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Treatment of Fillers with Organofunctional Silanes, Technology and Applications

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Summary: The surface of mineral fillers and reinforcements can be modified by reaction with organofunctional silanes. When they are incorporated into polymers, four major consequences result from the chemical modification of the filler surface:

1. *The filler-polymer physical interactions* are affected. This has a strong impact on rheology and can be used to improve processing.
2. *The filler-polymer chemical interactions* are affected. The resulting interphase maybe designed to be chemically stable, to exhibit barrier properties or to have specific mechanical properties that may help transfering stresses from the matrix to the filler. Organofunctional silanes are preferred candidates for creating covalent bonds between the filler and the polymer.
3. *The filler-filler physical interactions* are affected. This can be best observed in composite materials that are highly filled with fine particles. The effect is highlighted by a striking modification of dynamic properties at low strain.
4. *The polymer structure close to the interphase* can be modified through cure control agents or crosslinking agents. Silanes are moisture-curable, environmentally stable molecules that can be used as accelerators, crosslinkers or co-monomers.

Introduction

The global market of silane surface treatments for fillers and reinforcements reached about 300 MM$ [1]in 1999.

It has been growing very significantly in the past 20 years, first to improve the abrasion resistance and electrical properties of technical rubber filled with kaolin and clay, later to improve stiffness and heat resistance of engineering thermoplastics with fillers like talc, wollastonite and mica, much more recently to improve dynamic properties and rolling resistance of automotive tires replacing carbon black with precipitated silica. This latter segment alone should generate a silane consumption of over 300 MM$ by 2005.

All these developments could only happen thanks to the broad ability of silanes to control and modify filler surfaces. It is now widely understood that silanes can react with the surface of most mineral fillers to impart designed properties. It is also well accepted

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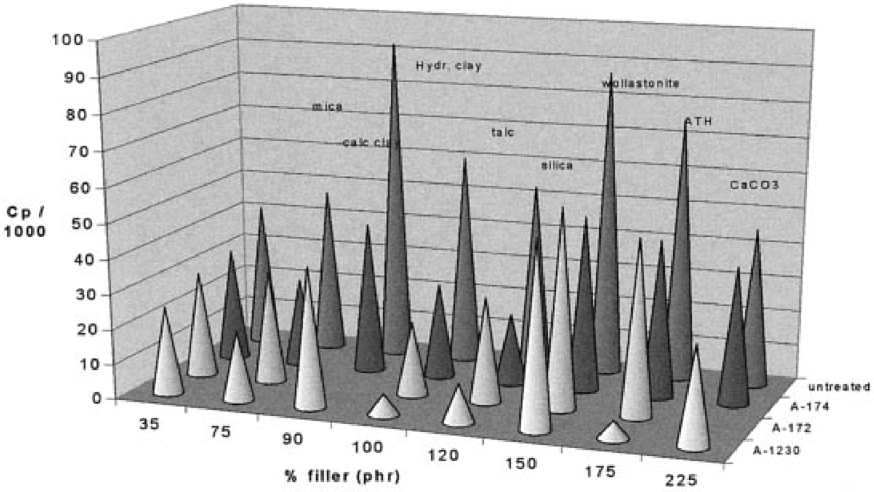
that the organofunctional part of the silane is preferably reacted with the polymer to achieve the best properties and that this covalent bridging mechanism controls surface properties like adhesion.

However more properties are affected by silane surface treatments. We shall review them briefly and we shall demonstrate how silanes can be selected and used to obtain optimum performance and processability.

Physical interaction between Filler and Polymer

The first benefit that can be observed when blending a silane-treated filler with a polymer is usually improved wettability : The filler adsorbs the polymer more completely and more rapidly because the silane treatment reduces the interfacial tension with organic liquids. As another result of improving the interfacial tension with the polymer, one also achieves a viscosity reduction of the filler/polymer system. Some examples of the viscosity reductions that can be expected from a suitable silane choice and treatment are presented in Fig. 1.

Figure 1. Viscosity reduction by silanes in selected systems



In water on the contrary, fillers are more easily dispersed if untreated. Silane treatments makes their surface hydrophobic and the interfacial tension is increased. To illustrate this effect, some contact angles with water[2,3] are reproduced in table 1.

Table 1. Wetting angle of water on silane treated surfaces

type of surface and silane treatment	Ref.	θ, °
Glass, untreated	2	0-15
Glass + $(CH_3)_3$ Si Cl	3	76-85
Glass + $C_{18}H_{37}(CH_3)_2$ Si Cl	3	65-85
Glass + $(C_3H_7)_2$ Si Cl_2	3	62-82
Glass + (t-C_4H_9) Si Cl_3	2	67-73
Glass + C_8H_{17} Si $(OMe)_3$	2	100
Calcined clay + C_8H_{17} Si $(OMe)_3$	2	162
Alumina trihydrate + C_8H_{17} Si $(OMe)_3$	2	148
Alumina trihydrate + CH_2=C(CH_3)-CO-O-$(CH_2)_3$-Si$(CH_3)_3$	2	72

As a result of increased interfacial tension with the silane-treated surface, the liquid water penetration into the interphase is hampered and a better resistance against humidity is achieved. Note that this is almost independent of the silyl reactive group, as long as the treatment conditions are set to ensure complete reaction between the silane and the filler. The major factor governing the hydrophobic effect is therefore the silane organic group. As from table 1 best results are obtained with octyl silanes. However, the benefit would disappear with time if the silane treatment itself was not chemically stable in a wet environment. Hence it is important to understand the chemistry of the silane reactions with the filler and the polymer.

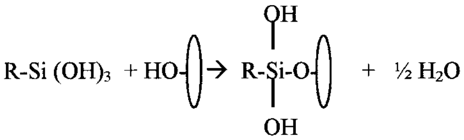
Chemical interaction between filler and polymer

The reactions between the silane, the filler and the polymer take place in presence of surface water :

The first reaction is the hydrolysis reaction of the silane. For example the reaction of a trimethoxysilane releases methanol and consumes water:

$$\text{R-Si(OMe)}_3 + 3/2\ \text{H2O} \rightarrow \text{R-Si (OH)}_3 + 3\ \text{MeOH} \qquad \text{(I)}$$

Then the resulting trisilanol reacts with a surface hydroxyl group of the filler (condensation reaction):



$$R\text{-}Si(OH)_3 + HO\text{-} \rightarrow R\text{-}\overset{OH}{\underset{OH}{Si}}\text{-}O\text{-} + \tfrac{1}{2} H_2O \qquad (II)$$

On one hand, in the equilibrium state the amount of OH-groups on the filler surface is the most important parameter governing the quantity of silane-filler covalent bonds. On the other hand, the reaction kinetics are related to surface catalysis. The rate-determining step for the chemisorption process is under most conditions the condensation reaction. Hydrolysis and condensation reactions are pH-dependant and are catalyzed by both acidic and basic conditions. Therefore it is not surprising to observe very large differences in reactivity on different surfaces. Table 2 shows the effectiveness of methacryl-propyl trimethoxysilane on different fillers.

Table 2. Flexural strength of filled polyester with 0.5% of Methacryl silane after 4 hours in boiling water.

Filler	OH population	Filler pH	Filler loading, phr	Flex Str. MPa, Untreated	Flex. Str. MPa, Silane-treated	% improvt.
Amorphous Silica	High	7	120	60	101	170
Calcined Clay	Low	5	100	61	97	160
Hydrous Clay	High	9	88	31	45	145
Mica	Low	8	40	18	24	135
Talc	Low	9	100	30	50	165
Wollastonite	Fair	10	150	53	86	160
Alumina Trihydrate	High	10	175	32	57	180

To increase the reactivity of silanes one may also use the inherent basic nature of aminosilanes. Combining aminosilanes with other compatible silanes can help achieving faster chemisorption on difficult substrates. To illustrate this point, fiberglass was treated with unsaturated- and aminosilanes separately and in combination. The fiber was then compounded with polypropylene and injection-molded into test specimens. The resulting properties are listed in table 3.

Table 3. Performance of amino- and unsaturated Silane blends in fiberglass-reinforced polypropylene[4].

Silane type	% silane in the size bath				
Vinyl tri(Methoxyethoxy)-	0.35		0.7		
Aminopropyltriethoxy-	0.30	0.30			0.6
Methacryloxypropyltrimethoxy-		0.30		0.6	
Physical properties					
Tensile Strength (MPa)	102	100	96	95	98
Tensile Elongation (%)	2.6	2.4	1.4	0.5	2.2
Flexural Strength (MPa)	112	110	110	106	110
Flexural Modulus (MPa)	4230	3940	4560	4310	4470
Charpy Impact (J/m^2)	35	33	23	23	25

After organofunctional silanes have build covalent bridges between the filler and the polymer, the bridge also has to be strong, that is resistant and stable. The data in table 2 illustrate the stability of silylated surfaces towards hydrolysis. The reason proposed by E.P. Plueddeman[5] is that the silane/water reaction is reversible, allowing rearrangements with the overall effect that the trifunctional silanes are able to re-adsorb on the filler surface after partial hydrolysis.

Retention of properties in hot water is very often used as an accelerated ageing test. More data on hydrolysis resistance are presented on table 4 for clay-filled nylon 6 compounds .

Such benefits could not be achieved without building a strong covalent bond between the filler and the polymer. We have seen how it is generated by reacting the silane with the filler. On the other hand the silane organic group must react with the polymer to complete the bridging process. A variety of Silanes with reactive organic groups are now commercially available to provide grafting mechanisms for many industrial treatment conditions (table 5)

Table 4. 50% Kaolin-filled nylon 6. Effect of aminosilane treatment on wet ageing

	Unfilled	Untreated kaolin	Silane treated
Flexural strength, MPa			
Initial	86	119	151
16 hours in 50°C water	39	69	100
7 days in 50°C water	28	45	66
Flexural Modulus, MPa			
Initial	1900	5900	6300
16 hrs in 50°C water	550	2400	2500
7 days in 50°C water	550	1200	1400
Tensile Strength, MPa			
Initial	62	70	78
16 hrs in 50°C water	42	43	61
Heat Dist.Temp. 1.8MPa, °C	57	131	128

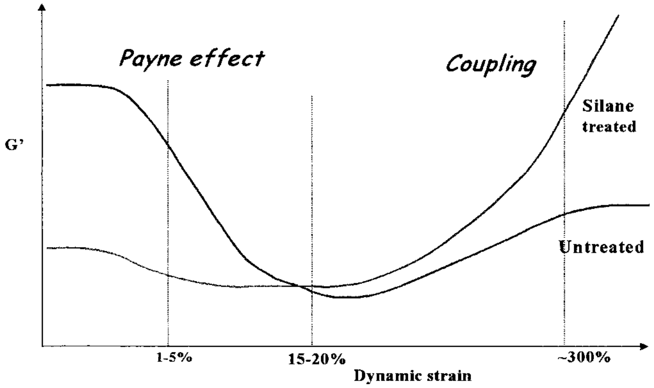
Table 5. available functional organic groups in commercial silanes

Organic function	Types	Polymer matrix
Amines :	-NH2, -NHR , -NR2, Φ-NH, -NH-CO-NH2	Phenolic, epoxy, urethane, melamine, polyamide, silicones
Unsaturated groups :	-CH=CH2, -OC=OCMe=CH2	Polyolefines, polyesters, peroxyde cured rubber
Epoxy	Glycidyl, cyclohexyl	Epoxy, carboxylic latex, PBT, polysulfide, PUR
Isocyanate	-N=C=O	polyurethane
Mercapto	-SH	Sulfur-cured rubber, PUR

Physical interaction between filler particles

We have discussed how the filler-polymer interaction can be controled by silanes in relation with interfacial tension. The reduction of interfacial tension translates on macroscopic scale as improved dispersibility and lower viscosity. However the modification of surface properties of mineral fillers can also have a significant influence on the attraction and re-agglomeration of individual filler particles. This effect can best be seen on very fine fillers at high fill ratio. In such systems the dynamic mechanical properties at low strain reflect the filler network properties. It was demonstrated by Payne that the elastic modulus and hysteresis (tan δ) are directly related to particle-particle interactions[6],[7]. The effect is illustrated on silica-filled rubber (Fig.2). In this case it is associated with an increase of the filler-rubber interaction (coupling effect).

Figure 2. Silane treatment effect on silica-filled rubber



Note that the same trends can also be observed on static properties.

As the filler-filler interaction is essentially of physical nature and the filler-polymer interaction can be associated to chemical interactions it is possible to combine both effects by a suitable combination of silanes or by a suitable selection of the silane molecule.

Polymer modification in the interphase

The interphase is the polymer phase close to the filler surface. It is the boundary layer where all the stresses and property gradients are concentrated. Many efforts were made to selectively modify these properties in order to reduce the stress concentration at the interface. The most promissing results were obtained by generating or increasing the crosslinking density in that layer. This can be achieved through the use of multiple-functional silanes. Silanes with a single reactive organic group are either chain-terminating or grafting agents. Silanes with multiple organic reactive groups can function as chain-extenders or crosslinking agents. An example of such a process is shown in table 6 where aminopropylsilane is compared to polyazamide silane for the treatment of glass fibers in a nylon composite.

Table 6 comparison of monofunctional and polyfunctional aminosilanes in fibreglass-reinforced nylon 6.6[8]

Glass treatment	No silane	Aminopropylsilane	Polyazamide silane
Flexural strength (MPa)	118	172	195
Flexural modulus (MPa)	55800	53000	69600
Tensile strength (MPa)	69	102	129

Filler treatment process in the laboratory

There has been considerable debate on how to treat fillers. Each case requires careful consideration of following parameters :

1. Filler pretreatment or direct addition into final compound
2. Filler preconditioning and optimal moisture content.
3. Silane addition level
4. Use of solvent
5. Temperature of addition
6. Silane cure conditions and temperature
7. Shelf-life of treated filler
8. Health and Safety
9. Fate of alcohol by-products

Based on practical experience, the following recommendations can be made to address the questions above in the laboratory:

1. For laboratory purposes, slurry pre-treatment is the most consistent method and optimal results can relatively easily be obtained. However, the method is expensive and requires intensive investments in production scale.
2. Except when dealing with very fine fillers (precipitated or fumed silica), 50 to 100 ppm of water based on filler are sufficient to ensure complete hydrolysis and condensation of most commercial silanes at 1% loading. This is a very low level and most fillers will contain 10 times more humidity in a « dry » stage. In practice it was found suitable to use the filler in a stage where most physically adsorbed water has been eliminated through drying at about 120-150°C. In some cases it can be useful to

enhance surface acidity or basicity to improve the chemisorption process.

3. The optimal addition level is most often much higher than the calculated « monolayer concentration » and not directly related to specific surface. Guidelines are presented in table 7.

Table 7. Guidelines for determining silane amount to be applied on fillers

Average particle size of mineral filler (microns)	Amount of silane (%w/w)
< 1	1 to 5
1 to 10	1.0
10 to 20	0.75
20 to 100	0.1 or less

4. Solvents must be used in the slurry process. Suitable solvents are alcohols and non-protonated solvents (esters, ketones except for aminosilanes). The optimal amount of solvent is the minimum amount that can be added to obtain a pumpable slurry. The solvent must later be eliminated by drying in a flash-proof oven. The benefit is that the process allows for complete silane reaction and elimination of alcohols as hydrolysis by-products. In some cases water can be used, but only aminopropylsilanes can be dispersed in water at high concentrations. All other silanes must be dispersed at maximum 8% to 10% silane concentration. The main benefit of water slurry is the reduction and possible elimination of VOC's.
5. The recommended addition temperature is in most cases room temperature. Some inert fillers like quartz or talc require moderate heating.
6. The silane grafting reaction rate is extremely variable and tests must be performed at several conditions of time and temperature to assess completeness of cure. As a general rule it is recommended to leave at least a few minutes to allow for complete silane coverage and rearrangement at the filler surface.
7. A completely cured silane layer on the filler is shelf-stable. However, decomposition reactions of the organic group of the silane may be catalyzed by the silane surface and this must be considered.
8. Health hazards are in principle not different from the liquid silane, but the occurrence of flying dust may be a factor able to increase the hazard of materials that are irritant to the eyes, lungs and throat. The release of alcohols that are flammable or may be toxic must be taken into consideration as well. Treated fillers can eventually be

considered as « flammable solids » if the alcohol emission is significant.

9. The generation of significant amounts of alcohol must be considered in the frame of VOC regulations.

Filler treatment process in the manufacturing plant

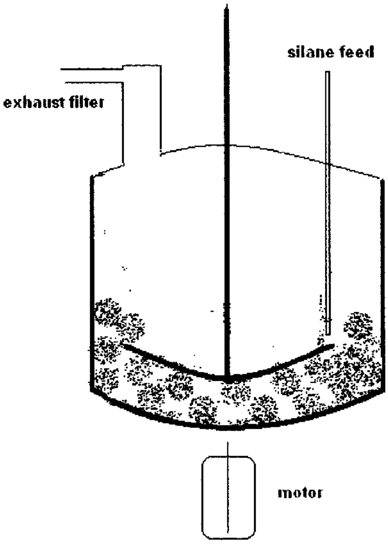
The industrial treatment processes include water suspension or slurry treatment, or dry addition.

The slurry treatment is identical to the laboratory process described above. It is used whenever the filler preparation includes a water dispersion. However it is limited by the drying temperatures required to eliminate surface water. In most cases these temperatures exceed 200°C and are not compatible with silane surface treatments.

The dry addition process consists of adding the silane, eventually diluted with solvent, to the dry filler. It requires a fast mixer that can disperse the small amount of liquid over the entire filler surface. Ideally the mixing speed and mixing device are selected to provide the highest possible shear rate without filler attrition. Suitable mixer types include blade mixer/fluidizers like Henschell or Papenmeier mixers. They should be temperature regulated, and preferably with variable speed. At first the filler is loaded in the cold mixer, then the mixer is run at full speed while silane is sprayed right above the blades (Fig.3). The temperature raises within a few minutes to about 50°C, and the mixer is stopped. The treated powder is discharged and a new batch cycle is started.

Depending on silane and filler reactivity the alcohol evolution can be significant. An exhaust filter and duct should be mounted on the mixer cover to equilibrate pressures at all times. Eventually the mixer may be run at low speed at the end of the treatment process to ensure complete reaction.

Figure 3. High Shear Powder Mixer



Treatment of materials sensitive to abrasion :

Materials like glass beads, porous or hollow fillers, or fibers shall not be treated under high shear or with liquids. The recommended procedure consists of loading the silane onto a porous carrier and to blend the dry concentrate at low shear with the filler. As carrier material, porous polyethylene is recommendable. Once the silane has been transferred to the filler the porous carrier can easily be separated by gravity and recycled.

Conclusion

The surface treatment of fillers using organofunctional silanes has a strong influence on several parameters :

Physical interactions between filler and polymer can be modified to control processing properties like wetting speed and efficiency, viscosity during compounding and filler dispersion.

Chemical interactions between the filler and the polymer leading to the formation of stable covalent bonds. The formation of a strongly chemisorbed layer protects the filler/polymer interface from hydrolysis, improves ultimate mechanical properties and improves ageing.

Physical interaction between filler particles can be designed to control rheological and dynamic mechanical properties. This interaction can be influenced independently of polymer-filler interactions.

Chemical modification of the polymer in the interphase can be introduced through silane crosslinkers or reactive plasticizers to minimize the impact of large property differences between filler and polymer.

The treatment of fillers is a relatively simple process if attention is payed on the reactivity between silane and filler. The surface reactivity is difficult to predict and should be mesured case by case. In the laboratory, it is simpler and more efficient to pre-treat fillers by the solvent slurry technique, whereas in production the most efficient process is direct addition of silane into final compound or pretreatment with neat silane.

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