

## Ways to improve performances of reinforced-polymers: from dispersion up to interphase control

by

Valerie Smits, SISC, Dow Corning Europe S.A.  
Pierre Chevalier, SISC, Dow Corning Europe S.A.

### Abstract

This work deals with the silane treatment of fillers to improve composites ultimate properties. The dispersion mechanisms as well as the way silane operates as hydrophobic agent up to interpenetrating network formation (IPN) are discussed. Silane filler-treatment was performed on talc and silica using a variety of silane functionalities. Treated fillers were compounded into talc reinforced thermoplastics and silica reinforced organic rubber. The results show that silane enhances filler wetting. Depending on the silane functionality, we can observe a torque reduction at compounding stage, a shrinkage reduction and also a significant change on  $\tan \delta$  leading to improved impact resistance. The effect of silane functionality on processing improvement and mechanical properties are discussed. Additionally, the influence of processing conditions such as processing temperature is investigated. A combined effect of silane functionality and processing conditions in enhancing composite ultimate properties is evident. Finally, the future research directions for a reinforcement step-change are discussed.

### Introduction

The current trend in thermoplastics market is "Engineering up for cost down". One interesting way to achieve this and optimize cost-performance balance is through technical design and control of the interphase between filler and polymer. The interphase is 3-D layer in the immediate vicinity of filler surface, possessing physical properties different from those of the two main phases in a composite while an interface is a perfect 2D surface dividing two distinguished components of a composite and is characterized by an abrupt change in properties.

Performance of composites depends on the characteristics of the filler, but also on its dispersion and polymer-

filler interactions, and more specifically on the properties and thickness of interphase between polymer and filler [1]. It is well known that the final performances of the composites depend upon the capabilities of the interphase to transmit the stress from the matrix to the filler. The response of the fiber-matrix interphase, which may only compose as little as 1% of the total volume of material, can control the overall mechanical performance (strength, durability, fatigue life) as well as micromechanical energy absorbing mechanisms of composites materials ([2], [3] and [4]). Organosilane is a key element in engineering composites performances as it will affect filler wetting and dispersion through surface energy modification but also allows an optimization of the interphase design.

The first challenge of processing a compound is the filler dispersion and organosilanes are widely used in filled polymer composites to help the wetting and dispersion of fillers ([5] and references therein). The particle agglomerates have to be broken down into smaller parts called aggregates (Figure 1). During mixing of the compound, mechanical shear induces dispersion and distribution of the filler in the matrix. The mechanism for dispersion has been extensively studied ([6], [7] and [8]). It is well established that silane, due to its dual reactivity between inorganic and organic functions (Figure 2) plays a key role in filler dispersion improvement. The silane treatment clearly decreases the dispersive and specific component of the surface energy but changes also filler-filler, polymer-filler interaction and agglomerate packing properties ([9] and [10]).

In reality, the role of a silane is more complex than a single surface energy modification. The conventional way to illustrate how silane react with a filler surface is to consider that silane through hydrolysis-condensation reaction and hydrogen bonding reaction with filler surface form a siloxane monolayer around the filler particle leading a clear interface between filler and polymeric matrix. However, inter-diffusion phenomenon and interpenetrated network (IPN) formation occur leading to the creation of an interphase rather than an interface as illustrated in Figure 3[11].

This work intends to review the use of silanes to improve the filler dispersion. The effect of silane on filler wetting, dispersion and its influence on processability and composites properties are demonstrated. The synergetic effect of silane chemistry with processing conditions to optimize composites properties is shortly investigated showing that the reinforcement step-change will come from the control of interpenetrating network formation in terms of interphase thickness and mechanical properties.

## Experimental parts

In the following example, we will illustrate silane effect on filler hydrophobation and dispersion and more specifically how silane enhances filler compatibility and dispersion with polypropylene resin.

*a/ Materials:* In this work, two different kinds of talc were considered (T1 and T2). The two talcs differ mainly by their particle size distribution and surface specific area. The particle size distribution was characterized by d50 (meaning 50% of particles are less than) while the surface specific area (S) was determined by N<sub>2</sub> adsorption using the Brunauer, Emmett and Teller (BET) theory [12]. Table 1 is summarizing the talc key characteristics for both talcs. The following silanes were used to modify talc: methyl-, vinyl-, phenyl-, methacryloxypropyl-, n-octyl-, glycidoxypopyl- and octadecyltrialkoxysilane. The chemical structures of those various silanes are illustrated in Figure 4. The polymeric matrix used in this study was a bloc copolymer polypropylene having a melt flow index of 13g/10' (@ 230°C – 2.16 kg).

*b/ Modification of fillers.* Talcs were surface-treated with silane using different weight percentages up to 15wt% through wet and dry treatment.

The silanized filler particles were then dispersed in polypropylene via extrusion as described below and the resulting composites were injection molded into test samples. The reaction steps involved are shown in Figure 5.

*c/ Preparation of composites blends.* Composites were prepared using a 20 mm co-rotating intermeshing twin screw extruder having a length over diameter (L/D) ratio of 40. The screw configuration was designed with a melting zone of about 10D and two mixing zones of about 10D each. The other part of the screw consists of conveying elements. Two gravimetric feeders were used to feed the polymer and the filler separately through a common feed port at 0D. The extruder was run with a flat temperature profile of 210°C and a screw rotation speed of 250 rpm. The extrusion output was set to 5kg/h. The feed rates were controlled so that composites of different weight fractions could be prepared. The composite was extruded through a 4mm strand die, followed by a water bath, and finally to a pelletizer. Torque level during compounding, illustrating processing energy, was recorded for each formulation. All the pelletized formulations were injection molded as ISO 527-2 Type 1A specimens and ISO 527-2 Type 5A specimens using molding conditions according to ISO 1873-2. 100x 100 mm<sup>2</sup> plates were also injected for shrinkage measurement.

*d/ Testing.* The specimens were stored under controlled conditions (humidity and temperature) for at least one week before testing.

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Filler surface hydrophobation was characterized by contact angle (VCA) measurement of a standard 1µm water droplet.

Dynamic mechanical analysis (DMA) was used to identify the behavior of the various polypropylene composites formulations through the determination of storage modulus as well as tan δ as a function of the temperature. A viscoelastometer (VA4000, 0.1dB-Metravib Instruments) was used in the tensile mode for recording the dynamic spectra versus temperature. The samples were carefully cut from tensile specimen ISO 527-2 Type 5A to approximately 20x4x2 mm. A tensile configuration was used with loading frequency and strain values of 10Hz and 5E-04 respectively. Samples were heated from -70°C up to 160°C at a rate of 2°C/min. The storage modulus (E') and loss tangent (tan δ) were recorded as a function of the temperature.

Charpy unnotched impact properties were measured at room temperature according to ISO 179-1. Samples were cut out of the ISO 527-2 Type 5A specimens.

The dispersion of the filler in the composites was observed by Scanning Electron Microscopy (SEM). Qualitative analysis was performed by simple observation of the images.

The molding shrinkage was evaluated by measuring the 100x 100 mm<sup>2</sup> plate 7 days after molding. Two types of shrinkage were recorded: longitudinal and transversal to flow direction. The shrinkage is defined by the following equation:

$$\%shrinkage = \frac{L_0 - L}{L_0} \times 100,$$

where

L<sub>0</sub> = mold length

L = length of molded part after post shrinkage

## Results and discussion

Talc together with calcium carbonate and silica were initially treated using n-octyl silane at a level of 15 wt%. The efficiency of silane treatment to hydrophobe filler surface was characterized *via* Contact Angle (VCA) measurements. The higher the contact angle, the more hydrophobic the filler surface is. Figure 6 clearly illustrates that fillers are becoming more hydrophobic after octylsilane treatment. The results are explained as following. The reactivity of alkoxy groups of the n-octyl silane with the filler particles through hydrolysis condensation allows the silane bonding on the filler surface, whereas n-octyl functionality gives a hydrophobic character to the filler surface. Based on this data, we can conclude that treated filler will be more compatible with an apolar polymeric matrix such as polypropylene.

N-octyl treated talc samples were then compounded in a lab scale twin screw extruder using 2 different filler contents: 7 and 30 wt%. Torque over time was recorded. The torque level is related to processing energy during com-

pounding step: the lower the torque, the lower processing energy required for compounding. Figure 7 shows that by treating talc, using both wet and dry treatment, the torque level is reduced by 10%. It is observed that n-octyl silane treatment reduce the torque level to the equivalent level of pure polypropylene. One can observe a slightly higher torque drop when using the wet treatment. This discrepancy was even more pronounced in the case of silica reinforced-polypropylene. This difference could be explained assuming that dry route leads to a coating onto the agglomerate surface while wet route leads to homogeneous silanization within the filler agglomerate.

The graph on Figure 8 shows torque level values as a function of silane amount for talc T1 at 30 wt% loading rate. This graph illustrates that the higher the silane level, the lower the torque. The reduction in torque level of treated-filler composites is directly linked to the n-octyl functionality coverage of the talc particles surface thus improving compatibility with polypropylene.

On similar T1 talc, a series of different silane surface treating agents were investigated. The list and chemical structure of those silanes are available in Figure 4. The torque levels observed during the compounding step are reported in Figure 9. The torque reduction could be explained based on solubility parameters concept. The different silanes used in this study have different polarities and compatibilities with polypropylene. Solubility parameters were calculated using Fedors' method [13] and are reported in Table 2. According to the same method, solubility parameter of  $8.1 \text{ (cal/cm}^3)^{1/2}$  was calculated for polypropylene. Since a good compatibility is observed when the solubility parameters differ by less than  $0.2 \text{ (cal/cm}^3)^{1/2}$ , we shall consider that all different tested silanes have poor compatibility with polypropylene. However, assuming that silane forms a multilayer surface around talc particles, we could consider that the polypropylene matrix is only contacting the outside surface layer of the treated talc made of the organic functional R-group. Therefore, we could only consider the R-group to calculate solubility parameters. Doing that, n-octyl and octadecylsilane show better compatibility with polypropylene as solubility parameters are in the  $\pm 0.2 \text{ (cal/cm}^3)^{1/2}$  window as illustrated in Figure 10.

The lowest torque level was obtained with octadecyltrimethoxysilane: by reducing the filler/filler interaction, we reduce torque level. So, octadecyltrimethoxysilane and n-octyltriethoxysilane act as a lubricant. However, we are not building polymer filler interactions using those two silanes as the alkyl chain is too short to get proper entanglement and there is no reactivity with the polypropylene matrix. In order to go beyond, one could consider that the interactions we might form between polymer and filler would basically enhance the reinforcing effect of a filler particle, thanks to the interpenetrating network formation between filler and matrix which could transfer stresses from the matrix to the filler. So, a

further step would be to create a covalent bond or interpenetrating network with polypropylene. This concept will be further described later. It is however important to point out that these interactions could increase the torque level as illustrated in Figure 11, essentially because of the coupling effect between the matrix and the filler.

Figure 12 and Figure 13 illustrate the effect of silane treatment on shrinkage measurements. The lower shrinkage level observed when talc is treated could be due to a higher nucleating effect of silane treated-talc on PP compared to untreated talc limiting the chain mobility of the polymer phase. DSC measurements confirm this assumption as the crystallization temperature is about  $2^\circ\text{C}$  higher when silane treated-talc is used. We also calculated the nucleating activity using Avrami's equation [14]. For dynamic crystallization kinetics of molten polymers in the presence of nucleating agent, the following equation is used:

$$\log(q) \approx \text{const} - \frac{B}{2.3 \times \Delta T^2}$$

with:

q = rate of crystallization;

$\Delta T$  being ( $T_m - T_c$ );

$T_m$  = melting temperature (K);

$T_c$  = crystallization temperature (K).

If we plot  $\log q$  versus  $1/\Delta T^2$ , B can be calculated from the slope of the curve. The activity of the filler  $\phi$  is described as the ratio of  $B^*$  on  $B^\circ$ :

$$\phi = B^* / B^\circ$$

with

$B^*$  being the value obtained for filled PP;

$B^\circ$  being the value of the unfilled PP.

The nucleation activity values are reported in Table 3 and we see a higher nucleation activity for treated-talc by up to 20%.

The filler dispersion was quantitatively evaluated using SEM. As illustrated in Figure 14, there is no clear dispersion improvement of talc in polypropylene matrix. This is most likely due to the fact that talc is already fairly dispersible into polypropylene. On the contrary, silica dispersion was evaluated in another study and we clearly observed the dispersion improvement of silica in organic rubber *via* sulfido-silane treatment as illustrated in Figure 15.

Mechanical performances of the polypropylene composites were evaluated using viscoelasticity measurements through a temperature sweep. Figure 16 and Figure 17 summarized the results for the 30wt% talc reinforced-polypropylene. We clearly observed that elastic modulus is higher at low temperature, improved at room temperature and preserved within the service temperature range. At the same time  $\text{Tan } \delta$  is increased. This increase in  $\text{Tan } \delta$

$\delta$  is leading to improved impact performance, as illustrated in Figure 18, enhancing the rigidity-toughness balance.

From those results, one can conclude on the influence of silane treatment on the performances of a talc reinforced-polypropylene composite:

- (1) The silane treatment reduces the processing energy at the compounding stage by up to 10%.
- (2) The shrinkage is also reduced in both directions through silanization of the surface filler.
- (3) The nucleation activity of talc is slightly increased by silane treatment.
- (4) The energy dissipation is improved while maintaining composites stiffness.

Those observations are most likely due to an improved filler wetting and compatibility with the polypropylene matrix. However, the mechanical properties of the composites still need a step-change to answer current market needs. Different approaches can be considered to further optimized composites properties.

The first approach would be to benefit from the potential synergetic effect of processing conditions and silane treatment. Indeed not only silane type affects the ultimate mechanical performances of the composites but also processing conditions through its influence on silane reactivity. This concept was demonstrated on a silica reinforced organic rubber. Mixing was done in a 370cc Banbury internal mixer. Three dump temperatures were considered: 140, 155 and 180°C. Wet gripping, breaking performances and rolling resistance were measured using DMA measurement. An increase in  $\tan \delta$  at low temperature correlates with better wet gripping and breaking performances while a decrease of  $\tan \delta$  at high temperature correlates with a reduction of rolling resistance. Figure 19 clearly illustrates the impact of mixing temperature during silanization on tire performances. Understanding and controlling silane reactivity during rubber mixing, we are able to optimize tire performances. So, processing conditions and silane reactivity control are two routes to affect ultimate composite materials performances.

As discussed previously, a second approach would be to design a proper interphase between the matrix and the filler. The optimization of the IPN formation is of primary importance, and hence selecting the proper organosilane with regards to its compatibility with the matrix and the filler is critical. By properly engineering the interphase, and more specifically by controlling interphase properties and thickness, we can positively affect fundamental mechanical properties and avoid traditional trade-off between composites strength and impact performances. This approach was demonstrated by J. G. Iglesias and al. as well as by A. Abu Obaid and al. on fiberglass reinforced thermosets. J. G. Iglesias and al. [15] studied the influence of different aminosilanes ( $\gamma$ -

aminopropyltriethoxysilane,  $\gamma$ -aminopropylmethyldiethoxysilane and  $\gamma$ -aminopropyltrimethylmonoethoxysilane) fiber coating on the strength of epoxy-based composite materials. From this study they concluded that the mechanical performance of glass reinforced epoxide composite materials are strongly dependent on the molecular structure of the interphase. A. Abu Obaid and al. [16] draw similar conclusions using blends of three different silanes: tetraethoxysilane, 3-glycidoxy-propyl-methyldi- and trimethoxysilane at different ratio to tailor the interphase of epoxy based composite material. Those two studies clearly show that the interphase properties can be altered using different types of silanes and/or blends and leads to better mechanical performances of the final composites performances. This gives the basis for future research directions to achieve a reinforcement step-change in composites materials. The objective is to chemically design the micro scale interphase structure and build a gradient of properties between filler particle and matrix to achieve the best strength and toughness balance.

## Conclusion and future work

This article reviewed how organosilanes can affect both dispersion and polymer-filler interactions. Through a practical example based on talc reinforced-polypropylene, we illustrated that depending on the functionality, amount, method of introduction; the silane can reduce processing energy, reduce shrinkage and improve slightly mechanical performances of the composites. Additionally, different routes to further optimize composites performances were exposed. (1) By controlling processing conditions and thereby silane reactivity, we can fine-tune ultimate composite material properties. (2) By designing a proper interphase between the matrix and the filler, an interpenetrating network can be engineered to optimize both rigidity and toughness of the composites. This gives the basis for future research directions to achieve a reinforcement step-change in composites materials.

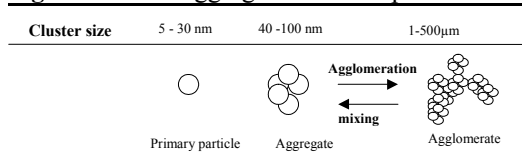
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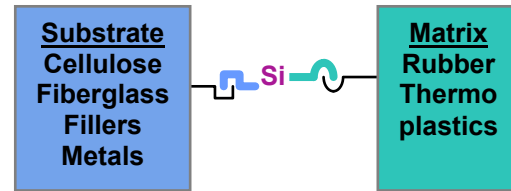
## Key Words

Silane, Filler treatment, Interface/Interphase, Interpenetrated network, reinforcement, filled polymer

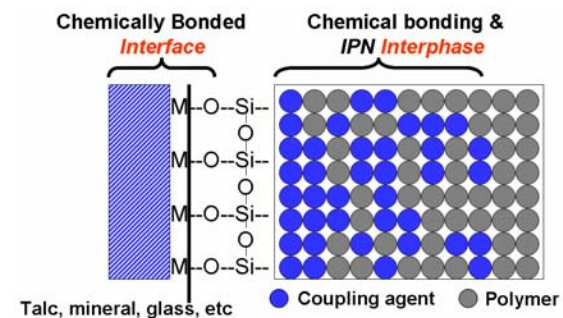
**Figure 1- Filler aggregation and dispersion.**



**Figure 2 - The silane dual reactivity**



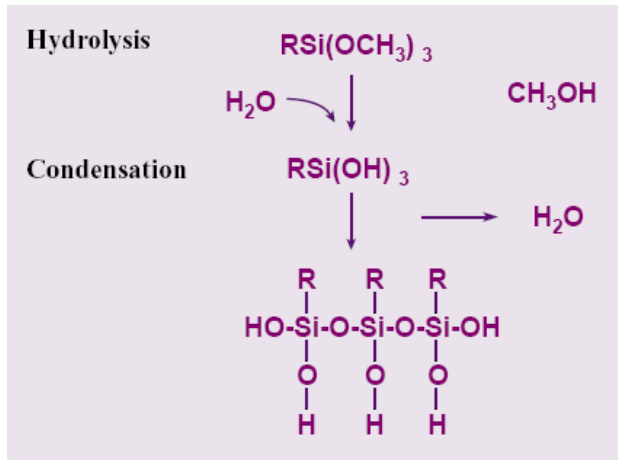
**Figure 3 – The inter-penetrating network (IPN) bonding mechanism.**



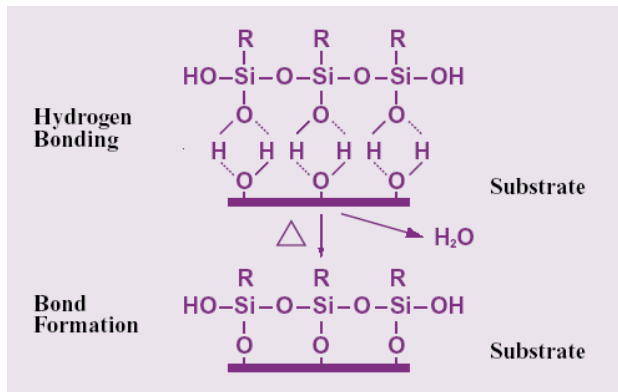
**Figure 4 - The chemical structure of studied alkoxy-silane. R-Si(OX)<sub>3</sub>**

Chemical name (R)	Chemical structure
Methyl-	
Vinyl-	
Phenyl-	
Methacryloxypropyl-	
N-octyl	
Glycidoxypropyl	
Octadecyl-	

**Figure 5** - Reactions steps for filler treatment

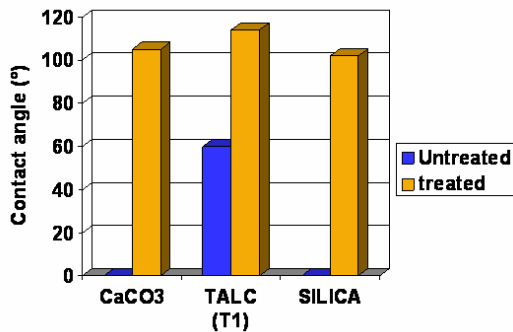


a/ Hydrolysis and condensation reaction of alkoxy silanes

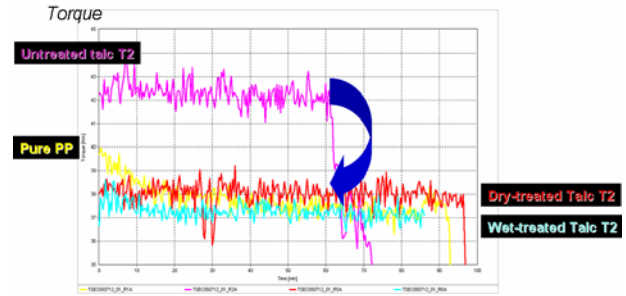


b/ Bonding to an inorganic surface

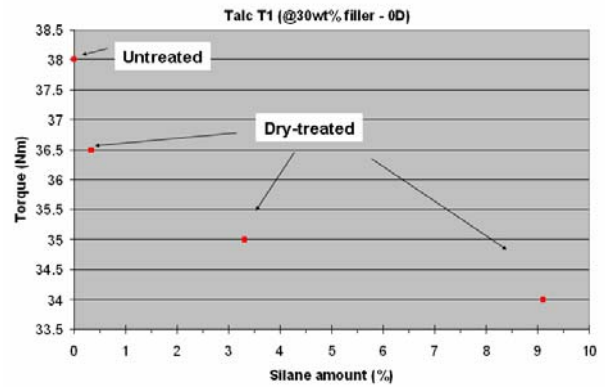
**Figure 6** - Surface hydrophobation - contact angle measurements for untreated and n-octyl silane treated fillers.



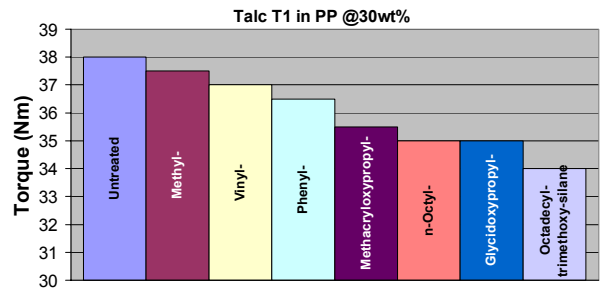
**Figure 7** - Processing energy reduction for T2 at 7wt%



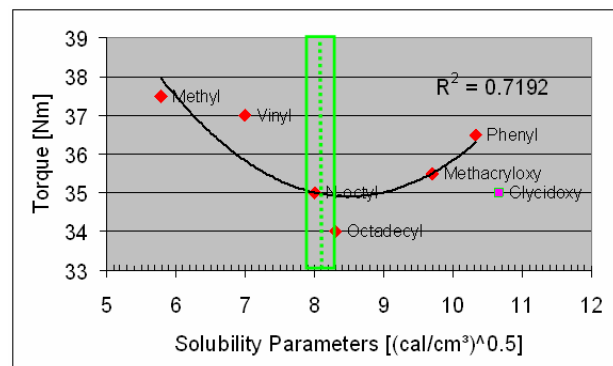
**Figure 8** - Processing energy reduction versus n-octyl silane treatment level for T1 @ 30wt% loading



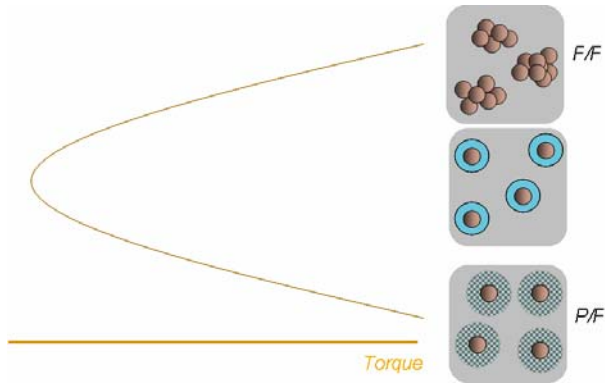
**Figure 9** - Torque reduction versus silane type for talc T1 @ 30 wt%



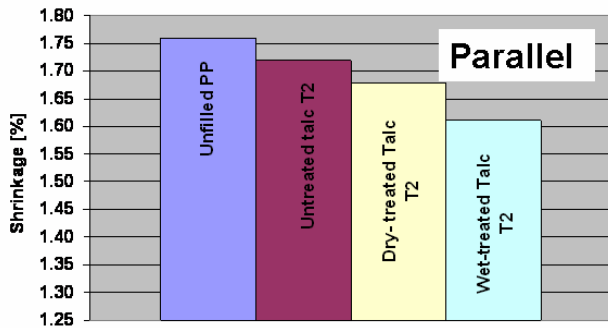
**Figure 10** - Torque versus Solubility parameter  $\delta$



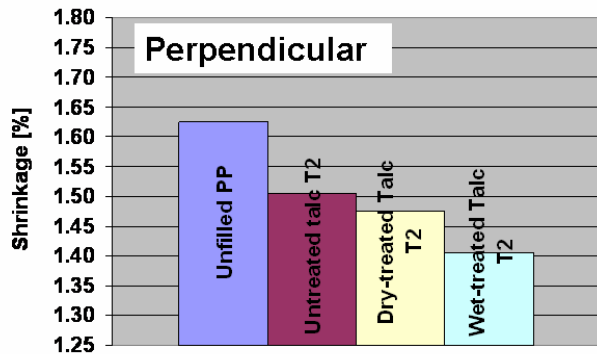
**Figure 11 - Torque versus polymer and filler interaction**



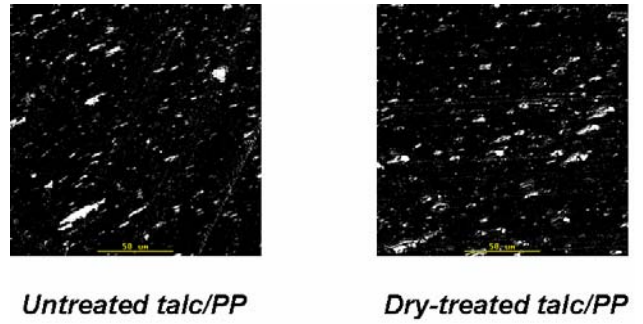
**Figure 12 - Effect of silane treatment on parallel shrinkage**



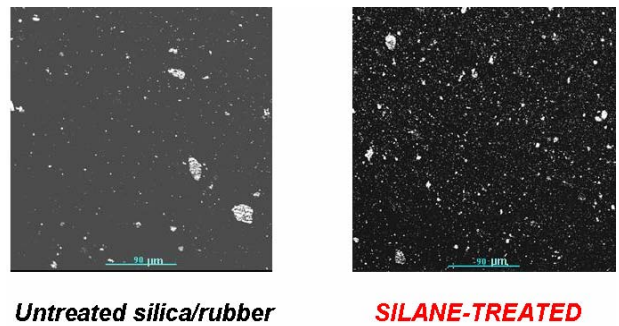
**Figure 13 - Effect of silane treatment on perpendicular shrinkage**



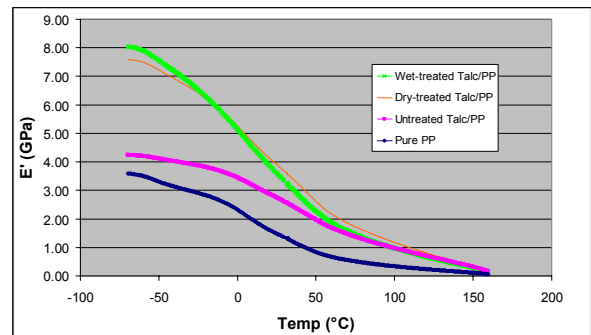
**Figure 14 - SEM picture of T2 reinforced PP composites, effect of silane treatment on filler dispersion.**



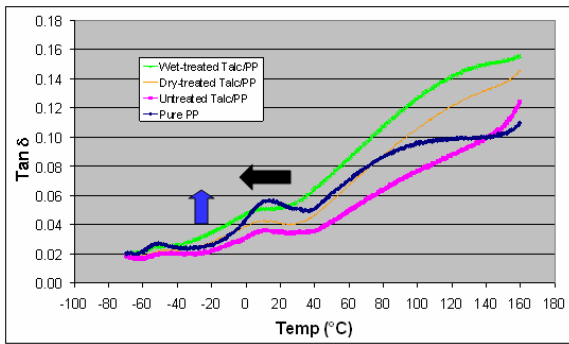
**Figure 15 - SEM picture of silica reinforced organic rubber, effect of silane treatment on filler dispersion.**



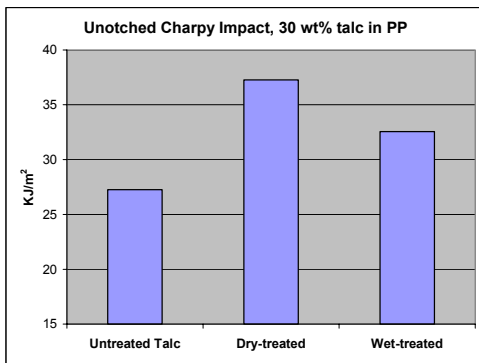
**Figure 16 - Thermomechanical properties – Storage modulus E' - for 30wt% T2 filled-polypropylene composite.**



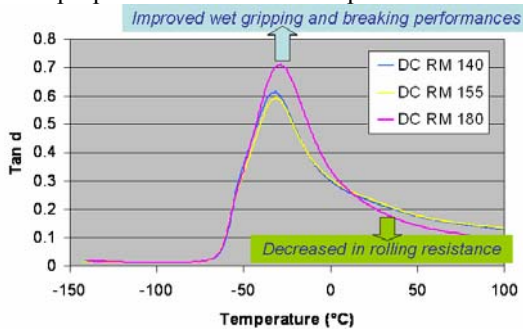
**Figure 17** - Thermomechanical properties – Loss tangent Tan  $\delta$ - for 30wt% T2 filled-polypropylene composite.



**Figure 18** – Un-notched impact strength for 30wt% T2 filled-polypropylene composite



**Figure 19** - Impact of temperature processing on viscoelastic properties of tire tread compound.



**Table 1** -Filler characteristics

	T1	T2
D50 ( $\mu\text{m}$ )	3.35	2
S <sub>BET</sub> ( $\text{m}^2/\text{g}$ )	5.4	16

**Table 2** Solubility parameters ( $\delta$ )

Chemical name (R)	Silane $\delta$ [( $\text{cal}/\text{cm}^3$ ) <sup>0.5</sup> ]	R-group $\delta$ [( $\text{cal}/\text{cm}^3$ ) <sup>0.5</sup> ]
Methyl-	7.29	5.79
Vinyl-	7.50	7.00
Phenyl-	8.81	10.33
Methacryloxypropyl-	8.99	9.70
N-octyl	7.62	8.01
Glycidoxypropyl	8.44	10.67
Octadecyl-	7.89	8.30

**Table 3** – Nucleation activity values for 7wt% reinforced-polypropylene

(using $^{\circ}\text{K}/\text{min}$ )	Untreated talc	Dry treated talc	Wet treated talc
$\Phi$	0.71	0.85	.80

**Author(s):**

**Valerie Smits**, plastics and rubber compounding specialist, Surface and Interface Solutions Center (SISC), Dow Corning Europe S.A.

Silane applications development and laboratory management for the plastic and rubber. Prior experience at Total S.A as Polyolefins Application Development and Technical Service Engineer.

**Pierre Chevalier**, Senior reinforcement specialist, Surface and Interface Solutions Center (SISC), Dow Corning Europe S.A.

Filler-coupling agent-polymer matrix systems and Sol-gel technology development for performances improvement. Other expertise: thermal & photo-activated cross-linking technologies, metathesis & radical polymerizations...