

Organomodified siloxanes

Improved fire protection

Flame-retardant plastics can save lives by delaying the spread of a fire, allowing valuable time for firefighting. But flame retardants based on metal hydroxide can achieve their full effect only if the right processing aids are used in the production of the flame-retardant compounds. Jointly with its partners, Evonik has developed suitable formulations and has demonstrated their efficiency in standards-compliant flame-retardant tests.

[TEXT Kathrin Lehmann]



FIRES AREN'T ALL alike. Strange as it may sound, there are highly problematic and less problematic fires. Highly problematic fires, particularly in buildings, are those that spread via electrical installations. These propagate the fire into rooms that would otherwise be well protected, for example, by a concrete wall or ceiling. Also highly problematic are fires that spread quickly and those in which toxic gases may form.

To prevent and delay fires, fire retardants are used in a variety of products such as plastics, textiles, wood products, paints, and electronic and electrical devices. Appropriate standards define the protective action that the industry must provide for each application (see box on flame-retardant classes).

Due to rising global safety standards and the increasing use of flammable materials, the market for flame retardants is becoming increasingly important: according to a study by the market research institute Ceresana, it is now estimated to be worth €1.9 billion. Flame retardants must be precisely adapted for the specific application, which is possible only in close collaboration with producers, processors, and users of the end products.

In cable insulation, producers incorporate the fire retardant during extrusion. However, fire retardants complicate the processing of plastics; they may also be highly corrosive or abrasive toward com- ▶▶

In a fire, smoke emission hinders firefighting and evacuation of the building. The longer a fire is delayed from spreading and the less smoke formed, the more time remains for occupants of buildings to escape and for timely intervention of the fire department to minimize physical injury and damage to property. Flame-retardant plastics play an important role here, for example, in preventing the spread of the fire through cable ducts (right) which usually extend through the entire house



Figures 1-3 refer to an ethyl-vinyl acetate compound with a magnesium hydroxide Mg(OH)₂ content of 65 percent. Fig. 1 and 2: as processing aids in the production of polymer compounds by extrusion of polymers and fire retardants, TEGOMER® additives increase the MFI (melt flow index) of the mixture and reduce its Mooney viscosity. This reduces the extruder head pressure and the resulting torque (fig. 3). As a result, throughput increases while power consumption and maintenance costs are reduced

Figure 1. Melt flow index (MFI)

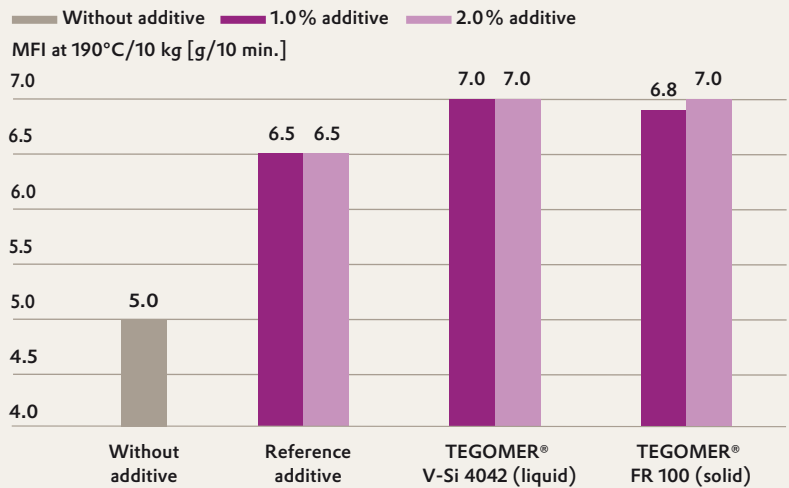


Figure 2. Mooney viscosity

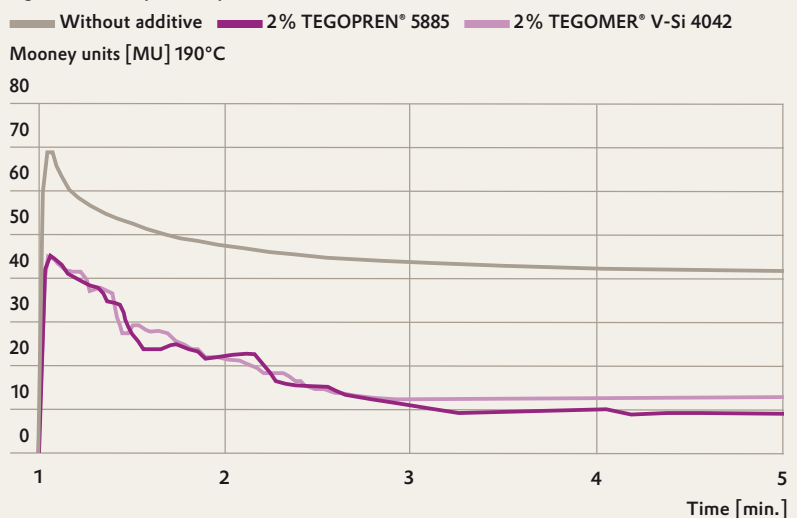
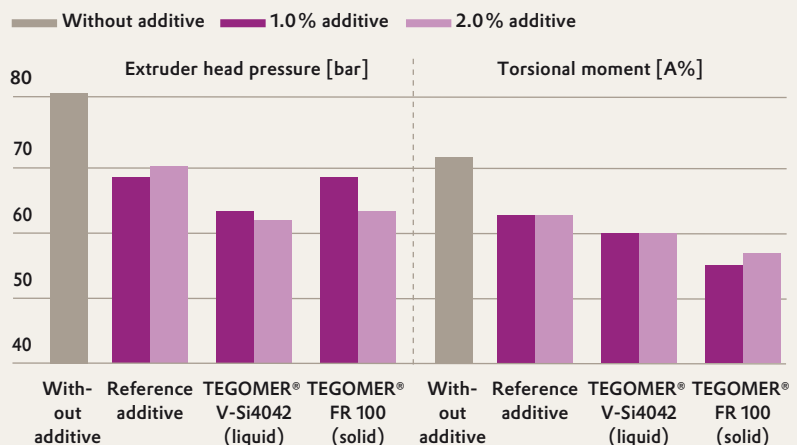


Figure 3. Extruder head pressure (left) and torsional moment (right)





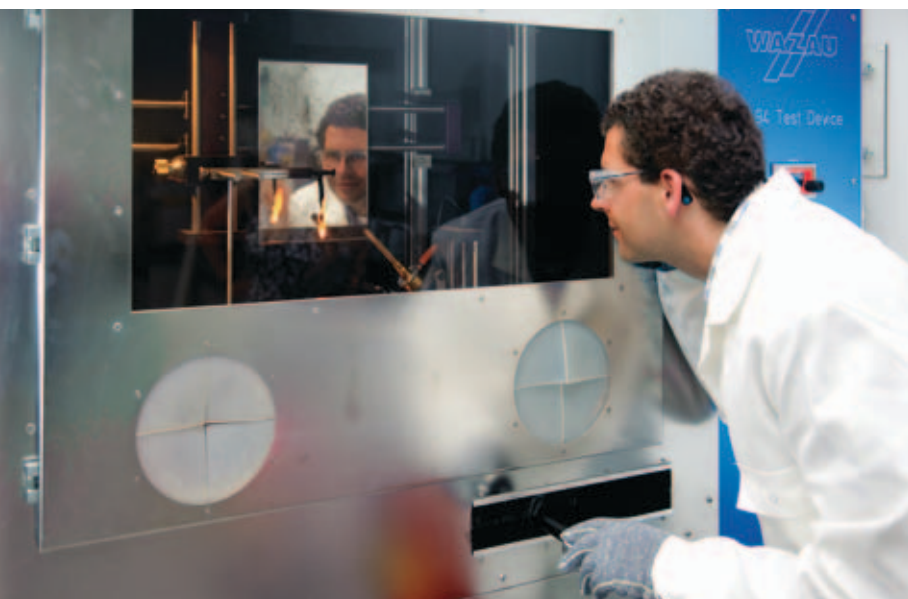
▶▶▶ pounding machines. For nearly ten years, therefore, Evonik has been supplying cable compounders with TEGOMER® additives, based on organomodified siloxanes, that serve as processing aids in the extrusion process. These have been proven to reduce power consumption and extruder head pressure because they act as a kind of internal lubricant, lowering the viscosity of the compound (fig. 1-3), which reduces friction and therefore maintenance costs.

But there is still much potential in the additives for further improving the flame-retarding action of metal hydroxides. In strategic partnerships, Evonik has systematically investigated how the action of these flame retardants can be further optimized by the use of additives and how they do not only improve the compounding process. They are much more than just processing aids.

Metal hydroxides: the flame retardants of choice

Metal hydroxides are among the most commonly used flame retardants worldwide. In a fire, they produce neither toxic gases nor soot particles. The compounds used are mainly aluminum hydroxide ($\text{Al}(\text{OH})_3$ or aluminum trihydrate, ATH) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$ or magnesium dihydrate, MDH). In the event of a fire, the metal hydroxides release water on heat uptake: the water cools down the material by evaporation. This delays the spread of the fire without generation of toxic gases.

However, if the metal hydroxides are to show the desired effect, they must be mixed with the flammable polymer in high proportions of more than 60 percent. ATH has the additional disadvantage for polymer processing that it releases water at temperatures as low as around 190°C. The melting point of the polymer, which is relevant to extrusion, lies in many cases relatively close to this value, as for EVA (ethylene vinyl acetate) or PE (polyethylene). MDH, on the other hand, releases water only above 300°C, and is therefore used even in PP (polypropylene) or PA (polyamide).



In the new plastics test center in Essen, officially opened in February 2012, Evonik has available all the facilities needed to give plastics an abrasion-resistant or flame-retardant finish. These include a compounding test center, a processing test center, and also a facility for testing in accordance with the specifications of the UL 94 flammability standard (bottom photo)

Evonik has for many years forged strategic partnerships for flame retardants, for example, with Nabaltec, a specialist in ATH production. Last year approval was received for a research project on flame retardants in cable insulation, with funding from the state of North Rhine-Westphalia; Evonik's partners in this project are the compounder and cable manufacturer Nexans and the magnesium hydroxide producer Penoles. Nexans possesses test facilities that not only test the flame retardancy of compounds but also of entire cable bundles. Cable bundles of this kind are found for example in the wire harnesses of cars, and also, especially, in the ducts of buildings. Evonik has now also built its own test facilities: the new plastics test center in Essen now possesses a facility that allows testing in accordance with the specifications of the UL 94 standard of the flammability of plastic materials, using the compounds produced there on twin-screw extruders.

Together with Nabaltec, Evonik has tested various formulations using ATH into which organomodified siloxanes have been mixed. Again jointly with Nabaltec, Evonik has also developed and tested new ATH formulations that, thanks to the additives, allow better dispersion in the polymer during extrusion. The additives must be adsorbed on the ATH particles in the correct way. There are two possibilities here: post-treatment of the ATH with the organomodified silanes (OMSs), or the use of the OMSs during compounding for in-situ hydrophobization of the metal hydroxides. The results from the formulation trials and test series were positive for both of these approaches.

To act effectively as a flame retardant, ATH must normally be mixed with a polymer in a proportion of 63 to 65 percent to attain the highest UL 94 flame retardancy rating of V-0. Thanks to the additives from Evonik, the same efficiency can be achieved with a lower percentage of ATH; this was previously possible only by using a higher ATH concentration. Depending on the required flame retardancy rating, the proportion needed is 59 to 61 percent only. These values have been confirmed in tests, on equipment of the type used in the categorization of materials by the flame retardancy rating. >>>

FLAME-RETARDANT CLASSES

The UL 94 test

Various methods have been established for the classification of flame retardants and their use in polymer compounds such as cable insulation. In the UL 94 tests, test laboratories expose defined test materials to open flames. The power and duration of the flame are also specified.

There are various levels that a flame-retardant compound of a plastic can attain in the UL 94 tests:

V-2: extinction of a vertically clamped sample within 30 seconds

V-1: same as V-2; in addition, there must be no dripping of a fused polymer

V-0: same as V-1; in addition, the flame must be extinguished within ten seconds





Positive side effects of Evonik additives: kinking in the cable strand, which can complicate the drawing of cables over long distances as in multistory buildings, does not occur. Additionally, the continuous printing of the cable that is necessary is not negatively impacted as in the case of other additives such as cheap silicone oils

Plastic insulation with additives from Evonik: in a (flame retardancy) class of its own

The use of organomodified siloxanes extends the compounder's formulation freedom by two to four percent, which is a significant gain. The available measurement data (fig. 4 and 5) show that the additives enable compounders to improve their plastics insulations by one to two flame-retardant classes. This is an inestimable advantage in a market where standards have become increasingly stringent over the last few years.

Moreover, with additives from Evonik, the combination of flame retardant and polymer also scores better on all other parameters than a pure ATH-polymer mixture. The additive ensures that the metal hydroxide is more effectively dispersed in the melt. For example, the greater freedom of formulation allows significant reduction in stress whitening of the cable insulation when bent. Moreover, twisting (kinking) of the cable strand, which is particularly likely when cables are drawn over long distances, as in cable ducts of multistory buildings, does not occur. Water absorption can also be reduced, which improves the quality of the insulation by reducing conductivity.

In connection with flame retardancy, the additives also bring about better char formation, which is the development of a crust on the surface of the burnt material. This is an important property: in the event of a fire, this encrustation prevents the ambient heat, or even direct fire, from penetrating rapidly into the internal layers of the cable. This also allows more time for evacuation and firefighting, and extends ▶▶



Compound formulations are tested in the test facility in conformity with the UL 94 flammability standard. EVA that is flame retarded with 65 percent MDH or ATH and contains TEGOMER® additives such as processing aids develops less heat (fig. 4) and releases less smoke (fig. 5) over the same period than flame-retarded EVA without TEGOMER®. This gives the fire department time to extinguish the fire, and the occupants of the building time to escape

Figure 4. Heat release rate EVA 19, 65 wt.%

— ATH without additive — ATH + 2% TEGOMER® V-Si 4042 comp.
 — MDH without additive — MDH + 2% TEGOMER® V-Si 4042 comp.

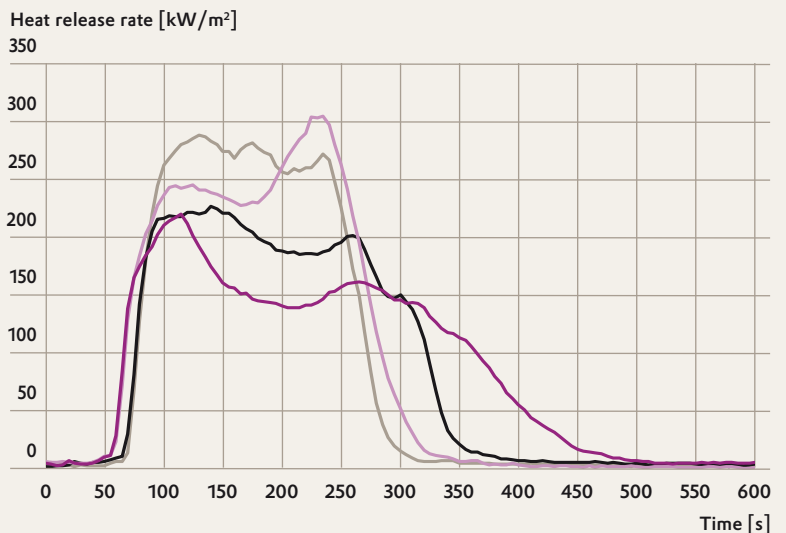
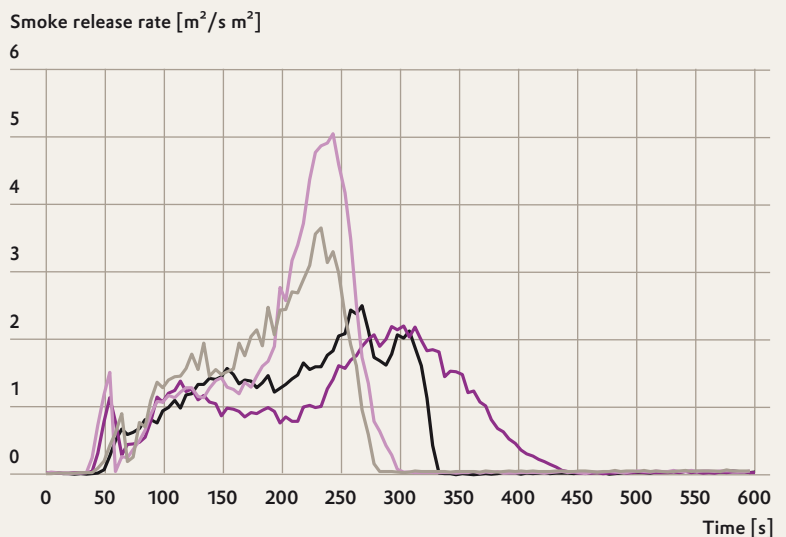


Figure 5. Smoke release rate EVA 19, 65 wt.%

— ATH without additive — ATH with 2% TEGOMER® V-Si 4042 comp.
 — MDH without additive — MDH with 2% TEGOMER® V-Si 4042 comp.



Cone calorimeter test on EVA flame retarded with 65 percent MDH. The TEGOMER® containing variant (right) shows significant char formation. This delays the advancement of the fire to a point where short-circuiting of the cable occurs; heat generation and gas emission are delayed, or occur to a significantly lesser extent. Additionally, the LOI (low oxygen index)

of the compound with TEGOMER® is 43, while the LOI of the variant without TEGOMER® is only 36. The higher LOI is another indication that the compound with TEGOMER® has the lower flammability, i.e., the flame retardancy is better than in the formulation without the additive



Without additive, LOI = 36



With 2% TEGOMER® V-Si 4042 used during compounding, LOI = 43

Degradation of EVA flame retarded with MDH (left) and ATH (right), without (above) and with (below) TEGOMER® at 400°C. TEGOMER® causes silicification of the material, with the formation of a skeletal framework that ensures mechanical stability and delays the progress of the fire

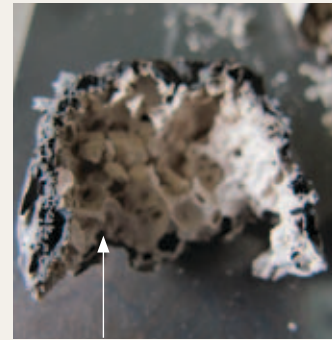
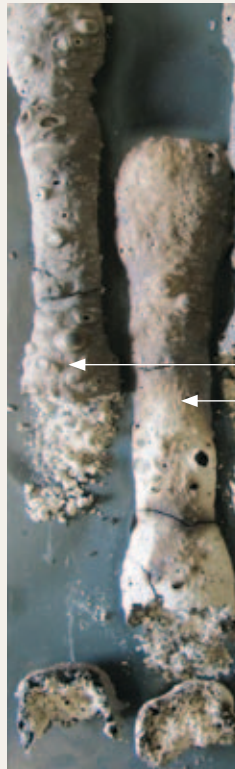
65% MDH



Without additive
2% TEGOMER®V-Si 4042 used during compounding



65% ATH



Without additive
2% TEGOMER®V-Si 4042 used during compounding



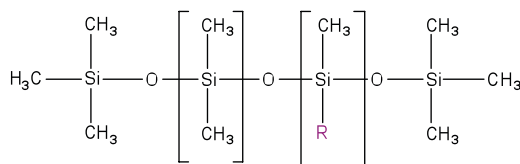
ORGANOMODIFIED SILOXANES

Versatility of application

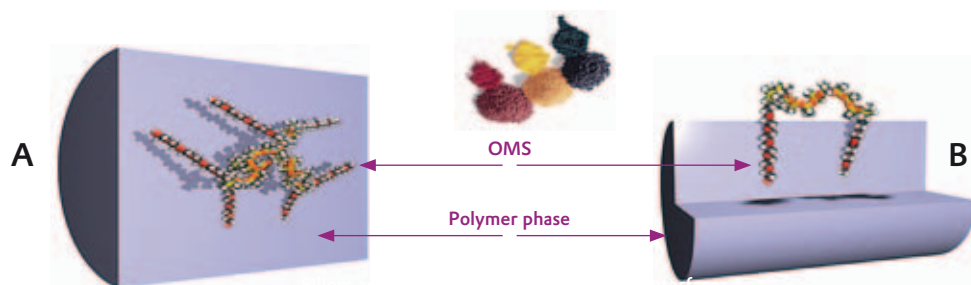
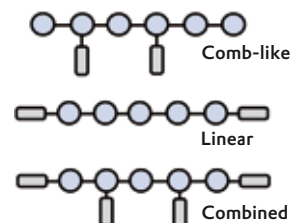
Additives based on organomodified siloxanes are used in many industrial applications. Examples are to be found in cosmetics, coating formulations, and in the production of PU foams. Siloxanes of this type are chemical compounds containing various organic functional groups as well as dimethylsiloxy units. Examples of such groups are alkyl, polyester, polyether, acrylate, hydroxyalkyl, and aminoalkyl groups. Organically modified siloxanes may be linear (with the organic groups at the two ends),

comb-like (with the organic groups at right angles to the siloxane chain), or a mixture of the two variants. The desired properties of the molecules can be attained through different combinations of these various options, as with a construction kit. Evonik possesses extensive expertise in the design of the chemical behavior of organomodified siloxanes. The products are marketed under the TEGOMER® and TEGOPREN® brand names.

Versatility: the properties of organomodified siloxanes can be fine-tuned as required via the organic groups and the architecture. For example, it can be controlled whether the siloxanes are homogeneously distributed within a polymer (bottom left) or are confined to the surface (bottom right)



R = Alkyl, polyester, acrylate, epoxy, hydroxyalkyl, aminoalkyl ...



▶▶ the interval after which a short circuit (due to burning away of the insulation) could cause further problems in the building, such as the trapping of passengers in an elevator.

The reason for the high mechanical stability of the material made from the ATH-polymer mixture lies in the additives. In the event of fire, they form oxides such as SiO_2 , H_2O , and CO_2 , which are non-flammable solids and gases. Due to the SiO_2 formed, silicification occurs, and because the additives are distributed as fine droplets through the entire cable sheath, a substructure remains that ensures the stability of the ash.

Due to the many advantages that organomodified siloxanes offer for flame retardants, the tests by Evonik and its partners have aroused much interest among cable manufacturers: flame retardants based on metal hydroxides are enhanced in quality by

additives that simplify and even widen the scope of their use. Such additives allow new applications in which, for example, MDH for polypropylene requires improved flowability in injection molding applications, which is ensured by the organomodified siloxanes. ◀◀



Kathrin Lehmann, of Evonik's Consumer Specialties Business Unit, is head of Technical Service and Development for additives in plastics and polymer applications at the new plastics test center in Essen. Following studies in synthetic chemistry at the Humboldt University of Berlin, she worked in technical service for a pigment manufacturer for five years. In 1999 she moved to Evonik, where she was responsible for the development of wetting and dispersing additives for coating applications. She took up her current post in April 2005. +49 201 173-2824, kathrin.lehmann@evonik.com