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Efficient and Versatile

Pelletized Silicone Additives for Thermoplastics

Manufacturers and processors of thermoplastic compounds have tough international competition. So, they are looking for ways of lowering their costs and creating more added value. A highly efficient silicone additive, which is universally suitable for all thermoplastics and easy to process, can help.

In the plastics industry, silicone additives are known for their friction-lowering effect. For this reason, they have been used in the compounding of thermoplastics since the 1970s [1]. Adding silicones, generally polydimethylsiloxanes, can enhance the processing and surface properties of plastics significantly [2].

Polydimethylsiloxanes offer several advantages over organic additives with a similar effect. At 20 mN/s, their surface energy is extremely low. That's why silicones are insoluble in the melts of almost all organic polymers and accumulate at the interfaces. Silicone additives also outperform organic ones in terms of thermal stability and low-temperature flexibility.

Formulation with 70 % Silicone

Prior to the turn of the millennium, the use of silicone additives was quite conservative. This was due to problems associated with the products in use at the time. Silicone fluids tend to exude from the plastic. If silicone escapes from the plastic surface, so-called blooming can occur. This can complicate subsequent processing steps such as coating and laminating, as the exuded silicone can creep onto the surfaces of neighboring parts and thus contaminate the surroundings.

If, however, the additive is an ultra-high-molecular silicone polymer [3], blooming is not an issue. The high molecular weight makes it virtually impossible for the silicone to exude. The downside is that high molecular weight complicates the silicone polymer's processability. Due to its extremely high viscosity, it can only be incorporated into thermoplastic compounds with great difficulty.

Low-voltage cables with sheating of polyolefins (figures: Wacker Chemie)

Silicone masterbatches, which have been available since the late 1990s, solve this handling problem. Here, a thermoplastic polymer that is compatible with the thermoplastic to be modified serves as a carrier for the silicone. This masterbatches are easy to process, because they consist of solid pellets. However, compounders must keep a specific additive masterbatch in stock for each thermoplastic.

Genioplast Pellet S silicone pellets from Wacker Chemie AG, Munich, Germany, came on the market in 2004 and represent the current state of the art. This additive, which is also easy to process, consists of a pelletized, highly concentrated silicone polymer formulation [4]. The product's silicone content is 70 %. Pyrogenic silica, whose properties are tailored to the polydimethylsiloxane, serves as the carrier.

Impact due to the Carrier

As well as the silicone active, the carrier significantly contributes to the effect of the pelletized silicone-polymer formulation. Pyrogenic silica has several functions [4]:

- Firstly, it provides the silicone-polymer formulation with the high level of stability under load required for compounding. The pellets retain their shape, so long as they are not exposed to excess pressure. Their incorporation poses no problems in a co-kneader or twin-screw extruder if they are conveyed via a spiral conveyor or flex-wall metering device.
- Secondly, pyrogenic silica ensures that the additive is compatible with all thermoplastics and thermoplastic elastomers. Compounders thus only require a single silicone additive to optimize a whole range of different thermoplastics. This is a big advantage over silicone masterbatches.
- Thirdly, the silica anchors the silicone active in the polymer compound. Due to its high molecular weight, the silicone polymer generally does not migrate out of the polymer matrix. The anchorage makes the additive's effect permanent and creates additional protection against undesired blooming. In the plastic, the pyrogenic silica acts as the anchor by bonding to the siloxane backbone via physical interactions on the one hand, and, on the other, mechanically interlocking with the organic polymer.

At the applications laboratories of Wacker, the additive's effects on various thermoplastics – such as polyolefins, different engineering plastics and thermoplastic elastomers [5] – were tested. The test compounds included talc-filled polypropylene systems, as used in vehicle interiors, and halogen-free, flame-retardant polyolefin blends for cable sheathing.

Constituent	Amount in parts by weight
Polypropylene: medium impact copolymer	68.2
Polyolefin elastomer: density 0.87 g/cm^3 MFR 5 g/10 min (190°C, 2.16 kg)	10.0
Talc: D50 3.7 µm, D95 10.2 µm (Sedigraph method, ISO 13317-3)	20.0
Black pigment: carbon black MB	1.0
Scratch-resistance additive: -- none (reference) -- Genioplast Pellet S -- competitor product	0 (reference); 1 or 2 or 3
Calcium stearate	0.2
Other additives (antioxidant, UV-stabilizer)	0.6

Table 1. Composition of the tested PP/talc systems: the friction-lowering competitor products 1 and 3 are silicone-based and competitor product 2 is organic

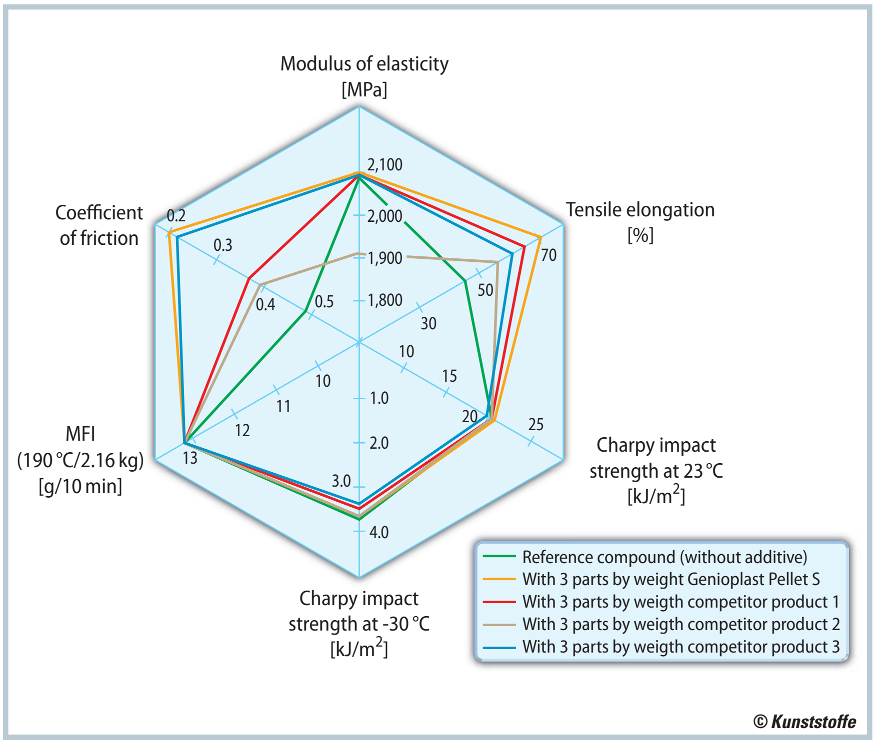

Fig. 1. Comparison of effects of polypropylene compounds with and without friction-lowering additives (compounds from Table 1, values according to common DIN-standards)

Scratches Are Less Visible

In cars, the door, pillar and trunk panels, as well as the housing of the center console and parts of the dashboard, are usually made of talc-filled polypropylene (PP/talc). The automotive industry expects the surfaces to provide a look of quality throughout the vehicle's entire service life. This requires high scratch and abrasion resistance and good look-and-feel. Furthermore, the plastic should not release any substances into the environment. In addition to blooming, fogging – condensation with deposits on the windscreen – and unpleasant odors are not welcome in the interior. The molded parts must also be sufficiently impact resistant and balanced regarding their stiffness and flexibility.

Laboratory testing [5] thus focused on these properties. The tests compared the silicone pellets with one organic and two silicone-based competitor products. A standard PP/talc formulation – to which the additives to be tested were added – served as the base and reference (**Table 1**). Test plates were produced from the compounds in an injection molding machine. Their surface quality was assessed according to industrial standards and their mechanical properties were tested. Further tests covered fogging behavior and the influence of the additives on the flow properties of the polymer melt.

Figure 1 illustrates the key results. Genioplast Pellet S significantly reduces the coefficient of friction. The surface feels smooth and dry. The silicone pellets improve elongation without reducing the modulus of elasticity or impact strength. Mechanical and flow properties remain unchanged.

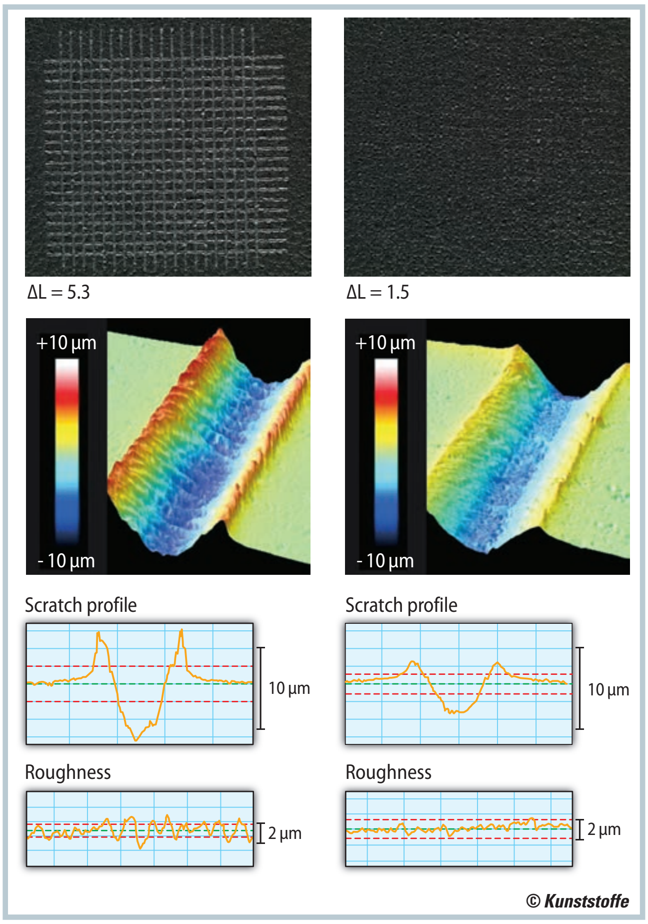

Fig. 2. Grained polypropylene-talc test plates underwent the Erichsen scratch test and were then examined by confocal microscopy. Results for the reference compound at the left side, results for the compound to which silicone pellets had been added at the right side. The silicone additive reduces the depth and roughness of a scratch

The reduced surface friction provides the plastic with greater scratch and abrasion resistance. This effect is clearly evident with the addition of 3 % of the pelletized silicone polymer, as shown by the inspection of a scratch with the aid of a confocal microscope [5] (**Fig. 2**): the contour of the scratch is flatter and the surface inside the scratch is less rough.

The silicone pellets also performed very well in all other tests – such as visibility of scratches, mar resistance as per GME 60280, rubbing resistance with a crockmeter as per ISO 105-X12 and fogging behavior as per DIN 75201 – whereas the organic competitor product displayed weaknesses.

These results verify that the active ingredient of the silicone pellets does not migrate out of the polymer matrix. Unpleasant odors, fogging and blooming can thus be ruled out. This effect can be explained by the fact that the silicone macromolecules are securely anchored in the polymer matrix. Due to its low surface energy, the active migrates to the interfaces as desired and the ends of the long siloxane chains protrude from the plastic.

The addition of silicone pellets can have a positive influence on the surface properties of many engineering plastics and thermoplastic elastomers, too. These plastics also become more scratch and abrasion resistant.

Easier Extrusion, Better Flame Resistance

Polymer compounds for the manufacture of sheathing for low-voltage cables are based on polyolefins (**Title figure**). They are often rendered flame-retardant with aluminum hydroxide (ATH). During extrusion, these highly filled compounds can briefly heat up so much that ATH and other less thermally stable auxiliaries start to

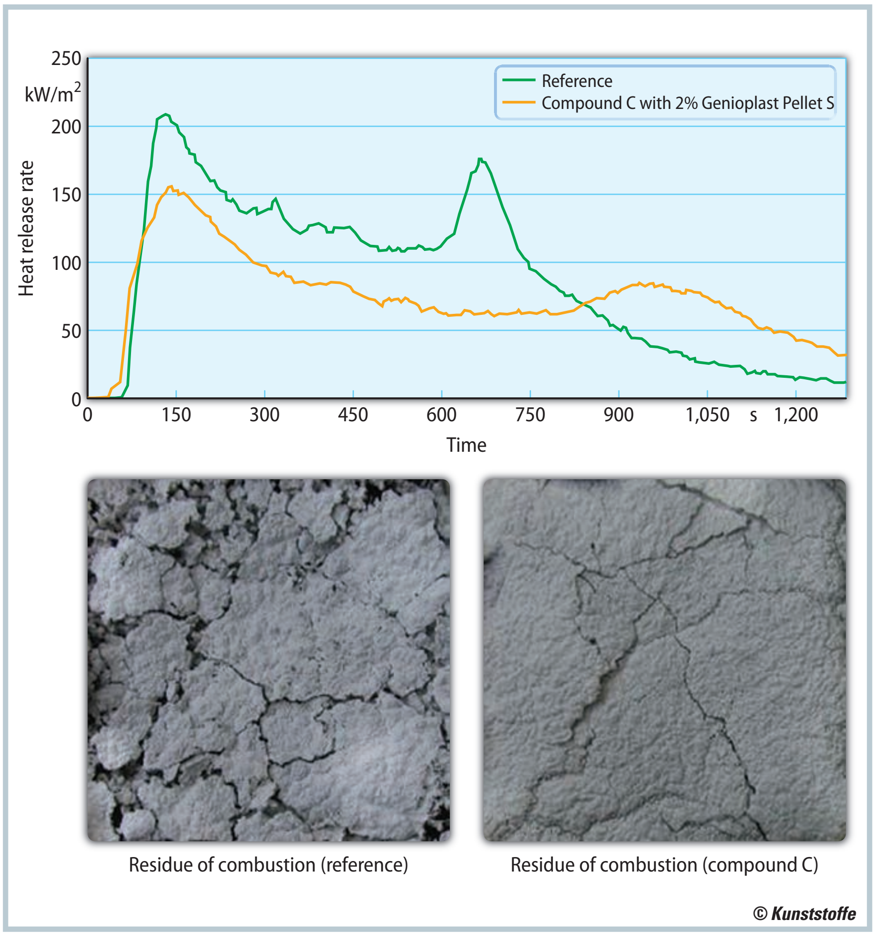

Fig. 3. In ATH-filled, polyolefin-based polymer compounds, the pelletized silicone additive promotes ATH's flame retardancy, as shown by cone calorimetry (top image). The additive facilitates char-layer formation: combustion residue of the reference compound without additive (bottom left), combustion residue of a polymer compound with Genioplast Pellet S (bottom right)

Constituent	Amount [phr]			
	Reference	Compound A	Compound B	Compound C
EVA (18% VA)	73	73	73	73
m-LLDPE	19	19	19	19
MAH-g-LLDPE	8	8	8	8
ATH	160	160	160	160
Antioxidant	0.75	0.75	0.75	0.75
Genioplast Pellet S	0	1	3	5

Table 2. Composition of tested cable-sheath compounds in parts per 100 parts rubber (phr)

	Reference	Comp. A	Comp. B	Comp. C
Extrusion parameters[1]				
Torque [%]	72	70	68	66
Die pressure [bar]	33	28	28	26
Current consumption [A]	38.9	37.8	36.9	35.5
Compound properties				
Tensile strength [MPa]	12.7	12.4	12.4	12.2
Elongation at break [%]	69	81	83	77
Melt flow index, MFI (190°C / 21.6 kg) [g/10 min]	11.4	11.6	12.9	13.5
Coefficient of friction	0.52	0.33	0.31	0.27
Flame retardance characteristics				
Oxygen index (LOI) [% O^2]	32	32	33	33
Time of ignition [s]	68	–	–	61
Peak heat release [kW/m²]	203	–	–	151
Total heat released [MJ/m²]	110	–	–	102
Total smoke formation [m²/m²]	866	–	–	313
Burning time [s]	1,217	–	–	1,820

1 Compounding with KraussMaffei Berstorff ZE 25 twin-screw extruder (screw diameter 25 mm, L/D 47, extruder speed 200 rpm, throughput 10 kg/h)

Table 3. Extrusion parameters and properties of the tested cable-sheath compounds (the flame retardance characteristics data (with the exception of LOI) was determined by cone calorimetry)

decompose. This can result in die drool and fluctuating wall thicknesses in the extruded cable sheath.

Application testing of different ATH-filled polyolefins shows that the addition of silicone pellets offers clear advantages for the manufacture and processing of the compounds. It increases the plastic's quality and synergistically promotes ATH's flame retardancy. This is further illustrated by the test results for a compound that is representative of the cable industry. **Table 2** summarizes the formulations and **Table 3** outlines the determined extrusion parameters and material properties.

The additive reduces the melt viscosity. As a result, the die pressure at the extruder is lower, so a lower torque is sufficient for extrusion and power consumption drops. Furthermore, the extrusion can be run more gently, so that the temperature peaks are less extreme. In addition, the silicone active improves ATH's bonding to the polymer matrix and thus facilitates better dispersion. Both the gentle process and the good dispersion reduce die drool.

The pelletized silicone additive also had a positive effect on the plastic's flame-retardant characteristics. As shown by the cone-calorimetry results (**Figure 3**), the additive reduces the peak and total heat release and cuts down on smoke formation. The reason behind this is the more compact and less brittle char that deposits on the burning test specimen as a crust. This combustion residue hinders oxygen transport and heat transfer.

Requirements on flame retardant characteristics are also high in the case of aluminum composite panels (ACP). Such lightweight panels find use in the construction industry as siding for office, commercial and industrial buildings. The composition of the plastic core of these sandwich-like panels is similar to that of the compounds from which cable sheathing is extruded. Several ACP manufacturers already use the silicone additive as a processing auxiliary and to improve flame retardance.

Conclusion and Outlook

As shown by the test results, the silicone additive, which is universally suitable for all thermoplastics, principally has two effects: on the one hand, added in small amounts, it serves as a processing auxiliary and thus cuts costs. At a slightly higher dosage, on the other hand, it also enhances key performance properties of the plastic, thus providing a way of creating more added values. Thanks to its favorable properties, the additive is well-established in the plastics industry. And that is not all. Recently also a grade called Genioplast Pellet P plus approved for food-contact use has become available as well [6]. ■

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References & Digital Version

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