

# Nanocomposites as a New Class of Flame Retardants

AWARD WINNER

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by

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## Ethylene-vinyl acetate (EVA), enhanced with very low loading levels of nanofillers, provides an efficient system for flame retardant cables.

Fire hazards are mainly the result of a combination of different factors including ignitability, ease of extinction, flammability of the generated volatiles, amount of the heat released on burning, rate of heat release, flame spread, smoke obscuration and smoke toxicity. The most important fire hazards are heat, smoke and toxic gases.<sup>1</sup>

A high rate of heat release causes a fast ignition and flame spread. It also controls the intensity of the fire and is therefore much more significant than ignitability, smoke toxicity or flame spread. The escape time available to fire victims is also controlled by the heat release rate.

Smoke production is another significant fire hazard. People become disoriented in the dark smoke and therefore cannot see building exits. Also, fire fighters have severe problems attempting to rescue people in dark surroundings.

The acute toxicity of fire gases is mainly controlled by carbon monoxide (CO) content. CO is responsible for over 90% of people killed by fires.<sup>2</sup> Each year, about 5000 people are killed by fire in Europe and in the USA the number is over 4000. The direct property losses are about 0.2% of gross domestic product and total costs of fires are around 1% of gross domestic product.<sup>3</sup> Therefore it is vital to develop well designed flame retardant materials to reduce these fire hazards.

Polymers are used in more and more fields of applications and specific mechanical, thermal and electrical properties are required of them. An important property is the flame retardant behavior of the polymers, which can be fulfilled traditionally by the following methods:

- Use of intrinsically flame retardant polymers like PVC or fluoropolymers.
- Use of flame retardants like aluminium trihydrate, magnesium hydroxide, organic brominated compounds or intumescent systems to prevent the burning of polymers like PE, PP, PA or other polymers.

These flame retardant systems sometimes exhibit the following disadvantages:

- The applications of aluminium trihydrate (ATH), and also magnesium hydroxide, require a very high portion of the filler within the polymer matrix; filling levels of more than 60% weight are necessary to achieve a suitable flame retardancy, e.g., for cables and wires. Clear disadvantages of these filling levels are the high density and the lack of flexibility of the end products, the low mechanical properties and the problematic compounding and extrusion steps.
- In Europe, there are at least reservations about a general use of brominated compounds as flame retardants.
- Intumescent systems are expensive and the electrical requirements can restrict the use of these products.

A new class of materials, called nanocomposites, avoids the disadvantages of traditional flame retardant systems. A

nanocomposite is a two-phase material with a suitable nanofiller (usually a modified layered silicate) dispersed in the polymer matrix at a nanometer ( $10^{-9}$  m) scale.

### Nanocomposite Properties

Compared with virgin polymers, nanocomposites show tremendous improvements, with the content of the modified layered silicates often ranging between just 2% and 10% weight. The following list indicates some of the most important improved properties:

- Mechanical properties such as tension, compression, bending and fracture.
- Barrier properties like permeability and solvent resistance.
- Optical properties.
- Ionic conductivity.

A review in the January 2000 issue of *Materials Science and Engineering*, discusses these improvements.<sup>4</sup>

Other highly interesting properties of polymer-layered silicate nanocomposites concern their increased thermal stability and ability to promote flame retardancy at very low filling levels. The formation of a thermal insulating and also low permeable char to volatile combustion products caused by a fire is responsible for these improved properties.<sup>5, 6, 7, 8</sup>

The low filler content in nanocomposites that results in the dramatic improvement in thermal stability is of high interest to the wire and cable industry, as end-products can be made more economically and with easier processing.

### The Experiment

In an experiment, commercially available layered silicate based on montmorillonite modified by dimethyl-distearylammonium cations from **Süd-Chemie** of Germany was used as the nanofiller. Ethylene-vinyl acetate (EVA) copolymers (**Exxon's** Escorene types) with different percent weight vinyl acetate were also used in the study. Such copolymer types have demonstrated their ability to promote nanocomposite formation by melt blending with nanofillers.<sup>9, 10, 11</sup>

Additionally, aluminium trihydrate ATH (Martinal OL 104 LE) from **Martinswerke GmbH** of Germany was used in the experiment.

Depending on the nature of the filler distribution within the matrix, the morphology of the EVA nanocomposites can evolve from an intercalated structure with a regular alternation of layered silicates and polymer monolayers to an exfoliated (delaminated) structure with layered silicates randomly and homogeneously distributed within the polymer matrix. The easiest and technically best way to produce these types of materials is kneading the polymer in the molten state with a modified layered silicate such as montmorillonite. The native  $\text{Na}^+$  interlayer cation within the silicate has been exchanged

by a quaternary alkylammo-nium cation. The modified filler is called a nanofiller and is much more compatible with the polymer matrix.

Mixing during the experiment was done on several compounding machines. Rolling mill and internal mixers were used as discontinuous compounding machines. A BUSS co-kneader (with a rotating and simultaneously oscillating screw, 11 L/D and 46 mm screw diameter) was used as a continuous compounding machine. A processing temperature of 160°C (320°F) was used for all the different compounding machines.

Information on the nanocomposite morphology (Figure 1) was obtained by transmission electron microscopy (TEM) and X-ray diffraction (XRD) observation. Exfoliated silicate sheets were observed together with small stacks of intercalated montmorillonite. This structure may be described as a semi-intercalated, semi-exfoliated structure that does not change principally with the vinyl acetate content of the EVA matrix. Even a larger amount of stacks are observed for EVA with lower vinyl acetate contents.<sup>10</sup>

Also, there were no great differences in nanocomposite morphology relative to the different compounding routes.

## Experiment Results

**Thermal Stability:** Thermogravimetric analysis (TGA) is widely used to characterize the thermal stability of a polymer. The mass loss of the polymer due to volatilization of products generated by thermal decomposition is monitored as a function of a temperature ramp. Non-oxidative decomposition occurs when the heating of the material is done under an inert gas flow like helium or nitrogen. However, use of air or oxygen allows the monitoring of oxidative decomposition reactions.

The experimental conditions of the degradation highly influenced the reaction mechanism of the degradation. The thermal stability of EVA-based nanocomposites was investigated as partially intercalated and partially exfoliated structures independent of the EVAs used.<sup>10</sup>

TGA under helium (non-oxidative decomposition) and under air (oxidative decomposition) were investigated. EVA is known to decompose in two consecutive steps. The first step is identical in both oxidative and non-oxidative conditions. It occurs between 350°C and 400°C (662°F and 752°F) and is linked to the loss of acetic acid. The second step involves the thermal decomposition of the obtained unsaturated backbone either by further radical scissions (non-oxidative decomposition) or by thermal combustion (oxidative decomposition). In helium, the EVA nanocomposite has a negligible reduction in thermal stability compared to the virgin EVA or the EVA filled with Na-montmorillonite (microcomposite). In contrast, when decomposed in air, the same nanocomposite exhibits a rather large increase in thermal stability because the maximum of the second degradation peak is shifted 40°C (104°F) to higher temperatures while the maximum of the first decomposition peak remains unchanged (Table 1).

In this case, the explanation for the improved thermal stability is the char formation occurring under oxidative conditions. The char acts as a physical barrier between the polymer and the superficial zone where the combustion of the polymer is occurring. The results in Table 1 on the maximum temperatures at the main degradation peak for EVA nanocomposites demonstrate that the obvious optimum for thermal stabilization is already obtained at a layered silicate level of 2.5% to 5.0% weight.

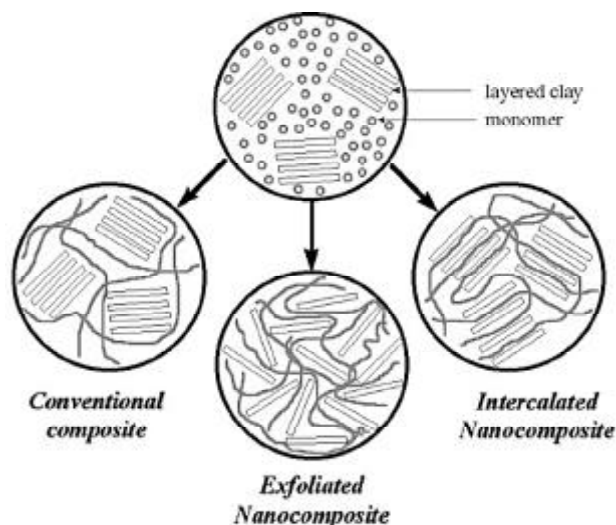


Fig. 1 — Microcomposites showing intercalated & exfoliated morphologies of nanocomposites.

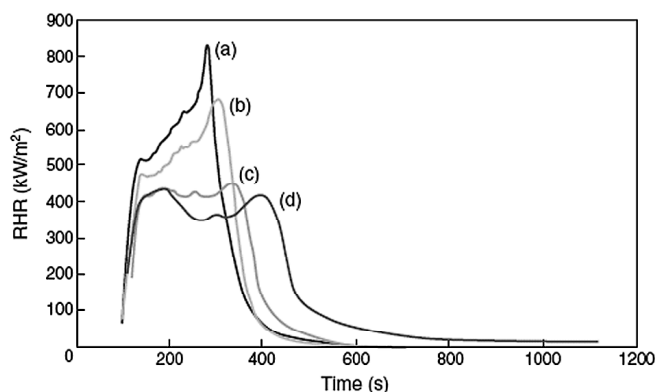
Table 1. Maximum temperature of the main degradation peak (DTG) in air, 20°C/min. for EVA & EVA nanocomposite. EVA: Escorene UL00328 with 28% by weight VA.

Nanofiller content (percent weight)	Maximum Temperature peak main degradation peak
0	452.0°C
1	453.4°C
2.5	489.2°C
5	493.4°C
10	472.0°C
15	454.0°C

**Flammability Properties:** From an engineering point of view, it is important to know what hazards within a fire must be prevented. Only then can strategies for measurements and improvements be developed. Extensive research at the National Institute for Standards and Technology (NIST) in the USA, led to the following conclusion that allows significant simplification of the problem for hazards in fires: The heat release rate, in particular the peak heat release rate, is the single most important parameter in a fire and can be viewed as the “driving force” of the fire.<sup>12</sup>

Therefore, today the universal choice of an engineering test for flame retardant polymers is the cone calorimeter. The measuring principle is oxygen depletion with a relationship between the mass of oxygen consumed from the air and the amount of heat released. The cone calorimeter is utilized in achieving certification to ASTM E 1354 and ISO 5660 standards. In a typical cone calorimeter experiment, the polymer sample (a plate of 100 x 100 x 5 mm) in an aluminium dish which is exposed to a defined heat flux (which is normally 35 kW/m<sup>2</sup> or 50 kW/m<sup>2</sup>). Simultaneously, the properties of heat release rate, peak of heat release, time to ignition, total heat released, mass loss rate, mean CO yield, mean specific extinction area, etc., can be measured.

The flame retardant properties of the EVA nanocomposites have been determined using cone calorimetry under a heat flux of 35 kW/m<sup>2</sup> (Figure 2 on next page). Under such conditions, simulating a small fire scenario, the effect of the nanofiller is already observed for 3%. A decrease by 47% of the peak of



**Fig. 2** — Rate of heat release versus time measured with a cone calorimeter (heat flux: 35 kW/m<sup>2</sup>) for various EVA (Esorene UL 00328 with 28% vinyl acetate content) based materials: (a) Virgin EVA & EVA with 5% of nanomontmorillonite (micro-composite); (b) EVA + 3% nanofiller; (c) EVA + 5% nanofiller; (d) EVA + 10% nanofiller. Note: All % are by weight.

heat release as well as a shift towards longer times are detected for a nanocomposite containing 5% by weight of the nanofiller when compared to the virgin matrix EVA. Increasing the filler content to 10% does not further improve the reduction of the peak of heat release. As a decrease in the peak of heat release indicates a reduction of the burnable volatiles generated by the degradation of the polymer matrix, such a drop clearly indicates the flame retardant effect due to the presence of the nanofiller and its “molecular” distribution throughout the matrix. The flame retardant properties are further improved by the fact that the peak of heat release is spread over a much longer period of time. The flame retardant properties are due to the formation of a char layer during the nanocomposite combustion. This char acts as an insulating and non-burning material that reduces the emission of volatile products (fuel) into the flame area. The silicate layers of the nanofiller play an active role in the formation of this char, but also strengthen it and make it more resistant to ablation.

Cone calorimeter experiments with a heat flux of 35 kW/m<sup>2</sup> also show that virgin EVA is completely burned without any residue. In contrast to the previous result, an early strong char formation is found for the EVA nanocomposite within an analogous cone calorimeter experiment. But now this char is stable and does not disappear by combustion.

Finally, compared to the virgin EVA matrix, the nanocomposite burns without producing burning droplets (UL 94 vertical procedure),<sup>14</sup> a characteristic feature that further limits the propagation of a fire. This is an important characteristic for products to be classified within the new Euroclasses that regulate flame retardancy.

**NMR investigation and FR mechanism:** The degradation of EVA and the EVA-nanocomposites was investigated utilizing solid phase CP-MAS-<sup>13</sup>C-NMR spectroscopy. The principles and measurement method are described in detail by Le Bras et al.<sup>16</sup>

EVA (Esorene UL 00112 with 12% vinyl acetate content by weight) and also a nanocomposite based on EVA (Esorene UL 00112 with 12% weight vinyl acetate content) with 5% of the nanofiller were irradiated within a cone calorimeter by a heat flux of 50 kW/m<sup>2</sup>. Samples were taken out from heat flux after 50, 100, 150, 200 and 300 seconds and the presence of EVA and char formation were measured.

The following results were obtained:<sup>17</sup>

- Before irradiation of EVA and EVA-nanocomposite:
  - 33 ppm => - CH<sub>2</sub> - by polymer backbone
  - 75 ppm => - CH<sub>3</sub> by acetate group
  - 172 ppm => - C = O by acetate group (small signal)
- After irradiation of EVA:
  - 50 seconds: New signals at 130 ppm (char: aromatics and polyaromatics) and 180 ppm (- C = O with beginning of oxidation), EVA signals present
  - 150 seconds: no signals => no organic material present
- After irradiation of EVA-nanocomposite:
  - 50 seconds: New signals at 130 ppm (char: aromatics and polyaromatics) and 180 ppm (- C = O with beginning of oxidation), EVA signals present
  - 100 seconds: char-formation and EVA signals present
  - 200 seconds: char-formation & EVA signals present
  - > 300 seconds: no signals => no organic material present

Obviously the formation of nanocomposites clearly promotes char formation and delays the degradation of EVA.

**Intercalation versus Exfoliation:** Often it is reported within the literature that exfoliation is the most effective structure for maximal enhancements of properties improved by nanocomposites. Therefore, it was of interest to shift the ratio of the mixed intercalated/exfoliated structure that is observed within EVA-nanocomposites<sup>10</sup> to the exfoliated structure. This was accomplished through the melt-compounding of EVA (Esorene UL 00328) with 5 phr of the nanofiller on a twin-screw extruder. Two screw designs were used. One screw was for maximum mixing using mixing elements and the second screw was for maximal dispersion using kneading blocks. The screws were used from 300 to 1200 rpm. TEM and XRD demonstrate that for the highest shear rate (1200 rpm) and highest friction (second screw), the mixed structures are shifted to the exfoliated structure. However, cone calorimeter data show that there are no changes on the peak heat release rates for all the melt-compounded nanocomposites. Obviously, the mixed intercalated/exfoliated structures within the EVA nanocomposites already have the maximal reduction in peak heat release rates.

## Combination of Traditional ATH Filler with a Nanofiller

To achieve typical flame retardancy for cables required by the most important international cable fire test (IEC 60332-3-24)<sup>15</sup>, a weight ratio of 65% weight of ATH and 35% weight of a suitable polymer matrix like EVA must often be used for cable outer-sheaths.<sup>13</sup>

Therefore, the performances of two compounds were compared. Both compounds were prepared on a BUSS co-kneader (46 mm screw diameter, 11 L/D). One compound was made with a 65% ATH and 35% EVA Esorene UL 00328 and the second compound was made by 60% ATH, 5% nanofiller and 35% EVA Esorene UL 00328. Both compounds were investigated by TGA in air and by cone calorimeter at 50 kW/m<sup>2</sup>. TGA in air clearly showed the delay in the degradation by the small amount of nanofiller.

The char of the EVA/ATH/nanofiller compound created by the cone calorimeter was very rigid with only a few small cracks, but the char of the EVA/ATH compound is much less rigid (less mechanical strength) with many large cracks. This is

also the explanation why the peak heat release rate in the case of the nanocomposite was reduced to 100 kW/m<sup>2</sup> compared to 200 kW/m<sup>2</sup> for the EVA/ATH compound. To obtain the same decrease for the peak heat release rate by the flame retardant filler ATH only, the weight content of the ATH must be increased to 78% within the EVA/ATH compound. The great improvements in flame retardancy by the nanofiller also provides the potential to decrease the level of ATH within the EVA polymer matrix. To maintain 200 kW/m<sup>2</sup> as a sufficient peak heat release level, the weight content of ATH can be decreased from 65% to 45% by the presence of only 5% nanofiller in the EVA polymer matrix. Reduction in total amount of these fillers also results in improved mechanical and rheological properties for typical EVA-based cable compounds.

### Coaxial Cable Passing UL 1666 with a Nanocomposite-Based Outer Sheath

There are many applications for indoor cables that pass the riser test defined by UL 1666 with a 145 kW burner in a two-story facility. This very severe fire test defines the following most important points of measurements:

- Maximum temperature of 850°F at 12'.
- 12' maximum height for flames.

Halogen cable compounds are often used to pass this fire test. But more and more, flame-retardant, non-halogen (FRNH) cables are requested by the market for passing the riser test. Cables based on nanocomposites compounds demonstrate promising performance for this fire test.

An example of FRNH cables passing UL 1666 is shown in **Figure 3**. The outer sheath is based on a FRNH nanocomposite with an EVA/ATH/nanofiller composition. The analogous FRNH coaxial cable is also tested with an outer sheath based on EVA/ATH. In both compounds, the relation of polymer/filler was the same. **Table 2** indicates the results.

The improved flame retardant properties are due to the formation of a char layer during the nanocomposite combustion. This insulating and non-burning char reduces the emission of volatile products from the polymer degradation into the flame area and thus reduces the maximal temperature and height of the flames.



**Fig. 3** — Coaxial cable with an FRNH nanocomposite-based outer sheath.

**Table 2.** Fire performance of FRNH coaxial cables with EVA/ATH & EVA/ATH/nanofiller outer sheaths.

UL 1666 Requirements	EVA/ATH Compound	EVA/ATH/Nanofiller Compound
Maximum Temp at 12': < 850°F	1930°F	620°F
Max. Flame Height: < 12'	> 12'	6'

### Conclusion

The thermal properties of EVA are improved by very low loading levels of a suitable nanofiller within the polymer matrix. For EVA nanocomposites, TGA in air shows a delay of the degradation, and the peak of heat release measured by a cone calorimeter is dramatically reduced. Char formation with nanocomposites is improved and provides better flame retardancy. The results are also valid for EVA nanocomposites in combinations with metal hydroxides like aluminum trihydrate, and this allows for new flame retardant compounds for cables with reduced total filler contents. Also, a coaxial cable having an outer sheath based on flame-retardant, non-halogen nanocomposites passes the UL 1666 riser test.

To learn more, contact the author or **Circle 205**.

**WCTI**

### References:

- <sup>1</sup> M. Hirschler, *Polymeric Materials: Science and Engineering*, Vol. 83, ACS Meeting August 2000, Washington, DC
- <sup>2</sup> V. Brabrauskas, *Fire and Materials*, 19, 1995, 205
- <sup>3</sup> G.C. Stevens, Conference "Flame Retardants 2000," London, Elsevier Applied Science
- <sup>4</sup> M. Alexandre, Ph. Dubois, *Materials Science and Engineering*, 28, 2000, 1
- <sup>5</sup> G. Beyer, *Polymer News*, November 2001
- <sup>6</sup> M. Le Bras, G. Camino, S. Bourbigot, R. Delobel (editors), *Fire Retardancy of Polymers: The use of Intumescence*, Royal Society of Chemistry, Cambridge, 1998, page 196 ff
- <sup>7</sup> J.W. Gilman, T. Kashiwagi, E.P. Giannelis, J.D. Lichtenhan, *SAMPE J.*, 1997, 4
- <sup>8</sup> J. Lee, T. Takekoshi, E.P. Giannelis, *Mater. Res. Soc. Symp.*, 457, 1997, 513
- <sup>9</sup> G. Beyer, M. Alexandre, C. Henrist, R. Cloots, A. Rulmont, R. Jérôme, Ph. Dubois, *World Polymer Congress, IUPAC Macro 2000, 38th Macromolecular IUPAC Symposium*, Warsaw, 2000
- <sup>10</sup> G. Beyer, M. Alexandre, C. Henrist, R. Cloots, A. Rulmont, R. Jérôme, Ph. Dubois, *Macromol. Rapid Commun.*, 22, 2001, 643
- <sup>11</sup> M. Zanetti, G. Camino, R. Thomann, R. Mülhaupt, *Polymer*, 42, 2001, 4501
- <sup>12</sup> V. Babrauskas, R.D. Peacock, *Fire Safety J.*, 18, 1992, 255
- <sup>13</sup> M.J. Herbert, S.C. Brown, Conference "Flame Retardants 1992," London, Elsevier Applied Science
- <sup>14</sup> UL 94, *Test for flammability of plastic materials for parts in devices and appliances*, 1966-10-00, UL Inc.
- <sup>15</sup> IEC 60332-3-24, *Tests on electrical cables under fire conditions - Part 3-24: Test for vertical flame spread of vertically-mounted bunched wires or cables; Category C*, 2000-10-00, International Electrotechnical Commission
- <sup>16</sup> Le Bras et al, *Polymer Degrad. & Stab.*, 64, 1999, 425
- <sup>17</sup> G. Beyer, 12<sup>th</sup> BCC conference "Flame retardancy of polymeric materials," 2001, Stamford, CT, USA

### Author Profile...

**Günter Beyer** joined **Kabelwerk Eupen AG** in 1984 and is responsible for the fire testing stations, materials development and qualification of new materials. He gained his Ph.D. at the university **RWTH Aachen** in Germany in 1984 and has published more than 60 scientific papers mainly in the field of material science and flame retardancy of polymers. He has been invited for plenary presentations and as chairman on many international conferences. His main research interest for the moment is related to nano-structured flame retardant compounds.

### Company Profile...

In business since 1747, **Kabelwerk Eupen AG** manufactures cables as well as pipe and foam products.

