

**A New Filler Dispersion Aid
for the Plastics and Rubber Industry**

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Abstract: The performance of reinforced polymers depends on the filler and the polymer-filler interaction at the interface. As such, the filler dispersion is critical and will be detailed in this paper. Silanes are widely used as coupling agents and adhesion promoters, as well as dispersing aids for fillers. We will review the dispersion mechanism, the effect of silane treatment of fillers, as well as the fundamentals of silane chemistry and filler treatment. Additionally, the new Dow Corning® Z-6173 Filler Dispersion Aid offers traditional alkoxysilane functionality. The properties and benefits of this new filler surface treatment will be discussed.

The properties of filled or reinforced polymers generally depend on the size, shape, and surface characteristics of the filler particles. For a given system, one of the most important parameters impacting the mechanical, electrical or optical performance is the filler dispersion. It is well known that large agglomerates tend to form a flaw which leads to mechanical failure.

Silanes are widely used as coupling agents and adhesion promoters, but also as dispersing aids for fillers in polymer matrices. As such, silica is traditionally surface-treated with silanes to improve the reinforcement of tire rubber. Silanes are also commonly used for treating ATH, MDH and TiO₂ in plastics. However, the role of silane on the dispersion process is assumed, but there is no evidence for its mode of action.

Expanding on the extensive knowledge base of filler dispersion and polymer-filler interaction developed with rubber and plastic compounds, we wish to review the dispersion mechanism of fillers, the factors affecting the dispersion, and the effect of the silane treatment on fillers. We will also review silane chemistry and application to fillers, as well as the attributes of the new filler dispersion aid for plastics and rubber, Dow Corning Z-6173 Filler Dispersion Aid.

The Dispersion Mechanism

The first challenge of processing the compound is the filler dispersion. The agglomerates must be broken down into smaller parts called

aggregates, but not to the level of primary particles (Figure 1). An optimal particle size distribution must be achieved to attain the best performance in a specific application.

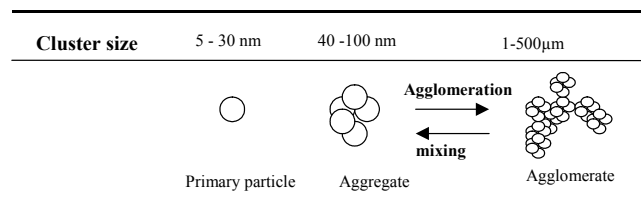


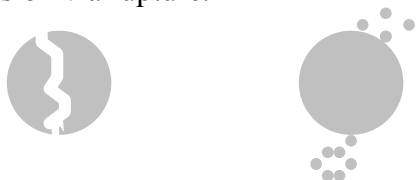
Figure 1. Filler aggregation and dispersion.

During mixing of the compound, mechanical shear induces dispersion and distribution of the filler in the matrix. In dispersive mixing, the objective is to break down agglomerates, and possibly aggregates, to fragments of uniform size. These fragments must be evenly distributed within the matrix to ensure uniform properties of the final compound. However, breaking down the filler particles in this manner often proves difficult. Even in the case of silica-filled rubber for tire treads, where extra efforts are made to disperse the filler, as much as 15-20% of the total amount of a highly dispersible silica remains in the macro dispersion state (agglomerate larger than 5 µm).¹

Dispersive mixing is governed by competition between the hydrodynamic forces acting on the particulate agglomerate and the cohesive forces holding that agglomerate together. Hydrodynamic forces are determined by the strength and geometry of the flow field produced by shear stress. Particle-particle interaction forces and the

packing arrangement of individual particles within the agglomerate determine agglomerate cohesivity.

The mechanism for dispersion has been extensively studied.²⁻⁴ Two modes of dispersion are identified: the bulk rupture (an abrupt breakage of the agglomerate into multiple large fragments) and the erosion (a sequential removal of small fragments from the agglomerate periphery) (Figure 2). The bulk rupture mechanism is favored with high hydrodynamic stress (high shear); this mechanism is sudden and leads quickly to agglomerate size reduction. The erosion mechanism is slower, but leads to a smaller final aggregate size. Increasing the hydrodynamic force leads to a shift from dispersion via erosion to dispersion via rupture.



$\sigma_{\text{cohesion}} < \sigma_{\text{hydrodynamic}}$ $\sigma_{\text{cohesion}} > \sigma_{\text{hydrodynamic}}$
 Figure 2. Schematic mode of agglomerate dispersion.

Factors Affecting Filler Dispersion

Several physical and chemical factors can affect the dispersion process: the structure and cohesivity of filler agglomerates, the surface activity of the filler, the chemical interactions between polymer and filler, and any infiltration of the polymer into the agglomerate.

Structure (i.e, the packing arrangement of the primary particles of the filler) is an intrinsic parameter mainly dependent on the filler synthesis route. Mercury porosimetry characterizes this parameter and gives pore size distribution with good resolution.

Cohesivity of the agglomerates depends on the strength of the individual bonds between neighboring particles and the number of such bonds that must be broken to release a fragment. The strength of individual bonds is determined by particle composition and surface characteristics (electrostatic, van der Waals and hydrogen-bonding) as well as interactions from secondary

species, such as silanes, grafted or adsorbed onto the particles. For instance, silanes can decrease the agglomerate cohesivity through a shielding of inter-aggregate interaction, thus decreasing the hydrodynamic stress needed to break the agglomerate.

Infiltration of the matrix into the agglomerate occurs as soon as the filler and polymer are mixed. The role of infiltration of the agglomerate by the polymer is one of the first order parameters of filler dispersion. It can have a positive or negative impact on the ability of the filler to disperse. For instance, if it creates bridges between aggregates, the cohesivity of the agglomerates is reinforced, resulting in a delay of the dispersion as observed in CaCO₃ and silica-filled silicone resins.⁵

The surface activity of the filler is defined through its surface energy γ , and is composed of dispersive (γ_s^d) and specific (γ_s^{sp}) components.

$$\gamma = \gamma_s^d + \gamma_s^{sp}$$

The dispersive component (γ_s^d) is based on London forces, and is representative of polymer-filler interaction.

The specific component (γ_s^{sp}) characterizes the interaction between filler particles. Table 1 gives some examples of γ_s^d for untreated and treated fillers.

Table 1. Dispersive Component of Filler Free Surface Energy and Effect of Surface Treatment⁶

Filler	γ_s^d (mJ/m ²)
Carbon black	51
Mg(OH) ₂	95
Mica	70
Talc	130
TiO ₂	76
CaCO ₃	200
CaCO ₃ treated with stearic acid	48-53
SiO ₂	105
SiO ₂ esterified w/ alcohols C ₁₆ -C ₁	46-87
SiO ₂ vinyl silane treatment	84

Table 2. Polymer Filler Contact Area of 100 g Polymer at Several Filler Volume Fractions

Filler	Density g/cm ³	Specific Area m ² /g	Volumetric Area m ² /cm ³	Filler/Polymer Contact Area M ² /100 phr of polymer		
				5.0%	10.0%	20.0%
Alumina	3.7	103	381.1	542	1,144	2,575
Silica	2.1	200	420	1,053	2,222	5,000
Carbon black	1.8	120	216	632	1,333	3,000
Clays	2.6	25	65	132	278	625

The Effect of Silane on Dispersion

Silane treatment of fillers is known to improve the dispersion, but the mechanisms of action are not fully understood. Does it modify the infiltration of the polymer into the agglomerates or does it transform only the surface chemistry of the filler?

Effect on infiltration. The silane impact on infiltration of a polymer into agglomerate is not widely depicted in the literature. Scurati et al.⁷ have investigated dispersion through erosion kinetics studies, in which the reduction in size of a single agglomerate of known density, prepared by filler compaction, was monitored in a controlled flow field. Their work focused on the effect of silane pretreatment of the agglomerates. They observed that after treatment, the aggregate size decreases and the infiltration rate of polyolefins into a TESPT (Bis-triethoxysilyl-propyl-tetrasulfane) treated filler is slower than for untreated filler. These results can be interpreted as being due to the changes of polymer-filler interaction and agglomerate packing properties. This work also shows a dramatic effect of the silane on the erosion kinetics (Figure 3).

Effect on surface energy. Several studies on the influence of surface properties and surface treatment on filler-filler and filler-polymer interactions of silica filler treated with different silanes are reported in the literature.^{8,9} The silane treatment clearly decreases the dispersive and specific component of the surface energy.⁸

Effect on interface/interphase contribution to bulk performance. Submicronic fillers are generally classified as reinforcing fillers because if well dispersed, they can develop a large interface with

the polymer (Table 2). For instance, a volume fraction of 20% of 200 m²/g silica could generate more than 5000 m² of interface in 100 g of polymer. The silanization of the surface with an organosilane may influence a layer of 1 to 5 nm thick corresponding to 5 to 25 g of influenced polymer in every 100 g, thus contributing to the dynamic mechanical performance enhancement of, for example, silica-filled matrices.¹⁰

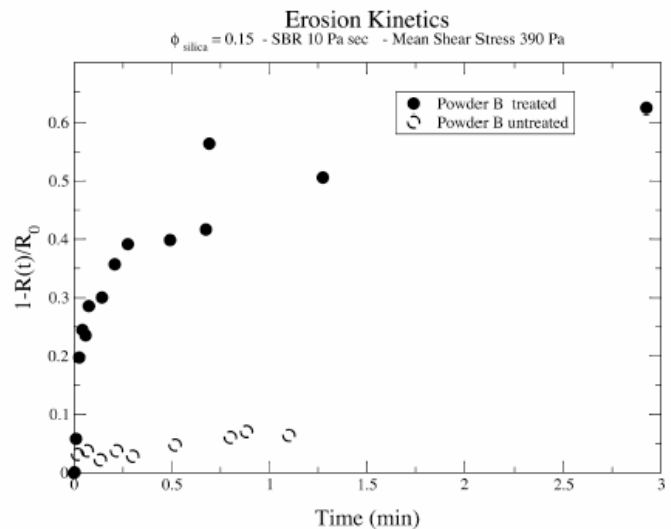
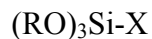


Figure 3. Kinetics of low viscosity polymer infiltrations into silica filters.⁷

However, the role of a silane is more complex than a single surface energy modification. Inter-diffusion phenomenon and interpenetrating network (IPN) formation in the interphase region occur and are critical for the final performance. Optimization of the IPN formation is therefore of primary importance, and hence, selecting the proper organosilane with regard to its compatibility with the matrix and the filler is critical.

Silane Chemistry and Filler Treatment

Silanes can transform the surface of a filler and improve compatibility in polymer matrices due to their dual functionality. A typical silane coupling agent/dispersing aid consists of:



where (RO) is a hydrolyzable group, such as methoxy, ethoxy, or acetoxy, and X is an organofunctional group, such as an alkyl, amino, epoxy, methacryloxy or vinyl. A silane coupling agent will act at the interface between the inorganic substrate (such as mineral, glass, or metal) and the organic material (such as an organic polymer, coating or adhesive) to bond, or couple, the two dissimilar materials (Figure 4).

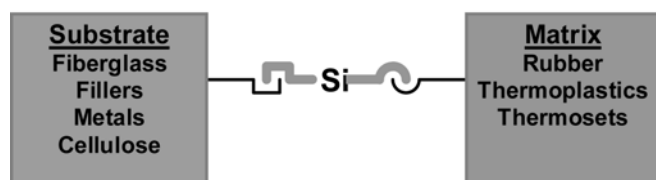


Figure 4. The silane coupling mechanism.

Dispersing aids such as silanes, as well as alkoxy-functional siloxanes, can be applied to mineral fillers by pretreatment or in situ mixing (during compounding with a resin or rubber). In either case, the reaction of the dispersing aid to the filler occurs in two primary reactions: hydrolysis and condensation (Figure 5).

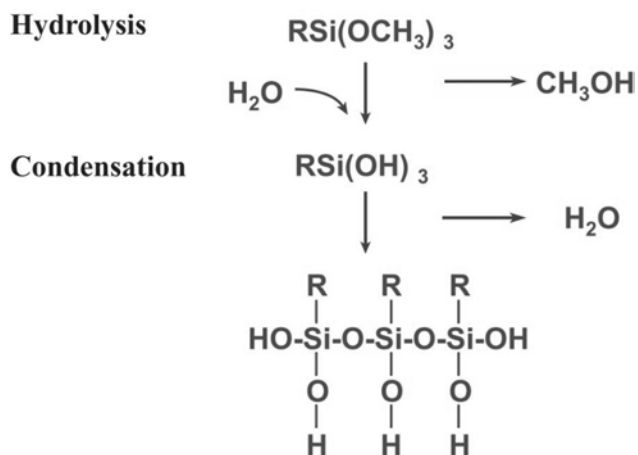


Figure 1. Hydrolysis and condensation of alkoxy silanes.

After hydrolysis, the silanol groups coordinate with the metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water (Figure 6).

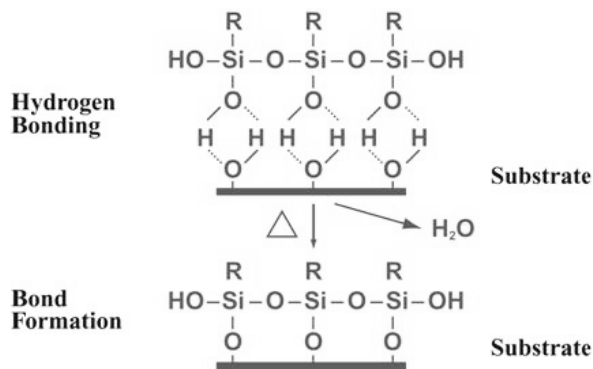


Figure 6. Bonding to an inorganic surface.

Silanes and alkoxy functional siloxanes react well with silicon and aluminum hydroxyl groups. Other metal hydroxyl groups may be reactive to a lesser extent, but often benefit from treatment. Figure 7 shows the general effectiveness of silane treatment of various fillers.

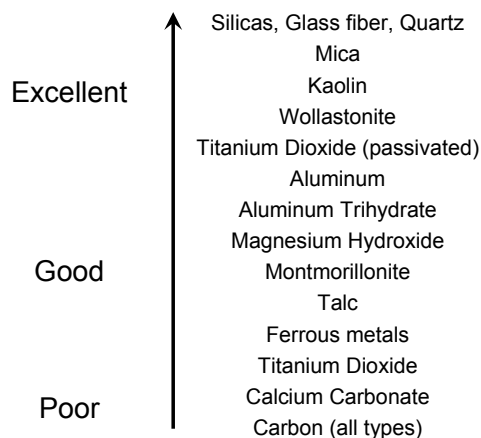


Figure 7. Effectiveness of silane bonding to filler surface.

A New Dispersion Aid

In addition to traditional, monomeric silanes for filler dispersion, Dow Corning Z-6173 Filler Dispersion Aid was developed to address the unmet needs of mineral filler producers and resin masterbatchers/plastic compounders. Dow Corning Z-6173 Filler Dispersion Aid has many of the same attributes as traditional silane coupling

agents, but also includes additional benefits. Properties include:

- Low viscosity liquid, which can be easily applied.
- Lower methanol byproduct generation compared to traditional silane coupling agents, resulting in lower VOCs.
- High boiling point of actives to reduce loss when applying.
- Hydrophobation of the inorganic mineral surface (improves filler's compatibility in organic matrices).
- Improved value.

Conclusions

Organosilanes are widely used in filled polymer composites to improve the dispersion of fillers. The exact role of the silane is not fully understood, but depending on the functionality, amount and method of introduction, the effect of these mineral filler surface treatments can be observed at different levels by:

- Accelerating or slowing the infiltration kinetic of the polymer matrix into agglomerates.
- Decreasing the agglomerate cohesivity, reducing the hydrodynamic stress needed to break the agglomerate and also limiting the re-agglomeration phenomenon.
- Generating an interface that can have a significant impact on bulk performance.

The selection of the organic functionality of the silane allows optimization of the final processing-performance compromise.

In addition to the new Dow Corning Z-6173 Filler Dispersion Aid, Dow Corning has more than 200 silanes and alkoxy-organo functional siloxanes¹¹ in development and commercially available to meet many different needs. Dow Corning continues to lead the development of silane technology and fundamental materials understanding, being supported by global technical expertise, including the Surface and Interface Solutions Center located in Seneffe, Belgium. Dow Corning can help optimize the filler performance in a polymer matrix and develop solutions with our customers.

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