of the organoclay increased from 30 to 36 Å after the TPU compounding. It seems that the TPU polymer also helps to bring order to the clay stacking with narrower peak and possible observation of d_{002} and d_{003} spacing/peaks. TGA studies of the TPU and TPU nanocomposite indicated the nanocomposite has higher heat stability particularly about 350 °C due to the heat-induced oxidative decomposition. Cone calorimetry study (Fig. 12.12) on TPU and TPU nanocomposite shows similar reduction of HRR with 5 % organoclay addition. However, the early ignition of the TPU nanocomposite is quite visible from the cone curve. This may be related to the early Hofmann elimination reaction of the quaternary ammonium compound within the organoclay under heat [2].

12.5 Synergy of Nanocomposite with Traditional Flame Retardant

Since fire burning is a very complicated process, it typically involves multiphase flame retardants to stop the flame. For plastics, the burning typically involved with plastic heat decomposition, diffusion of flammable gases from bulk to surface, and surface gas burning. It is very common to combine various flame retardants to reduce the flammability of the plastic to eventually extinguish the fire to achieve certain industrial rating like UL or IEC. Nanocomposite has demonstrated a great

potential in the flame-retardant formulations from traditional halogen-containing systems (PVC and Br-containing chemistry) to new low smoke zero halogen (LSOH) compounds.

PVC is one of the most used plastics with its excellent cost performance ratio and easy formulation and processing. However, regular organoclay made with quaternary ammonium modification cannot be used in PVC system due to unzipping of PVC by the presence of quaternary ammonium. Phosphate ester is a typical plasticizer and flame retardant in PVC. Therefore, we chose to evaluate flame retardance of the phosphate ester-modified montmorillonite in PVC system. Flame-retardant PVC formulations typically contain antimony trioxide (Sb_2O_3 or ATO) as synergist. ATO is a heavy metal oxide with unknown toxicity to human being. In addition, the current mining and extraction methods to obtain ATO have very negative impact to the environment. There is a strong demand to find ATO replacement in the PVC and other flame-retardant compounds. Phosphate ester-modified clay Charex 418515 was used in various FR PVC systems to study the efficiency as ATO replacement. Table 12.2 shows the PVC flame retardation study with Charex 418515 as atrial replacement to ATO. In this study, fire performance parameters like LOI (Limited Oxygen Index, PHRR, and Smoke Density, are used to evaluate the addition of Charex 418515 to the PVC formulations. The limiting oxygen index (LOI) is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer. Polymers or compounds with higher LOI will not easily burn since it will need more oxygen in the ambient condition to be on fire. Different phosphate esters were used as plasticizer and flame retardant. Phosflex 71B is more flame-retardant phosphate ester, and it can help the PVC to achieve LOI at 35. Three PHR (part per hundred of resin) of ATO was replaced with Charex 418515. Comparing PVC-1 and PVC-2, both of them have very similar measured LOI, PHRR, and smoke density. In addition, they

Table 12.2 FR and mechanical properties of FR PVC with ATO replacement by Charex 418515

	PVC-1	PVC-2	PVC-3	PVC-4
<i>Composition (PHR)</i>				
PVC	100	100	100	100
Phosflex 418	50	50		
Phosflex 71B			50	50
Charex 418515		3		3
Antimony trioxide	6	3	6	3
<i>Flammability</i>				
LOI	27.5	28.0	35.8	35.8
Peak HRR, kW/m ²	310	320	245	225
Smoke, SEA m ² /kg	1150	1140	1290	1150
<i>Physical properties</i>				
Tensile strength, MPa	18.2	17.3	22.9	24.8
Modulus, MPa	6.5	6.9	11.1	12.3
Elongation, %	480	450	380	390
Shore A hardness	89–85	89–85	94–90	92–88

also have comparable mechanical properties such as strength, stiffness, and hardness. Comparing PVC-3 and PVC-4, it is very encouraging to see the PVC-4 has the identical LOI as PVC-3 even with 3 PHR ATO replacement. PVC-4 also has somewhat reduced PHHR and smoke density. UL VW-1 wire flame retardation test evaluated the effectiveness of ATO replacement with Charex 418515. Formulation and testing results are listed in Table 12.3. With addition of 1.5 PHR Charex 418515, the wire samples achieved excellent flame retardation in significant reduced burning time and passed the UL VW-1 test.

Metal hydrates like aluminum trihydrate (ATH) and magnesium hydroxide (MDH) are the most common flame retardants for low smoke zero halogen (LSOH) cable formulations. Typical formulation will need 65 % of ATH or MDH to achieve certainly flame retardation standards. High loading level of the flame retardant in the formulation limits the compound processing and flexibility of the finished wires and cables. EVA and polyethylene are the most common polymers to formulate LSOH compounds. Combinations of organoclay with ATH were also studied by cone calorimeter tests. ATH and organoclay were premixed before compounding with EVA in a batch mixer at 145 °C for 15 min. Cone testing samples were prepared by compression molding and cut to fit the testing aluminum sample holder. With the same loading level of organoclay at 3 %, two loading levels of ATH were used at 58 and 60 %, respectively. A sample containing 65 % ATH was made and tested for comparison purpose.

From cone testing (at a heat flux 35 kW/m²) data on HRR (Fig. 12.13a), the samples containing organoclays show significantly reduced value. More importantly, the secondary burning of the samples containing organoclay was reduced and diminished eventually with higher ATH loading, like the combination of 60 % ATH with 3 % organoclay. This was attributed by the strong char formation of compounds containing organoclay in the burning process. In contrast, the sample containing only higher amount of ATH does not have strong char formation and had quite heat release and smoke generation associated with the secondary burning after the crack of the original char occurred. The rate of smoke production (RSP) (Fig. 12.13b) of these testing samples showed corresponding patterns like the HRR graph. Smoke generation associated with the secondary burning of the samples containing organoclay was nearly eliminated.

Table 12.3 UL VW-1 testing results with addition of Charex 418515

	Units	Control-1	Control-2	Formulation-1
OxyChem 240	PHR	100	100	100
DINP Jayflex 911	PHR	50	50	50
CaCO ₃	PHR	50	50	50
ATO	PHR		1.5	1.5
Charex 418515	PHR			1.5
Additive package	PHR	8	8	8
Max burn time	Sec	45	10	4
Paper flag burned	%	100	30	0
Rating		Fail	Fail	Pass

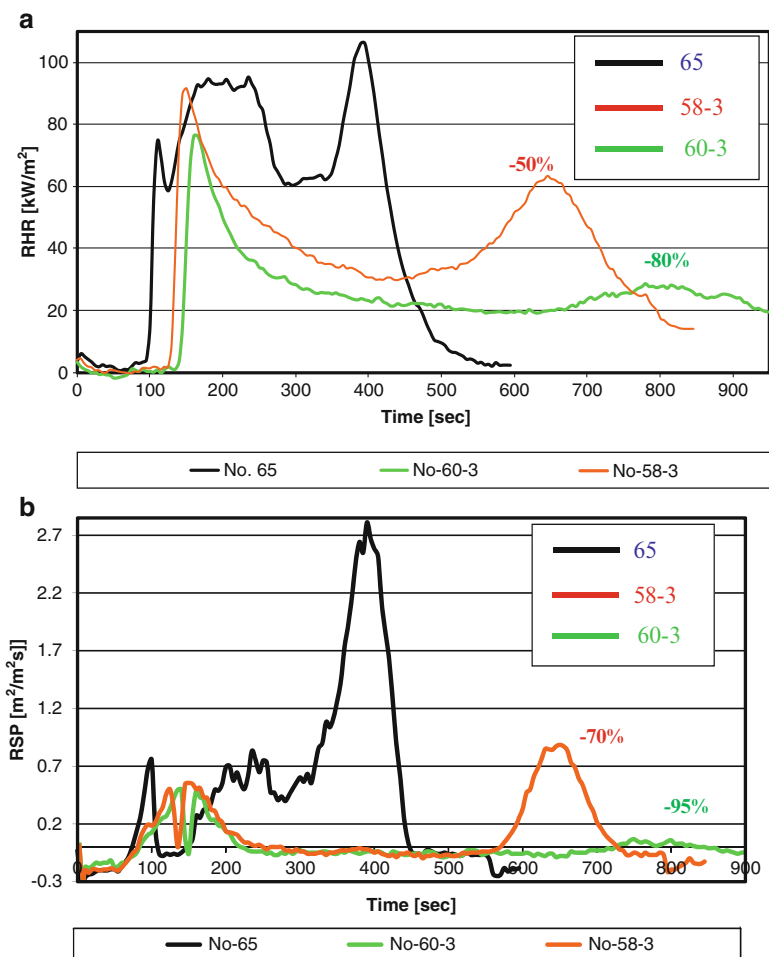


Fig. 12.13 (a) Heat release rate (HRR) of EVA-ATH compounds containing organoclay. 65: 65 % ATH, 35 % EVA ; 60-3: 60 % ATH, 3 % organoclay, 37 % EVA; 58-3: 58 % ATH, 3 % organoclay, 39 % EVA. EVA: Escorene UL 00328 with 28 % vinyl acetate content. Heat flux = 35 kW/m²; polymer plates of 100 × 100 × 3 mm³ within aluminum dishes. (b) Rate of smoke production (RSP) of EVA-ATH compounds containing organoclay. 65: 65 % ATH, 35 % EVA; 60-3: 60 % ATH, 3 % organoclay, 37 % EVA; 58-3: 58 % ATH, 3 % organoclay, 39 % EVA. EVA: Escorene UL 00328 with 28 % vinyl acetate content. Heat flux = 35 kW/m²; polymer plates of 100 × 100 × 3 mm³ within aluminum dishes

Combination of MDH with organoclay was carried in PP matrix. FR PP compounds containing MDH and organoclay were prepared in a corotating twin screw extruder [18]. Compatibilizer, like PP-g-MA, was used according to the MDH manufacturer's recommendations. UL 94 vertical test results indicate the addition of 2.5 wt% organoclay, and all the compounds pass the standard test with

self-extinguishing and non-flame dripping. Cone data (Table 12.4) indicates that the compounds containing organoclay can have delayed ignition compared with standard compound. Also the addition of the organoclay significantly increased the char yield from 34.6 wt% to 46.7 wt%. More importantly, the addition of organoclay reduced the CO release 50–75 %. CO₂ release rates for all compounds are essentially the same. CO has been recognized as one of the silent killers in fire due to its being colorless and odorless, and it often contributes to fire death [19]. The reduced CO yield from burning may be caused by the altered decomposition mechanism of the polymer once they enter the clay inner gallery. HRR and RSP results are shown in Fig. 12.14a, b. The benefit of the organoclay is reducing HRR and RSP on the compounds. The reduction features are quite high for the second burning.

Ammonium polyphosphate (APP) is another halogen-free flame retardant. APPs are inorganic salts of *polyphosphoric acid* and *ammonia*. APP is a common flame retardant using the intumescent mechanism. APP decomposes upon exposing to the heat of a fire-form ammonia and phosphoric acid. The phosphoric acid acts as a catalyst in the formation of carbonaceous char and releases nonflammable carbon dioxide which helps to dilute the air of oxygen. The formation of a coherent char is important for the intumescent FR system to pass any regulations. With sufficient amount of APP on the sample surface, it is possible to form a coherent char. However, the APP has certain processing limitation with possible degradation when surface concentrate reaches to high concentration. Addition of organoclay will bridge the carbonaceous char formed from the intumescent agent like APP to form coherent char. Thus, it is possible to a combination of organoclay with APP to create flame-retardant compounds. Table 12.5 lists our recent study in the combination of organoclay with APP in PP systems. All components were fed into a corotating twin screw extruder. UL94 rating increases with increased loading levels of APP from 24 to 28 %. When 1 % organoclay was added to the 24 % APP system, the compound

Table 12.4 UL-94 and cone results of MDH-PP compounds containing organoclay

Sample ID	Control	Nano-1	Nano-2
Co-PP	30.0	32.5	32.5
MDH	65.0	60.0	60.0
Ma-PP 1	5.0		5.0
Ma-PP 2	(5.0)	5.0	
Organoclay		2.5	2.5
UL-94 @ 1/16"	–	–	–
Rating	Failure	V-0	V-0
Time to ignition (s)	49.9	51.6	57.4
Peak RHR (kW/m ²)	238	222	235
Char yield (%)	34.6	46.7	46.7
Mass loss (kg/m ²)	3.19	2.80	2.79
CO yield	0.015	0.005	0.007
CO ₂ yield	2.54	2.46	2.53

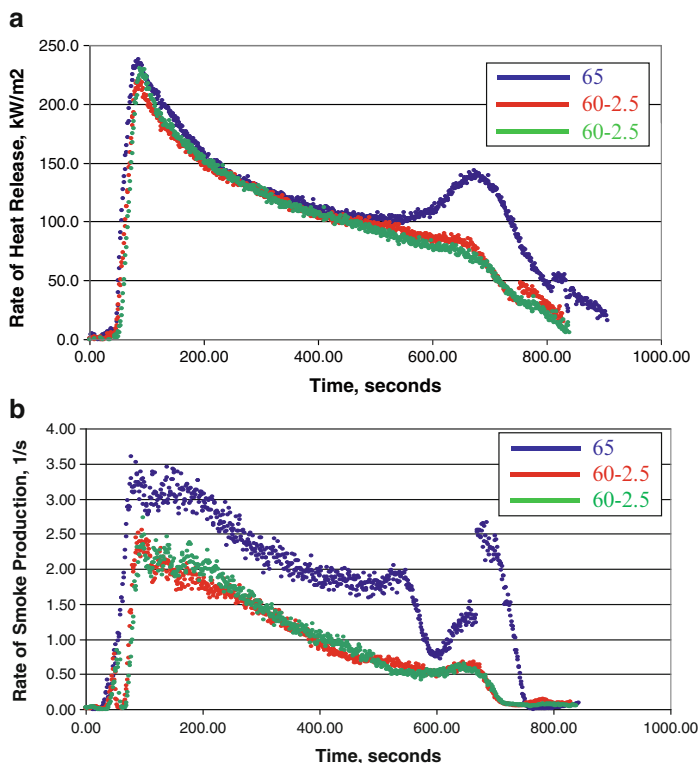


Fig. 12.14 (a) Heat release rate (HRR) of PP-MDH compounds containing organoclay and MDH. (b) Rate of smoke production (RSP) of PP-MDH compounds containing MDH and organoclay

Table 12.5 Effect of organoclay in PP/APP flame-retardant systems

Components	Sample-1	Sample-2	Sample-3	Sample-4	Sample-5	Sample-6
APP 752 (wt%)	24	26	28	24	24	24
PP (wt%)	76	74	72	75	73	72
Organoclay (wt.)	0	0	0	1	3	4
UL-94 rating (1/8 in)	V2	V-1	V-0	V0	V-0	Fail

could reach V-0 high FR rating which could be achieved with 28 % APP loading level. With further increase of the amount of organoclay to 3 %, the compound still achieved V-0 rating. However, once we increased the organoclay level to 4 %, the compound was no longer classified by the UL-94 test. Therefore, there is a limitation for the intumescent system to accept organoclay as char-forming agent. Once the organoclay level reached 4 %, there were too much organoclay on the surface; this could limit or interfere with char forming by the intumescent agents. Therefore, for intumescent system, it is necessary to start with low level of organoclay. Most

likely, low organoclay level will help the compounds to form coherent char during burning process to achieve good UL-94 FR ratings.

Combination of organoclay with ATH is EVA based. LSOH compound was the first commercial application reported by Kabelwerk Eupen. A coaxial cable containing an outer sheath made with EVA, ATH, and organoclay was studied under UL 1666 fire test. There are many applications for indoor cables passing the large-scale fire test UL 1666 (riser test for cables) with a 145 kW burner in a two-story facility. This very severe fire test defines the following important points of measurements:

1. Maximal temperature of fire gases at 12 feet: 850 °F
2. Maximal height for flames: 12 feet

Compounds with halogenated flame retardants are often used to pass this test, but more and more low smoke halogen-free cables are requested by the market for the riser test. Cables based on nanocomposites compounds demonstrate their promising performances for this fire test.

An example for LSOH cables passing UL 1666 is shown in Fig. 12.15. The outer sheath was based on a nanocomposite with an industrial EVA/ATH/organoclay composition. The analogous coaxial cable was tested with an outer sheath based on regular EVA/ATH compound. In both compounds, the relation of polymer/filler was the same and Table 12.6 presents the fire testing results. The improved flame-retardant properties were due to the formation of a char layer during the combustion process. This insulating and non-burning char reduced the emission of volatile products from the polymer degradation into the flame area and thus minimized the maximal temperature and height of the flames. The fundamental benefit of addition of organoclay in LSOH compounds has been transferred into real application and testing. The reduced heat release allows position lower gas temperature about the cable. This could reduce the fire risk hazard level in case of electrical fire.

European countries are leading the development and applications of LSOH compounds. The first halogen-free flame-retardant (HFFR) cables were introduced to London underground use in the early 1970s. HFFR was replaced by low smoke version in the late 1990s after the Düsseldorf Airport Fire in 1996. Furthermore, in 2010s, the technical and regulatory developments reached a new higher level when European Union Commission started to implement the new Construction Products Regulation (CPR). In a fire, the heat released from a burning article has been considered as the source to spread the fire to harm human life and damage properties. Reduction of heat released from burning articles will reduce the fire risk to provide safer products. The new European Construction Products Regulation (CPR), adopted in 2011, is now mandatory since July 1, 2013. This European regulation 305/2011 describes the conditions to make available a broad range of construction products including power, control, and communication cables for the market. The new CPR substitutes the old Construction Products Directive (CPD), which needed a revision because as a directive, it was not applied in a harmonized way throughout the European Union (EU). The new regulation will remove existing barriers to trade

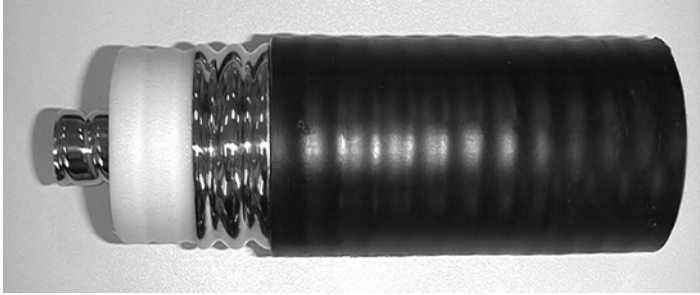


Fig. 12.15 Coaxial cable (1/2") with a nanocomposite-based outer sheath passing the UL 1666 cable fire test

Table 12.6 Fire performances of LSOH coaxial cables with EVA/ATH and EVA/ATH/organoclay outer sheaths

UL 1666 requirements	EVA/ATH compound	EVA/ATH/organoclay compound
Maximal temperature at 12 feet		
<850 °F	1930 °F	620 °F
Maximal flame height		
<12 feet	>12 feet	6 feet

in the EU where member nations of the EU each had their own fire standards (Fig. 12.16).

The European Commission's Fire Regulators Group, consisting of representatives from each member country, have reviewed various proposals to create a new fire performance hierarchy for products like cables installed in buildings within the governing document known as the *Construction Products Regulation* (CPR). Input was received from its own sponsored studies as well as from investigations by industry groups. The European Commission's FIPEC study (Fire Performance of Electrical Cables) presented a fire hazard assessment methodology for both communications and energy cables in buildings based primarily on modifications to the international cable fire test protocol according to different categories defined by IEC 60332-3 [20]. The revised testing procedures enabled measurements of heat release rate by oxygen consumption technique, smoke release rate, and the possibility of measuring toxic gas production rates by FTIR instrumentation. Parameters are flame spread (FS), peak heat release rate (PHRR), total heat released (THR), fire growth rate (FIGRA), smoke production rate (SPR), and total smoke production (TSP). The ranking of cables is summarized in Table 12.7 and the tests are described by the norm EN 50399. Products in Class A demonstrate the highest fire performances, while products with no fire performances are ranked in class F. This test setup will allow testing of cables in one of the most advanced test arrangements available in Europe.

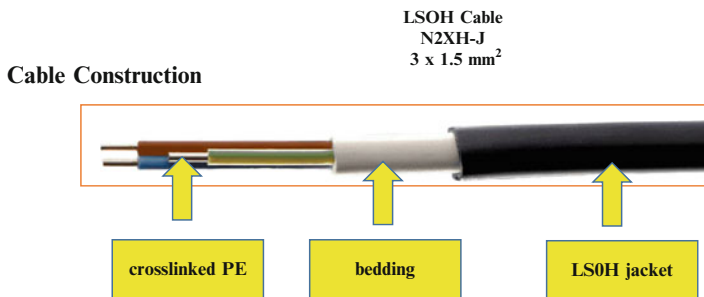


Fig. 12.16 LSOH cable construction for IEC and CPR testing

The value FIGRA is defined as the growth rate of the burning intensity, HRR, during a test. FIGRA is calculated as the maximum value of the function (heat release rate)/(elapsed test time). It should work as an indication of the propensity to cause a quickly growing fire. It is reported from cone calorimeter investigations that nanocomposites showed impressive reductions of peak of heat release rates and FIGRA, especially for higher external heat fluxes [21].

Two detailed test methods were developed for CPR: scenario 1 according to EN 50399-2-1 and scenario 2 according to EN 50399-2-2, the former being slightly more severe than IEC 60332-3-24, and the latter being much more severe and suitable for cables used in high hazard conditions. The conclusions reached by the FIPEC study were that current tests (e.g., IEC 60332-3-24, category C) are not sensitive enough to differentiate the enhanced fire performances needed for high-density telecommunication cable installations, and the parameter that has the most effect on the test results is the method of mounting cables on the ladder.

Cables with the following specification were tested according the FIPEC scenarios 1 and 2 (designation: NHXMH-J, $4 \times 16 \text{ mm}^2$; insulation: cross-linked polyethylene; filling sheath: a flame-retardant non-halogen compound; outer sheath: a flame-retardant non-halogen EVA compound either based on classic ATH only or based on a nanocomposite by combination of organoclays and ATH [22]). The values listed in Table 12.8 clearly demonstrate the improvements seen both for flame spread and FIGRA due to the nanocomposite-based outer sheath. In addition, during the fire tests (Table 12.8), there was no dripping of burning polymer from the cable with the nanocomposite-based outer sheath; this is an additional important requirement within the CPR regulation, and it shows that nanocomposites are essential to meeting the new fire test regulations.

12.6 New Development and Outlook

The use of nanocomposites based on organoclays in combination with metal hydroxides is now regularly seen in the cable industry. Kabelwerk EUPEN AG from Belgium, the inventor of this technology, has used it over a number of years for their

Table 12.7 New EU CPR for wire and cable flame retardance rating and classification

Class	Test method(s)	Classification criteria	Additional classification
A _{ca}	EN ISO 1716	PCS ≤ 2.0 MJ/kg (1)	
B1 _{ca}	FIPEC20 Scen 2 (5)	FS ≤ 1.75 m <i>and</i>	Smoke production (2, 6) and flaming droplets/particles (3) and acidity (4)
		THR _{1200s} ≤ 10 MJ <i>and</i>	
		Peak HRR ≤ 20 kW <i>and</i>	
		FIGRA ≤ 120 W s ⁻¹	
	EN 50265-2-1	H ≤ 425 mm	
B2 _{ca}	FIPEC20 Scen 1 (5)	FS ≤ 1.5 m; <i>and</i>	Smoke production (2, 7) and flaming droplets/particles (3) and acidity (4)
		THR _{1200s} ≤ 15 MJ; <i>and</i>	
		Peak HRR ≤ 30 kW; <i>and</i>	
		FIGRA ≤ 150 W s ⁻¹	
	EN 50265-2-1	H ≤ 425 mm	
C _{ca}	FIPEC ₂₀ Scen 1 (5)	FS ≤ 2.0 m; <i>and</i>	Smoke production (2, 7) and flaming droplets/particles (3) and acidity (4)
		THR _{1200s} ≤ 30 MJ; <i>and</i>	
		Peak HRR ≤ 60 kW; <i>and</i>	
		FIGRA ≤ 300 W s ⁻¹	
	EN 50265-2-1	H ≤ 425 mm	
D _{ca}	FIPEC ₂₀ Scen 1 (5)	THR _{1200s} ≤ 70 MJ; <i>and</i>	Smoke production (2, 7) and flaming droplets/particles (3) and acidity (4)
		Peak HRR ≤ 400 kW; <i>and</i>	
		FIGRA ≤ 1300 W s ⁻¹	
	EN 50265-2-1	H ≤ 425 mm	
E _{ca}	EN 50265-2-1	H ≤ 425 mm	
F _{ca}	No performance determined		

- (1) For the product as a whole, excluding metallic materials, and for any external component (i.e., sheath) of the product
- (2) **s1** = TSP₁₂₀₀ ≤ 50 m² *and* Peak SPR ≤ 0.25 m²/s
s1a = **s1** and transmittance in accordance with EN 50268-2 ≥ 80 %
s1b = **s1** and transmittance in accordance with EN 50268-2 ≥ 60 % < 80 %
s2 = TSP₁₂₀₀ ≤ 400 m² *and* peak SPR ≤ 1.5 m²/s
s3 = not s1 or s2
- (3) For FIPEC₂₀ scenarios 1 and 2: **d0** = no flaming droplets/particles within 1200 s; **d1** = no flaming droplets/particles persisting longer than 10 s within 1200 s; **d2** = not d0 or d1

(continued)

Table 12.7 (continued)

- (4) EN 50267-2-3: **a1** = conductivity <2.5 $\mu\text{S}/\text{mm}$ and $\text{pH} > 4.3$; **a2** = conductivity <10 $\mu\text{S}/\text{mm}$ and $\text{pH} > 4.3$; **a3** = not a1 or a2. No declaration = no performance determined
- (5) Air flow into chamber shall be set to 8000 ± 800 l/min
 FIPEC₂₀ scenario 1 = EN 50399-2-1 with mounting and fixing as below
 FIPEC₂₀ scenario 2 = EN 50399-2-2 with mounting and fixing as below
- (6) The smoke class declared for class B1_{ca} cables must originate from the FIPEC₂₀ Scen 2 test
- (7) The smoke class declared for class B2_{ca}, C_{ca}, D_{ca} cables must originate from the FIPEC₂₀ Scen 1 test

Table 12.8 Flame-retardant properties of cables by FIPEC scenarios 1 and 2 according to EN 50399

	NHXMH-J 4 × 16 mm ²	NHXMH-J 4 × 16 mm ²
	Classical purely ATH-based outer sheath	Nanocomposite-based outer sheath
<i>FIPEC scenario 1</i>	Flame spread=0.49 m	Flame spread=0.48 m
20.5 kW flame	PHRR = 27.1 kW	PHRR = 22.9 kW
0 min burning time	63.2 W s ⁻¹	FIGRA = 20.3 W s ⁻¹
<i>FIPEC scenario 2</i>	Flame spread=1.85 m	Flame spread=1.21 m
30 kW flame and plate	PHRR = 58.6 kW	PHRR = 55.8 kW
30 min burning time	FIGRA = 53.5 W s ⁻¹	FIGRA = 47.9 W s ⁻¹

range of flame-retardant non-halogen cables. The company also has worldwide patents on this technology. Other companies will follow this way for their flame-retardant product ranges. In Europe, one can expect a wider application of the nanocomposite-based flame-retardant technology driven by the enhanced requirements of the Construction Product Regulation (CPR). It is also likely that countries including China, South Korea, and Japan which are following the European trends toward non-halogenated flame-retardant products will adopt this technology in the near future.

Nanocomposite materials were developed in the last two decades. Significant progress has been made to adopt the technology in the standard plastic processing methods. Currently, most of the commercial uses of nanocomposites are based on layered silicates. However, with more research on carbon nanotube and graphene materials, one would expect these materials will move into the market place with new featured properties. Design of advanced flame-retardant plastics has taken advantage of this new class of materials. Flame-retardant plastic compounds using nanocomposite technology offer significantly improved char forming and reduced toxic substance emission while keep the same processing as the traditional flame retardant. With the implementation of the new fire retardation standard like the CPR in EU, we expect the growth of the use of nanocomposites in flame-retardant compounds will be substantial in the coming years. Development with other nano-sized

additives is also emerging, such as tubular nanoclay, graphene, and three-dimensional zeolite-like inorganic frameworks.

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