



REVIEW

Silane Effects on in-Rubber Silica Dispersion and Silica Structure (α_F)[†]

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The degree of silica dispersion in a rubber matrix is an important issue in the rubber industry because silica agglomerates in rubber compounds are difficult to disperse compared to carbon black due to the polar characteristics of the silica surface. Considerable effort has been made to improve the degree of silica dispersion, such as the use of bifunctional organosilane, intermesh rotor type mixer, milling technique, *etc.* Wolff and his coworkers introduced the in-rubber filler structure (α_F) for quantitative measurements of the filler structure. This paper reviews his research on the in-rubber structure of carbon black and silica and reports our recent results on silane-treated silica.

Key Words: In-rubber silica structure (α_F), Bifunctional silane, Silica, Carbon black.

INTRODUCTION

Currently most major green tire tread manufacturing companies use intermesh type rotor mixers for the mechanical dispersion of silica particles in rubber compounds. Other efforts to improve silica dispersions aim to increase the compatibility between the silica surface and rubber chain, which involves the use of chemicals, such as *bis*-(3-triethoxysilylpropyl) tetrasulfane (TESPT) and *bis*-(3-triethoxysilylpropyl)disulfane (TESPD), which are well-known organo bifunctional silanes in the market. The addition of silane into silica filled rubber compound reduces the viscosity of the compound, which results in improved processability of the compound. This also results in a chemically-bonded silane-silica structure, which reduces the polar characteristics of the silica surface and improves the dispersion of silica particles. The silane treatment of a silica surface should clearly affect the structure of silica in rubber.

The structure of the filler can be presented in several ways, such as Wolff's in-rubber filler structure (α_F)¹⁻⁵, Payne effect^{6,7}, *etc.* Wolff expressed α_F , as the slope derived from the ratio between the increase in rheometer torque of the filled compound ($D_{\max}-D_{\min}$) and that of the unfilled compound ($D_{\max}^0-D_{\min}^0$), which is directly proportional to the filler loading, as expressed in eqn. 1:

$$\frac{D_{\max} - D_{\min}}{D_{\max}^0 - D_{\min}^0} - 1 = \alpha_F \frac{m_F}{m_P} \quad (1)$$

where α_F is the in-rubber structure of the filler, $D_{\max}^0-D_{\min}^0$ is the torque difference of the unfilled compound, $D_{\max}-D_{\min}$ is the torque difference of the filled compound, m_F/m_P is the filler to polymer weight ratio. Wolff *et al.*^{4,5} reported that the α_F was constant over the entire range of carbon black (BET 140 m²/g) filled in NR and NBR systems. On the other hand, in the case of a silica (BET 134 m²/g) filled system, α_F increased with increasing filler concentration. Their research focused mainly on the filler-filler interaction in rubber compounds.

Since Rauline^{8,9} presented the use of a silica combination with TESPT for practical 'green tire' applications, there have been many studies on silane-modified silica rubber compounds in the tire tread compound. On the other hand, they focused mainly on the effects of the silica reinforcement¹⁰, silica dispersion¹¹⁻¹⁵, moisture/temperature effects on coupling with silane¹⁶⁻¹⁸, accelerator effects on the cure properties^{19,20}, effects of polymer blends²¹⁻²⁴ *etc.*

Silica consists mainly of silicon-oxygen ($\equiv\text{Si-O-}$) bonds with hydroxyl groups (-OH) on silica surface, whereas carbon black (CB) consists mainly of carbon-carbon single and double bonds ($\equiv\text{C-C}\equiv$, =C=C=). Silica particles exhibit a strong silica-silica interaction owing to its polar ($\text{Si}^{+8}\text{-O}^{-6}$) character due to differences in electro negativity between Si (3.5) and O (1.9). In contrast, carbon black shows a weak C=C interaction due to the presence of a π - π bond, thereby showing good compatibility with rubber chains, which contain a double bond. The

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π - π bonds and/or oxygen on the carbon black surface interact with double bonds (π - π) in the rubber chain, which shows good compatibility with the rubber chain. Therefore, the dispersion of carbon black is better than that of silica in the rubber matrix. On the other hand, modification of the silica surface with silanes, particularly with bifunctional organosilanes, such as TESPT and TESP, assists in the dispersion of silica agglomerates in the rubber chain^{14,25-28}. The chemical reaction between silica and silane as well as silane and rubber alters the network of the rubber matrix²⁸⁻³⁰. Hence, the filler network constant α_F of silane-modified silica is different from carbon black filled systems. This makes an interpretation of the in-rubber structure of the modified silica system more difficult. Few studies have examined in-rubber structure of silane-modified silica since Wolff's presentation at the Charles Goodyear Medal award in his 1996 presentation³.

This paper reviews Wolff's in-rubber structure of the filler α_F and compared their results with the results of other researchers including this laboratory^{31,32}.

SBR/CB sulfur cure system³³⁻³⁷: Fig. 1 shows the Δ torque (D_{\max} - D_{\min}) relationship with the carbon black (N330) loading at constant concentrations of curing agent in the SBR compound with various sulfur levels. This gives straight lines with different slopes, whose extensions intersect in a common point on the x-axis.

A linear correlation was observed between Δ torque (D_{\max} - D_{\min}) and the carbon black loading at a constant concentration of accelerator (CBS).

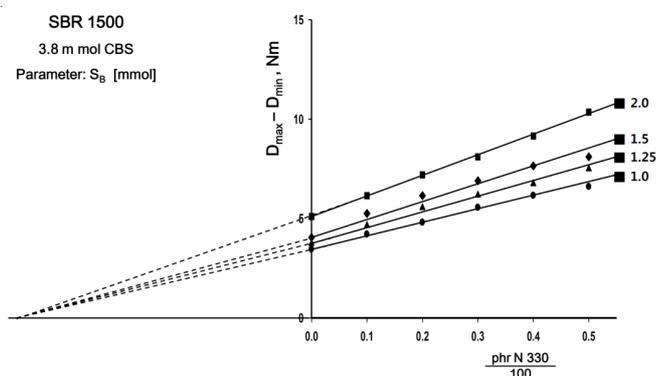


Fig. 1. Δ Torque (D_{\max} - D_{\min}) vs. CB loading of the SBR compound with various sulfur levels at a constant accelerator concentration/redraw from the work of Wolff³

SBR/Silica sulfur cure system^{38,39}: Fig. 2 shows the Δ torque (D_{\max} - D_{\min}) relationship with silica (130 m²/g) loading at constant concentrations of curing agent in the SBR compound with various sulfur levels. This does not give straight lines due to interference with sulfur.

No linear correlations were observed between Δ torque (D_{\max} - D_{\min}) and the silica loading at constant concentrations of curing agent.

SBR/Silica peroxide cure system³⁹: Silica does not interfere with the reaction mechanism of dicumyl peroxide curing, which has a radical reaction mechanism. At a constant dicumyl peroxide concentration, there was a linear correlation between Δ torque (D_{\max} - D_{\min}) and silica (175 m²/g) loading. Fig. 3 shows straight lines with different dicumyl peroxide concentrations, which intersect at a common point on the

x-axis. The slope of the SBR/Silica compound increases with increasing dicumyl peroxide concentration.

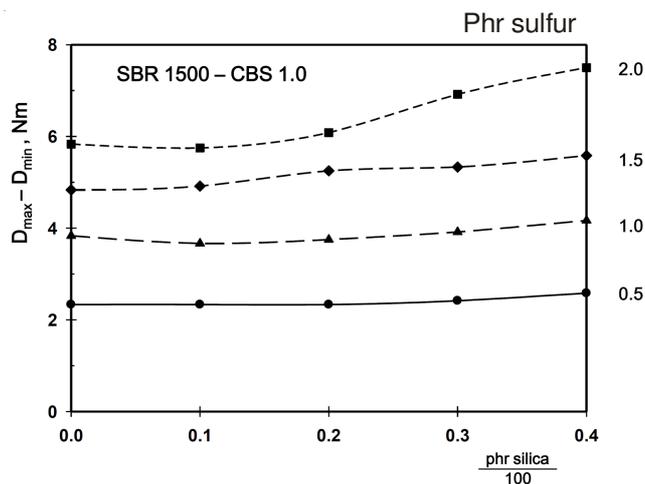


Fig. 2. Δ Torque (D_{\max} - D_{\min}) vs. silica loading of the SBR compound with various sulfur levels at a constant accelerator (CBS) concentration./redraw from the work of Wolff and Tan³⁹

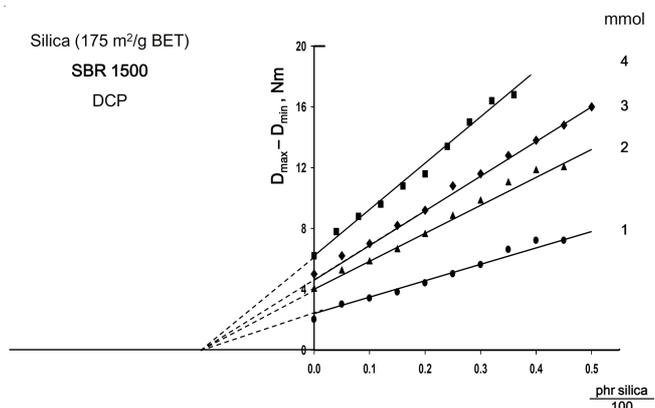


Fig. 3. Δ Torque (D_{\max} - D_{\min}) vs. silica loading of SBR compound with various peroxide (DCP) concentrations/redraw from the work of Wolff and Tan³⁹

Filler (Silica vs. CB)-Elastomer (non-polar vs. polar) interactions²: Fig. 4 shows plots for the normalized α_F as a function of the filler loading for CB (N110) and silica (BET 134 m²/g) in NR (natural rubber) and NBR (acrylonitrile-butadiene rubber). In the case of CB (N110), α_F was independent of the loading over the entire range for both NR and NBR. On the other hand, in the case of silica, the α_F was dependent on the filler loading. As the filler loading increased, the α_F increased sharply for both silica/NR and silica/NBR compounds. The increase in the α_F value was higher in the Silica/NR compound than the silica/NBR. This is an indication of the stronger filler agglomeration of silica in NR than NBR. At a critical silica loading, the sharp increase in α_F at a higher loading is an indication of the formation of a strong silica network^{40,41}. This critical loading is dependent on both the attractive potential and the distance between aggregates. The later onset of the sharp increase in α_F for silica/NBR was attributed primarily to the reduced specific interaction factor S_f (magnitude of inter-aggregate interactions or filler-filler networking) values of the silica through increased polymer-filler interactions

in the polar elastomer NBR. The rank of the adsorption energy is as follows: nitrile group > phenyl group > double bond⁴². The specific factor S_f is defined as the adsorption energy of a given probe divided by that of an alkane (real or hypothetical)⁴.

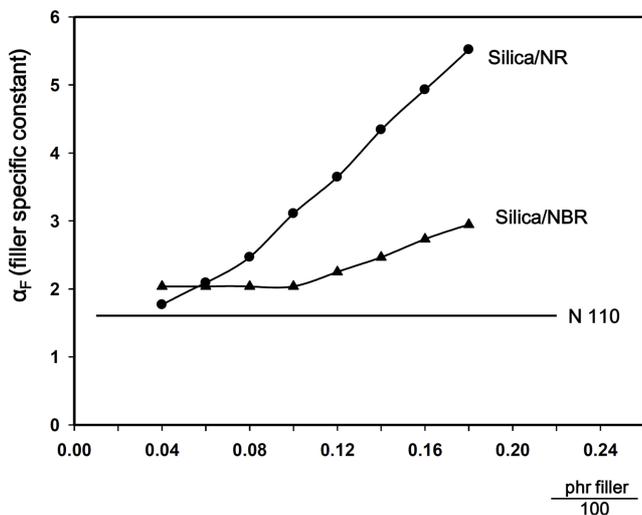


Fig. 4. Plots for the normalized α_F as a function of the filler loading for CB (N110) and silica (BET 134 m²/g) in NR (natural rubber) and NBR (acrylonitrile-butadiene rubber)/redraw from work of Tan *et al.*⁵

Second filler constant 'A'⁴³: The second filler constant 'A' was obtained from measurements of the ball rebounded as a function of the filler loading. The ball rebound decreased linearly with increasing filler loading.

The second filler constant 'A' can be expressed as follows:

$$R_0 - R = A \cdot \frac{m_F}{m_p} \quad (2)$$

where R_0 = rebound of the gum, R = rebound of the filled vulcanizate and A = second filler specific constant.

Fig. 5 shows the rebound difference ($R_0 - R$) as a function of the silica loading for peroxide-cured SBR. The rebound difference increased linearly with increasing silica (175 m²/g) loading.

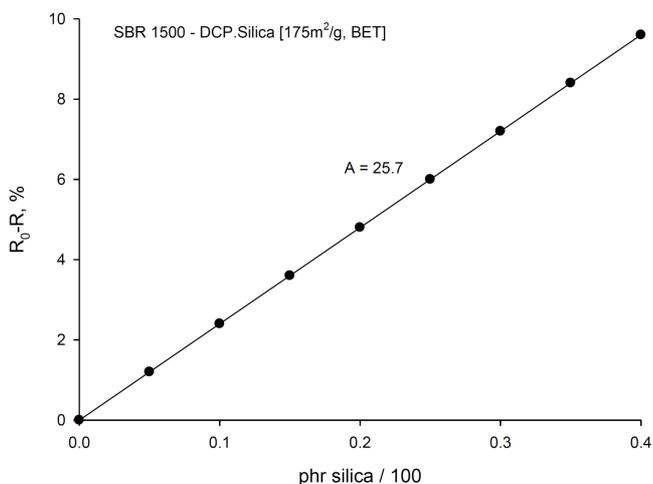


Fig. 5. Rebound difference ($R_0 - R$) vs. silica loading for peroxide-cured SBR/redraw from work of Wolff³

The second filler constant 'A' is also closely related to the filler surface area (Fig. 6).

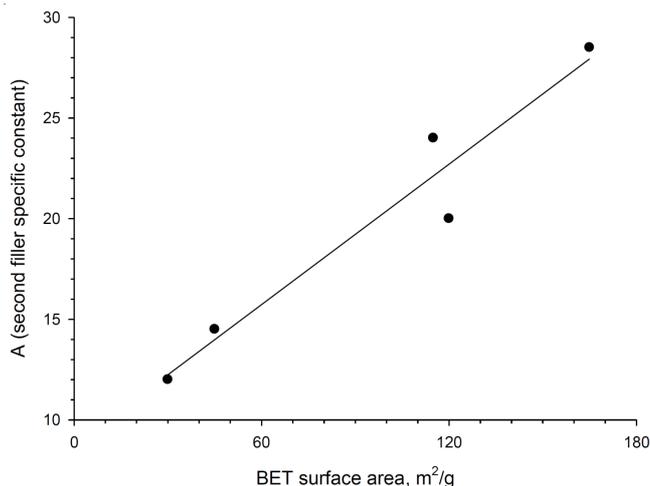


Fig. 6. Relationship between the second filler specific constant A and BET surface area for silica/redraw from work of Wolff³

Filler specific constant ' α_F ' vs. second filler specific constant 'A'³⁹: The differences between silica and CB can be compared with the relationship between the filler specific constant ' α_F ' and the second filler specific constant 'A' (Fig. 7). The silica groups and CB groups do not overlap. CB is independent of A, only dependent on α_F , but silica is dependent on both A and α_F . The α_F for the silica group ranged from 2.86 to 7.93. The α_F value of the low region silica is close to that of carbon black.

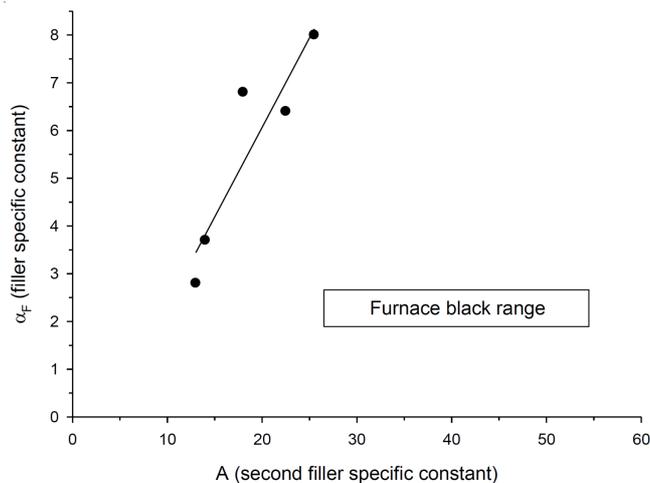


Fig. 7. Filler specific constant ' α_F ' vs. second filler specific constant 'A' for silica and CB/redraw from report of Wolff and Tan^{39,99}

Silane modified silica: The silanization of silica causes primary changes in their reinforcing characteristics (Fig. 8). The dispersive component of the surface energy γ_s^d decreases, even below the value of unmodified silica and the polar component γ_s^p becomes negligible. This prevents the formation of a silica network through hydrogen bonds. The addition of bifunctional organosilane (TESPT) forms a covalent silica-silane-rubber network, *i.e.* a strong 3-dimensional network.

Fig. 9 shows the effects of silane modification on the silica surface upon α_F and A. The in-rubber structure of the silica α_F was reduced from 5.6 to 1.9, which the level of CB as indicated in the rectangular box and the in-rubber surface area A was elevated from 20 to 46, which is similar to the level of CB.

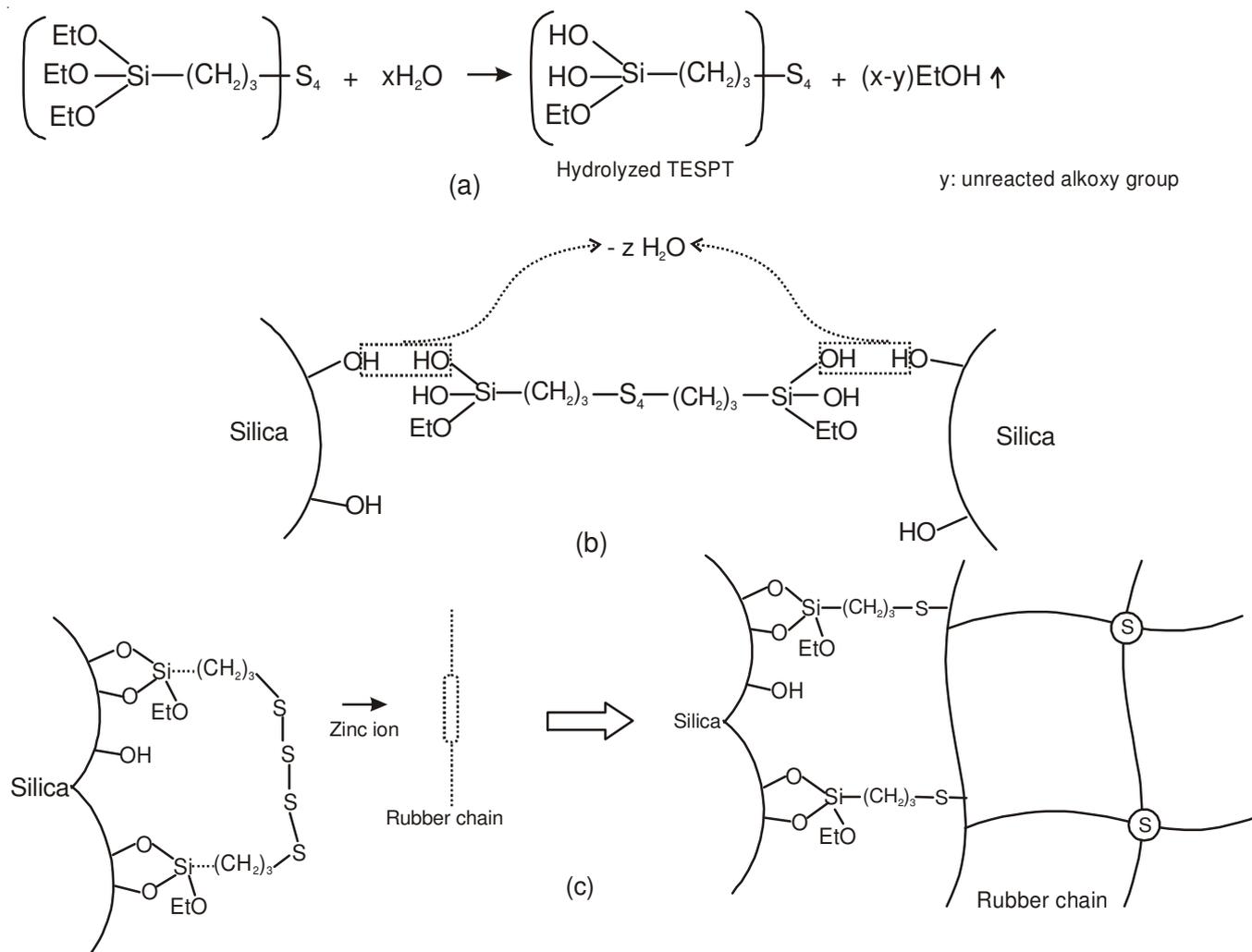


Fig. 8. Schematic diagram of (a) hydrolysis of silane, (b) condensation between hydrolyzed silane and the silica surface, (c) chemical reaction between sulfur and the rubber chain

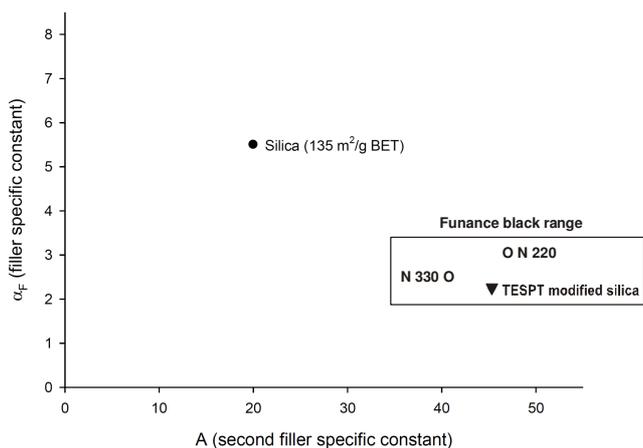


Fig. 9. Effects of silane modification on the silica surface upon α_F and A/redraw from work of Wolff³

Silica/silane loading effects on α_F ^{31,32}: The α_F value increased with increasing silica/silane loading (silane concentration 2, 4, 6, 8, 10, 12 %) (Fig. 10). A positive α_F value was observed from the compounds that contain a silane concentration > 6%.

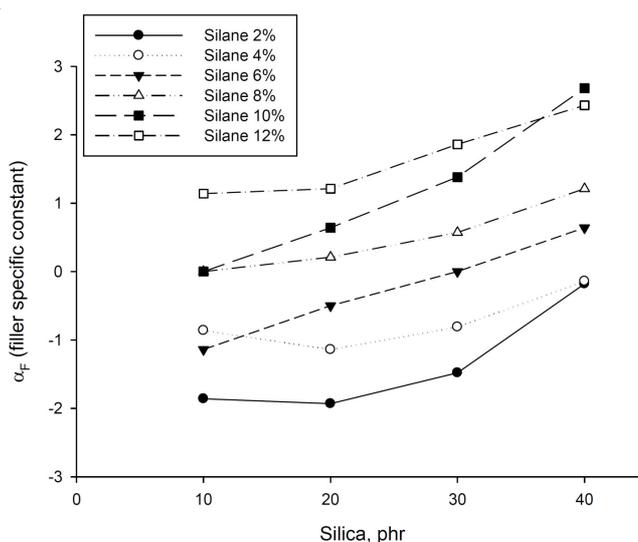


Fig. 10. Changes in α_F value as a function of the silica loading upon various silane loadings (2, 4, 6, 8, 10, 12 %)/redraw from work of Kim *et al.*³²

Silane concentration effects on α_F for silica/silane compound^{31,32}: Fig. 11 shows the changes in α_F value as a

function of the silane loading upon various silica loadings (10, 20, 30, 40 phr). The α_F value increased with increasing silane concentration. This is due mainly to the presence of sulfur atoms in TESPT, which acts as a sulfur donor^{11,25,29}. The treatment of the silica surface with silane reduces the silica-silica interaction, which decreases the α_F values³. On the other hand, the α_F value increased with increasing silane-treated silica loading. This appears to be due mainly to the increased polymer-polymer and silica-polymer interactions²⁹. Therefore, Wolff's theory should be re-expressed as follows (eqn. 3)³².

$$\frac{D_{\max} - D_{\min}}{D_{\max}^0 - D_{\min}^0} - 1 = \alpha_C \frac{m_F}{m_P} \quad (3)$$

where, D_{\max} and D_{\min} are the maximum and minimum torque of the filled rubber compounds, respectively, D_{\max}^0 and D_{\min}^0 are the maximum and minimum torque of the polymer, respectively, m_F and m_P are the filler and polymer mass in the compounds, respectively. α_C is a measure of the in-rubber structure of the compound, $\alpha_C = \alpha_F + \alpha_P + \alpha_{FP}$. α_F is a measure of the in-rubber structure of the filler-filler, α_P is a measure of the in-rubber structure of the polymer-polymer and α_{FP} is a measure of the in-rubber structure of the filler-polymer.

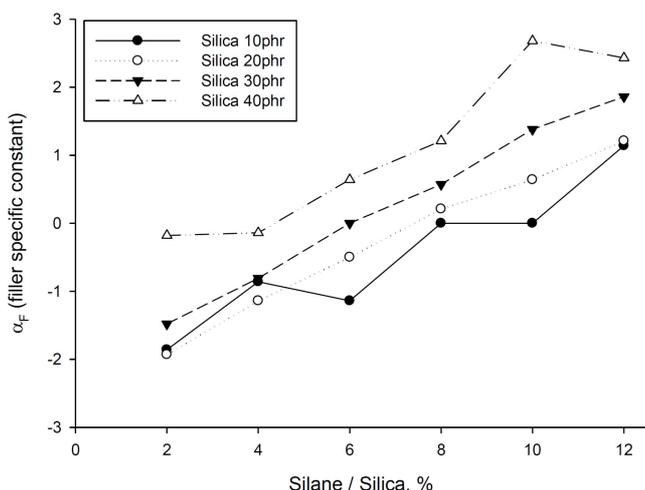
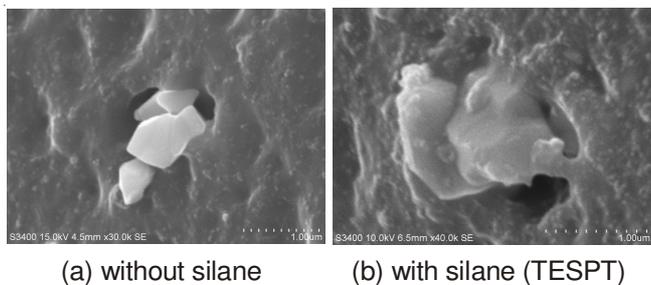


Fig. 11. Changes in α_F value as a function of the silane loading upon various silica loadings (10, 20, 30, 40 phr)/redraw from work of Kim *et al.*³²

Fig. 12 gives an example of α_{FP} compared to α_F which does not have a filler-polymer interaction. Fig. 8(c) shows the chemical structure of α_{FP} .



(a) without silane

(b) with silane (TESPT)

Fig. 12. SEM image of (a) without silane, (b) with silane (TESPT) coupled on the silica surface and rubber chain (α_{FP})

Concluding remarks: This paper reviews the Wolff's research results regarding the in-rubber structure (α_F) of carbon

black and silica and reported our recent research results of silane-treated silica systems. Owing to the formation of a 3-dimensional network structure in the compound *via* a chemical reaction of bifunctional silane with the silica surface and rubber chain, the filler network constant of silane-modified silica should be expressed by considering α_P and α_{FP} in addition to Wolff's α_F , *i.e.* $\alpha_C = \alpha_F + \alpha_P + \alpha_{FP}$. His interpretation of α_F , which focused mainly on the in-rubber filler structure, was updated by considering the network structure of the silane-treated silica system.

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