Effect of Fumed Silica Surface Area on Silicone Rubber Reinforcement

Fumed silica · Surface specific area · Silicone rubber · Reological proberties · Physical properties

The effects of fumed silica on the processability and vulcanizate properties of silicone rubber have been studied using fumed silicas with surface areas ranging from 90 to 417 m^2/g at a constant loading of 38 phr. The results show that all rheological properties of the compounds and mechanical properties of vulcanizates are strongly affected by the silica surface area. With increasing surface area, the viscosity of the compounds and the modulus of the vulcanizates increase markedly, the degree of dispersion of the filler, the tear strength and elongation at break are deteriorated, and the compression set is somewhat improved. While the bound rubber and tensile strength rise to a maximum at a surface area between 170 and 250 m^2/g, the extrudate appearance is poorer in this range. It was also found that lower surface area fumed silica favors discoloration.

Auswirkung pyrogener Kieselsäure mit spezifischer Oberfläche auf die Eigenschaften von Silikonkautschuk

pyrogene Kieselsäure · spezifische Oberfläche · Silikonkautschuk · rheologische Eigenschaften · physikalische Eigenschaften

Die Auwirkung von pyrogener Kieselsäure mit spezifischer Oberfläche von 90 bis 417 cm^2/g auf die Verarbeitung und Vulkanisateigenschaften von Silikonkautschuk wurde bei einer konstanten Dosierung von 38 phr untersucht. Die Ergebnisse zeigen, dass alle rheologischen Eigenschaften den Mischungen und die mechanischen Eigenschaften den Vulkanisate stark von der spezifischen Oberflächen des Füllstoffes beeinflusst sind. Mit steigender spezifischer Oberfläche nehmen die Mischungsviskosität und der Modul der Vulkanisate signifikant zu, während der Dispersionsgrad, die Reißfestigkeit und die Bruchdehnung sich verschlechtern, aber der Druckverformungsrest etwas verbessert wird. Bound Rubber und Zugfestigkeit erreichen zwischen 170 und 250 m^2/g ein Maximum, wobei sieh hier die Extrudateigenschaften verschlechtern. Es wird gezeigt, dass die spezifische Oberfläche ein primärer Parameter ist, der beim Compounding mit Silikonkautschuk berücksichtigt werden sollte.

Fumed silica is a major component of silicone rubber (high consistency rubber; HCR) products. It is by far the most active reinforcing agent for this polymer owing to its unique ability to enhance its physical properties. Chemically, fumed silica is an amorphous material. It consists of high purity silicon dioxide (SiO_2) tetrahedrally bound into an imperfect three-dimentional structure in which only short-range order exists. On its surface there are siloxane groups and a certain concentration of silanol groups, which can be classified as isolated, vicinal or geminal.

Morphologically, silica created in a combustion process consists of primary particles that are joined together, resulting in three dimentional branched chain aggregates. Fumed silica grades differ in surface area, which is related to the size of the primary particles, and also aggregate size, aggregate shape and in the distribution of each of these. The term "structure", widely used in the carbon black and rubber industries to describe aggregate morphology has also been adopted by the silica community. It was originally introduced in 1944, [1] to describe the ensemble of aggregates that is a stochastic distribution of the number and arrangement of the primary particles that make up the aggregates.

Commercially, many grades of fumed silica are available. It has been found practically, that for silicas without surface modification, specific surface area is one of the most important morphological parameters with regard to its end-use applications. Surface area is so important that it has been used as the principal parameter for grade classification of fumed silica.

There has been little work published on the effects of untreated fumed silica variables on silicone rubber compound properties since the review published in 1979 [2]. Much of the work since then has focused on the effects of silica surface chemistry and surface chemical modification on silicone rubber performance. One exception is the work of Cochrane and Lin [3], which examined silicas with three different surface areas, and found some relationships between surface area and some rubber physical properties. In a more systematic study of fumed silicas with BET surface areas ranging areas from 174 – 315 m^2/g, it was found that most mechanical properties were affec ted by the BET surface area of the silica, but that better correlation with performance could be achieved if the Carman Surface Area (CSA) was included as well [4]. CSA is thought to be a function of aggregate size and fractal structure, as well as primary particle size.

One of the consequences of the incorporation of silica into a polymer is the creation of an interface between a rigid solid phase and a soft elastomer phase. For fumed silica, whose surfaces exhibit very little or no porosity, the total area of the interface depends on the filler loading and the specific surface area of the filler. In a unit volume of compound, the interfacial area, ψ, is given by:

$$\psi = \phi\rho S \qquad (1)$$

where ϕ is the volume fraction of the filler in the compound, and ρ and S are the density and specific surface area of the filler, respectively. Thus, at constant loading, silica with higher specific surface area will result in higher total interfacial area in the compound.

In many practical applications, the silica surface is passivated by treatment *in situ* or *ex situ* with low molecular weight silanol compounds or other compounds that react

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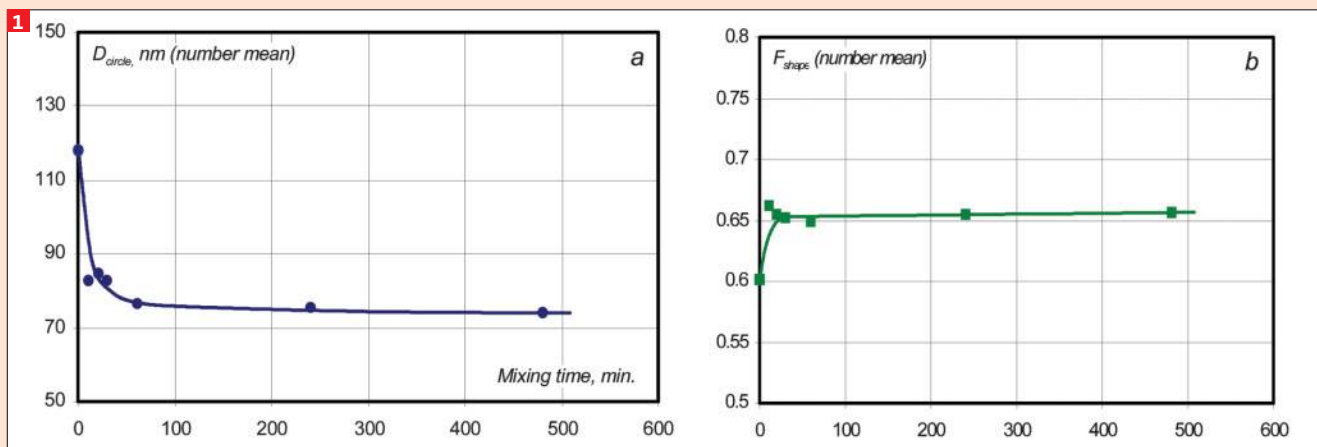157 Concord Road, Billerica
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1 Changes in (a) aggregate size and (b) structure during mixing
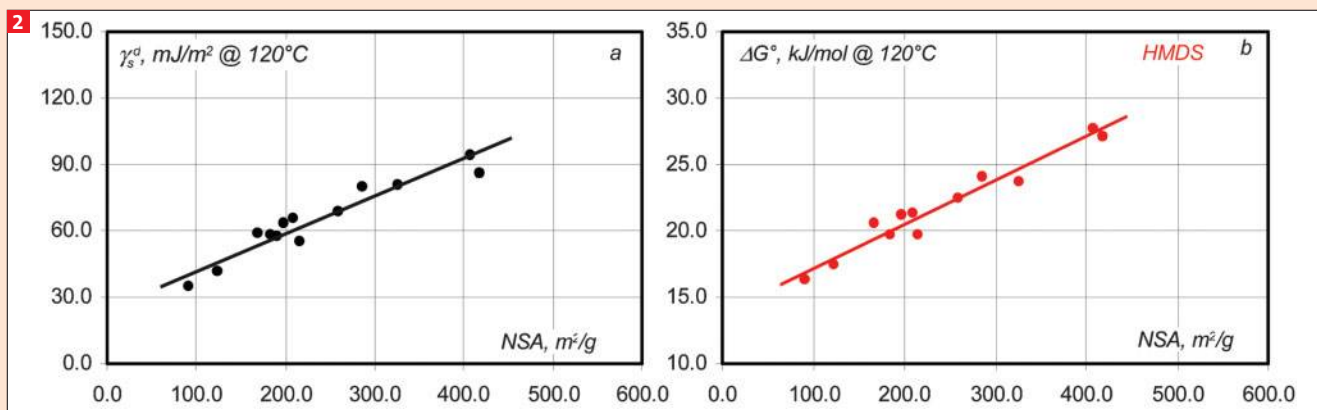
2 (a) Dispersive component of surface energy and (b) adsorption energy of hexamethyl disiloxane as a function of silica surface area

with the silanol groups on the silica surface. The purpose of this passivation is to reduce the concentration of silanol groups on the silica surface, which are largely responsible for strong filler-filler interactions through hydrogen bonding. In this study, the concentration of processing aid, which acts as the passivating agent, was kept constant as the total interfacial area increased. As a result, the degree of surface passivation that is achieved would be expected to reduce as the silica surface area is increased.

Surface Area vs. Structure of Silica

Many mechanical properties of filled elastomers have been explained in terms of the occlusion of rubber by filler aggregates. When structured fillers are dispersed in rubber, the polymer portion filling the internal voids of the filler aggregates is unable to participate fully in the macro-deformation. The immobilization (at least partially) in the form of occluded rubber, causes this portion of rubber to behave like filler rather than like the polymer matrix. As a result, the effective volume of the filler, with re-

gard to rheological and stress-strain behavior is increased considerably [5].

Knowledge of the effect of structure of fumed silica on rubber properties is still lacking and few test results have been cumulated for analysis. This is due to several reasons. First, compared with carbon black, there are no simple and reliable test methods for directly characterizing structure of fumed silica, although CSA has been used as an indirect measure of structure [3, 4]. Secondly, the availability of fumed silicas with similar surface areas but different structures is very limited. With regard to rubber compounding, there is a high degree of uncertainty about the breakdown of aggregates during mixing. Results presented in Figure 1 show that significant changes in aggregate size and structure occur during the first 10 minutes of mixing in a low viscosity polybutadiene. These results were obtained by pyrolyzing off the rubber after mixing. Similar changes could be expected in the poly-dimethylsiloxane (PDMS) fluids used for silicone rubber, which have similar viscosities to the polybutadiene.

Surface Area vs. Surface Activity of Silica

The reinforcing effect of silica particles should also depend on their surface activity. This factor, ill-defined as it is but widely used in the filler field, determines the polymer-filler, filler-filler and filler-ingredient interactions, and can impact the effectiveness of surface area and structure in rubber reinforcement.

Surface activity can, in a chemical sense, be related to different chemical groups on the surface. In a physical sense, variations in surface energy determine the adsorptive capacity and energy of adsorption. The surface chemistry of fumed silicas is much more clearly defined than that of carbon black. Besides the siloxane groups that comprise the basal composition of silica, there are different types of hydroxyl (silanol) groups on the surface. These silanols are the functional groups that determine the reactivity of silica with other chemicals. At any given loading, the total number of silanols available for reacting with other chemicals is determined not only by the concentration of silanol
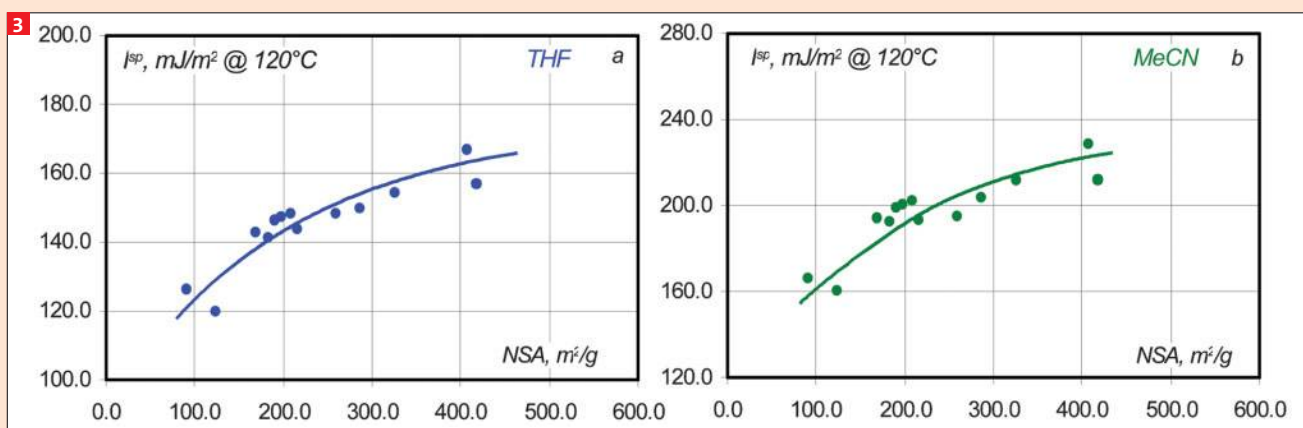
3 Polar components of the interactions between silica and (a) THF and (b) acetonitrile as a function of silica surface area

groups on the silica surface, but also by the surface area of the silica.

Physically, the interaction between two materials is determined by their surface free energies. It is known that several types of interactions exist between molecules close to each other, such as dispersive, dipole-dipole, induced dipole-dipole, hydrogen bonding, and acid-base. These result in different types of cohesive forces, which are the origin of the surface free energy. The surface free energy of a material can be expressed as the sum of several components, each corresponding to a type of molecular interaction (dispersive, polar, hydrogen bonding, etc). Since the effect of the dispersive force is universal, the dispersive component of the surface free energy, γ^d, is particularly

important. If a solid substance can have only dispersive interactions with its environment, its surface energy, γ_s, is identical with the dispersive component, γ_s^d. For most substances, the surface energy of a solid is the sum of γ_s^d and γ_s^{sp} that is the sum of the other components of surface energy, termed "specific" or "polar" components. By means of inverse gas chromatography (IGC), the γ_s^d of the filler can be measured from the adsorption energies of alkanes and the γ_s^{sp} can be estimated from the specific interaction parameter, I^{sp}, which is representative of the interaction between filler and a polar chemical [6]. According to Fowkes [7], the work of adhesion from dispersive interactions between materials 1 and 2, W_{12}^d, is determined by their dispersive components of surface energies:

$$W_{12}^d = 2\sqrt{\gamma_1^d \gamma_2^d} \qquad (2)$$

The γ_s^d of fumed silicas used in this study and their free energies of adsorption of hexamethyldisiloxane (HMDS) that is taken as a model compound of silicone rubber are plotted in Figure 2 as a function of the silica surface area. Presented in Figure 3 are the polar components of adsorption free energies of acetonitrile and THF. As can be seen, all these parameters increase with surface area of silica. This, according to Equation 2, suggests that from the point of view of filler surface energy, the filler-filler interaction increases linearly with surface areas of the fillers, and filler-polymer interaction is pro-

portional to their square-root. The high polymer-filler interaction of high surface area silicas is also demonstrated directly by their high adsorption energies of HMDS, which is chemically similar to the (PDMS) polymer. It should be noted that silica surface energies, especially the polar components, can vary significantly when the fumed silica is produced under different process conditions.

This study attempts to investigate the effect of fumed silica on rubber properties with a series of fumed silicas having a wide range of surface areas. The justification for this approach is firstly that industry experience has shown that surface area is a critical silica parameter governing the properties of filled rubber. Secondly, due to the dependent nature of structure and surface characteristics, a base line generated from surface area will provide a reference with which some specific factors or mechanisms involved in silicone rubber reinforcement may be further studied.

Experimental

Materials

The fumed silicas used in this study are listed in Table 1 together with their surface areas measured with nitrogen using the BET method. All silicas are commercial products from Cabot Corporation except silica A. The polymer employed was a low vinyl-containing poly-dimethylsiloxane (PDMS) with only terminal vinyl groups. The number average molecular weight of the polymer is about 700,000 and the polydispersity is close to 1.

Compounding and Curing

The basic formulation in this study is shown in Table 2. The feature of this formula is 38 phr silica with a small amount of processing

1 Specific surface areas of the silicas used

Silica	BET Surface Area, m²/g
Cab-O-Sil L90	90
Cab-O-Sil LM130	122
Cab-O-Sil LM150D-T	154
Cab-O-Sil LM150	167
Cab-O-Sil LM150D-B	183
Cab-O-Sil M7D	196
Cab-O-Sil M5	209
Cab-O-Sil HP60	216
Cab-O-Sil M75D	258
Cab-O-Sil HS5	285
Cab-O-Sil S17D	407
Cab-O-Sil EH5	417
Fumed silica A	193

2 Compound formulation

Material	Parts by Weight
Silicone Polymer (Vinyl terminated PDMS; MW~ 700,000)	100.0
Fumed silica	38.0
Processing aid (Hydroxy terminated PDMS: MW~ 400)	3.5
Crosslinker – STI type T (50 % bis-2,4-dichlorobenzoyl peroxide in PDMS)	1.97

aid, which is a short chain hydroxy-termi-nated PDMS. A silicone oil paste of 50 % bis-2,4-dichlorobenzoyl peroxide was used as crosslinker. The compounds were mixed in a Brabender Plasti-corder EPL-V with sigma blades at 30 rpm and a fill factor of 60 %. Once all the silica and processing aid had been incorporated, the temperature was raised to 120 °C and mixing was continued for 2 hours. The masterbatch was cooled to room temperature on a two-roll mill, then the crosslinker was added slowly. After 5 minutes, the compound was sheeted off. Compounds were cured at 100 °C. The cur-ing time was 10 minutes for the specimens of 2 mm thickness, and 15 minutes for the thick specimens (12.7 mm) used for com-pression set, hardness and dispersion test-ing. Post-curing was carried out in an air oven for 2 h at a temperature of 220 °C.

Rubber property testing

- Bound rubber:
  For bound rubber determination, 0.5g of uncured compound was cut into small pieces of approximately 1 mm and placed into a stainless-steel wire-mesh cage of known weight. The cage was then im-mersed in toluene in a bottle for 4 days at room temperature. The solvent was re-newed after one day. After extraction, the rubber and the cage were dried overnight in an exhaust hood at room temperature and then for 24 hours in a vacuum oven at room temperature. The bound rubber per-centage of the polymer, BR, was calculated according to the following equation:

$$BR\% = \frac{W_{fg} - W \cdot m_f / (m_f + m_p)}{W \cdot m_p / (m_f + m_p)} \times 100 \qquad (4)$$

where W_{fg} is the weight of filler and gel, m_f the weight of the filler in the compound (in phr), m_p the weight of the polymer in the compound (in phr), and W the weight of the specimen in dry state.
- Cure characteristics – ASTM D 2084.
- Extrusion – Extrusion was performed with a Brabender Plasti-corder single screw extrud-er equipped with a 19x1 mm die at 25 °C. The extrusion speeds were varied by changing the screw speed (rpm). Extruded samples were cured in air at 177 °C for 5 minutes.
- Surface roughness measurements – the surface roughness or shark-skin severity of the extrudates was measured by a portable glossmeter (Micro-TRI-Gloss, from Byk Gardner) at 60°. The extrudate roughness was also estimated visually by three independent observers, and the av-erage rating of the three is reported.
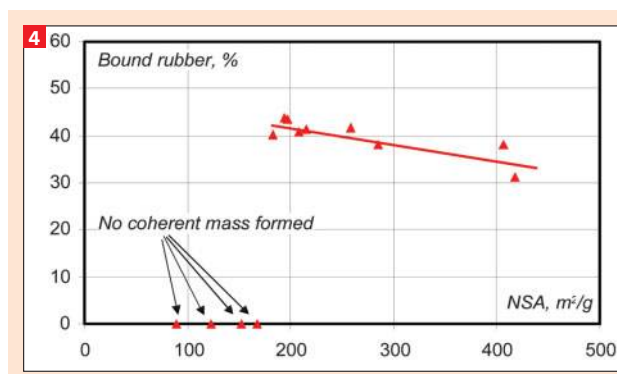
- Silica dispersion in vulcanizates – The dis-persion of silicas in the filled vulcanizates was measured using a DisperGrader (Tech-Pro) which analyzes a reflected image of a freshly cut surface. The presence of im-properly dispersed ingredients is shown by irregularities, which usually take the form of circular, convex "bumps" or con-cave marks on the surface. The size and frequency of these irregularities is used to judge the degree to which the compound falls short of an optimum dispersion. The dispersion level of the filler was compared with a series of electronically stored standards and then rated numerically from 13 (excellent) to 1 (very poor). It was found that the presence of air bubbles in silica-filled vulcanizates does not interfere with the rating of undispersed ingredi-ents.
- Dynamic modulus: The elastic moduli of the compounds were measured with a Rub-ber Process Analyzer (RPA 2000 from Alpha Technologies). The samples were cured in the RPA at 100°C for 10 minutes at a strain amplitude 0.14 % and frequency of 1.7 Hz, allowing the cure state to reach equilibrium. After the temperature was dropped to 30°C, a strain sweep was performed with strain amplitudes ranging from 0.42 to 147 %, at a constant frequency of 1.7 Hz.
- Hardness – ASTM D 2240.
- Stress-strain properties (stress at given elongation, tensile strength, elongation at break) – ASTM D 412.
- Tear strength – ASTM D 624, Die B.
- Compression set – ASTM D395, Method B. Aging condition: 177°C for 22 hrs.
- Color of the vulcanizates – The colors of the post cured compounds were meas-ured with a Gretag Macbeth Color-Eye 7000A (from Gretag). The samples for testing were discs with diameter of 25 mm and thickness of 10 mm. The color was ex-pressed using the CIELAB color scale which measures color using three coordinates, the L^*, a^*, and b^*. The L^* value represents

lightness (from white to black), the a^* val-ue represents red to green, and the b^* value represents yellow to blue.

Aggregate Dimensions by TEM

Cab-O-Sil LM150 was mixed with polybuta-diene (Mooney viscosity ML1+4 @ 100°C – 14) in an internal mixer. After specific mix-ing times, the silica was recovered by pyro-lyzing the filled compounds at 550°C in ni-trogen atmosphere for 4 hours. The recov-ered silica was dispersed ultrasonically in ethanol and dried on a conductive grid for transmission electron microscopy analysis. 2000 aggregates were measured and ana-lyzed using commercial image analysis soft-ware. D_{circle} is defined as the average diam-eter of a circle with the same area as the aggregate image. The shape factor, F_{shape}, is defined as the average ratio of the longest diameter, D_{max}, to the shortest diameter, D_{min}, of an aggregate image.
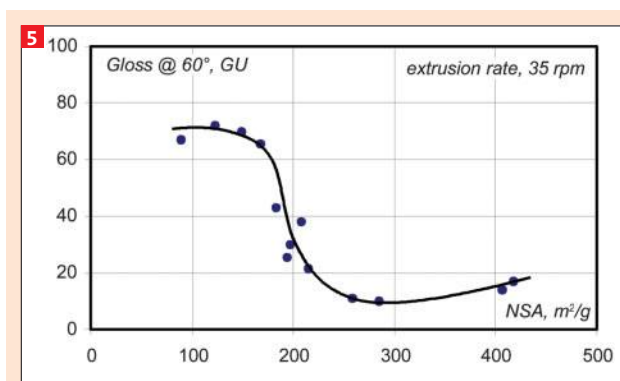
Surface Energy Measurements by Inverse Gas Chromatography

Gas chromatographic retention times for various probe molecules were measured at 120°C following the methods described elsewhere. [8] The energy of adsorption, and different components of the filler sur-face energy, were calculated by the meth-ods described therein.

Results and discussion

Bound Rubber

The results of bound rubber (Fig. 4) show that there is a critical surface area of fumed silica around 170 m²/g, below which no coherent mass could be obtained during solvent ex-traction. Bound rubber could not therefore be determined by the conventional test pro-cedure. Beyond the critical surface area, the bound rubber content seems to decrease with increasing silica surface area.
One of the necessary conditions for coherent mass formation in the swollen state of the

4 Bound rubber content as a function of fumed silica sur-face area

5 Surface roughness of extrudates as a function of surface area of fumed silica

compounds is that the filler aggregates must be held together by polymer, through polymer bridging or by entanglement of polymer molecules that are attached on the neighboring aggregates. For a given polymer system, the ability to form a coherent mass will be determined by the inter-aggregate distance. As the surface area of the filler decreases at a given loading, the average inter-aggregate distance increases. When this distance reaches a point at which polymer bridging between most of the aggregates cannot be achieved, the filler will be dispersed in the solvent along with any attached polymers. Consequently, no coherent mass would be expected. This explanation is based purely on geometric considerations, and assumes no difference in polymer-filler interactions between the different systems. An alternative explanation for the bound rubber results is based on the fact that the processing aid, which is a low molecular weight, hydroxy-terminated PDMS, is known to reduce polymer-filler interactions. Since the concentration of processing aid was constant between the different compounds, the silica surface coverage with low MW PDMS would be expected to be greater with lower surface area silicas. It is possible that the discontinuity in bound rubber with surface area represents the point at which silica coverage by processing aid is enough to prevent sufficient adsorption of high MW PDMS to form a coherent mass. In order to distinguish between these two explanations, further experiments are required with different formulations.
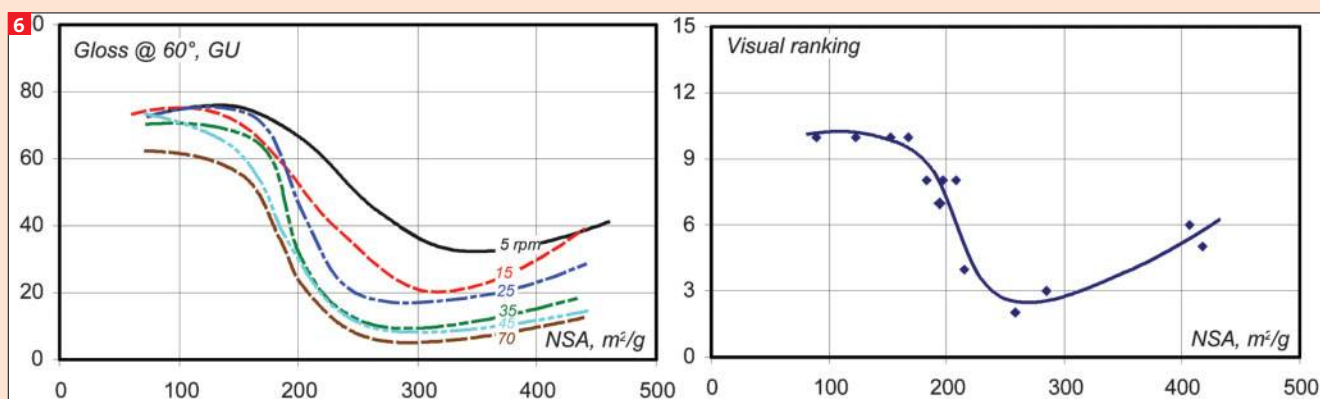
In a carbon black-hydrocarbon rubber system, it has previously been observed that a critical loading exists, below which a coherent mass of bound rubber does not exist [9]. Those results were explained in terms of a minimum inter-aggregate distance required for bridging of polymer chains, similar to the explanation given above. If the results presented here are compared with similar surface area carbon black-SBR compounds,

the critical loading for mass formation is lower for the carbon black system. This is probably due to the longer polymer chain length of SBR 1500, which is about three times that of the silicone rubber used in this study, and the higher polymer-filler interaction between SBR and carbon black.
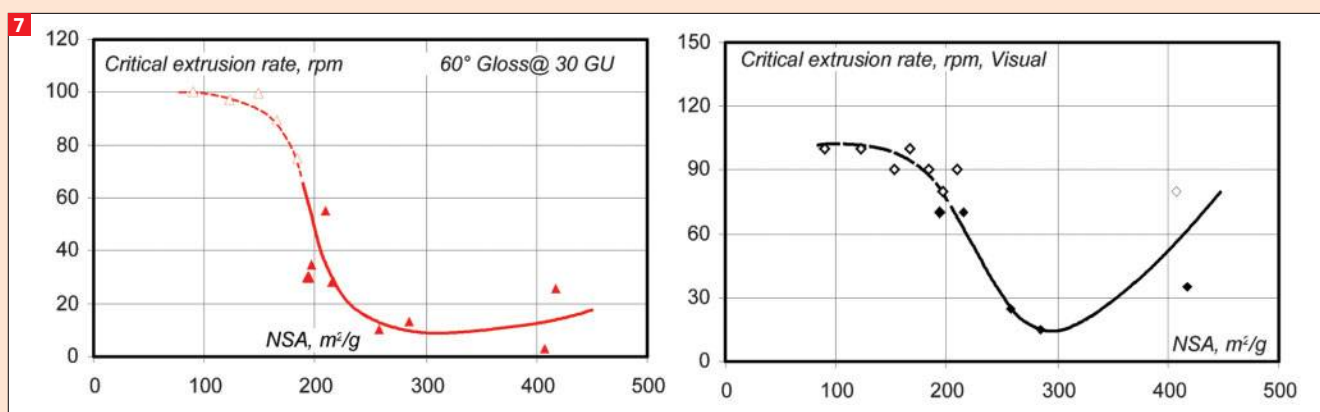
Our results show that beyond a critical fumed silica surface area, the bound rubber content decreases with increasing surface area. This is contrary to what might be expected from the interfacial area between polymer and filler, which is proportional to the surface area of the filler. It is also unexpected based on filler surface effects, since the surface activity of silica tends to increase with surface area, and the coverage with processing aid decreases. It can be explained in terms of dispersion quality and/or multiple adsorption. The poorer macro dispersion of high surface area silicas, as shown later, will certainly tend to reduce the effective surface area of the filler for bound rubber formation. However, even in a perfectly dispersed system, multiple adsorption of polymers can lead to reduced bound rubber. Once an appropriately-sized segment of a polymer chain becomes adsorbed to the filler, the whole polymer becomes part of the bound rubber. Further adsorption of other segments from the same polymer chain (multiple adsorption) takes up space on the filler surface, which could otherwise be used to adsorb other chains. As surface area of the filler increases, the inter-aggregate distance decreases, but in addition, the tendency for filler agglomeration or filler networking increases. Both of these effects would increase the probability of multiple adsorption. Thus the maximum bound rubber content on a surface area basis is achieved at the point where there is just enough bridging to form a coherent mass.

Extrudate Appearance

It is known that extrudate appearance can be affected by extrusion rate and temper-

ature. Generally, with decreasing temperature and increasing extrusion rate, the extrudate surface gets rougher. The results of gloss as a function of the silica surface area for extrudates extruded at a speed of 35 rpm (Fig. 5), show that with increasing surface area, the surface roughness of the extrudates increases rapidly between 170 m^2/g and about 300 m^2/g, beyond which the smoothness of the materials improves slightly. At low surface area, the roughness does not seem to change significantly. The results obtained at other extrusion rates (Fig. 6a), show that gloss becomes lower as extrusion rate increases. The overall surface appearances were also estimated visually (Fig. 6b), and there seems to be a good general correlation between these ratings and the surface gloss measured using a Glossmeter.

The effects of filler surface area and extrusion rate on the extrudate roughness can be explained on the basis of their effects on the elastic response or elastic memory of the compounds. It has been recognized that the surface appearance of the extrudate is associated with elastic recovery due to incomplete release of stress caused when long-chain molecules are orientated by shear in the die. The distortion of the extrudate increases with increasing unreleased stress and may, in some cases, even lead to the complete fracture of the extrudate (melt fracture). For a given compound, high temperature, which effectively reduces the relaxation time of the polymer, and lower extrusion rate, which allows the polymer enough time to relax in the die, both work to reduce the elastic recovery of the extrudate, giving a smoother surface. In terms of the polymer, the primary factor influencing the surface roughness of unfilled elastomers is the entanglement of elastomer molecules, which, in turn, is determined by their molecular weight and its distribution. Since the elastic memory occurs in the rubber phase alone [10], the surface roughness of the extrudate for any given polymer is generally improved by the addition of filler, due to the reduction of the elastic component of the compound and the decrease in effective relaxation time [11]. Fillers with higher structure will substantially increase the effective volume of the fillers [5, 12], leading to shorter relaxation times. In addition, filler agglomeration will further reduce elastic memory as long as the agglomerates are not broken-up under the shear stress during extrusion [13]. On the other hand, filler aggregates may serve as multi-functional crosslinks,

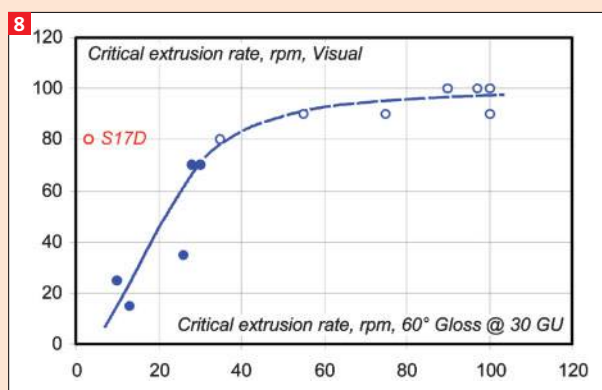**6** Surface roughness of extrudates measured (a) by glossmeter, and (b) visually

7 Critical extrusion rates for surface roughness, determined (a) by gloss measurements and (b) visually
The empty symbols represent the values extrapolated from the results obtained at the measured extrusion rates

due to the adsorption of polymer molecules, causing an increase in elasticity of the compounds. With these different mechanisms in mind, the dependence of extrudate appearance on silica surface area at constant loading can be explained as follows. At low surface area, where polymer bridging between filler particles is minimal, increasing surface area causes an increase in bound rubber, causing the elastic memory to increase somewhat, but this appears to be largely offset by the increased filler agglomeration which tends to reduce the elastic memory. Above the critical surface area where polymer bridging becomes significant, the effect of filler particles acting as extra crosslinks becomes dominant, leading to poorer extrudate appearance. At higher surface area, the effect of highly developed filler agglomeration becomes predominant, which, along with the reduction of bound rubber content, leads to an improved appearance of the extrudate.

Since the surface roughness of the extrudate is strongly affected by the extrusion rate, the critical rates of the compounds were also measured, taking 30 gloss units at 60° as criterion below which the surface is

considered to be rough. The critical rates were also estimated visually. The results shown in Figure 7 include some that were extrapolated from the results obtained at lower extrusion rates because even at the highest rate used in the study (70 rpm) the roughness of the extrudate was still below the criteria that we set. As expected, both the measured and visually estimated results generally show the same pattern: the critical rate decreases with surface area, passing a minimum and then going up slightly. It is more evident in the visual ratings. The

correlation between the measured data and those estimated visually was generally good (Fig. 8) but the compound filled with silica S17D is a clear exception. For this silica, the critical extrusion rate measured by glossmeter is extremely low and that obtained visually is even higher than 70 rpm, i.e. all extrudates looked smooth. It was also found that at low extrusion rate, the gloss of the S17D-compound was the lowest. With increasing extrusion rate, while the gloss of other compounds drops rapidly, the reduction in gloss is very small

8 Relationship between critical extrusion rate determined visually and that determined using a Glossmeter.

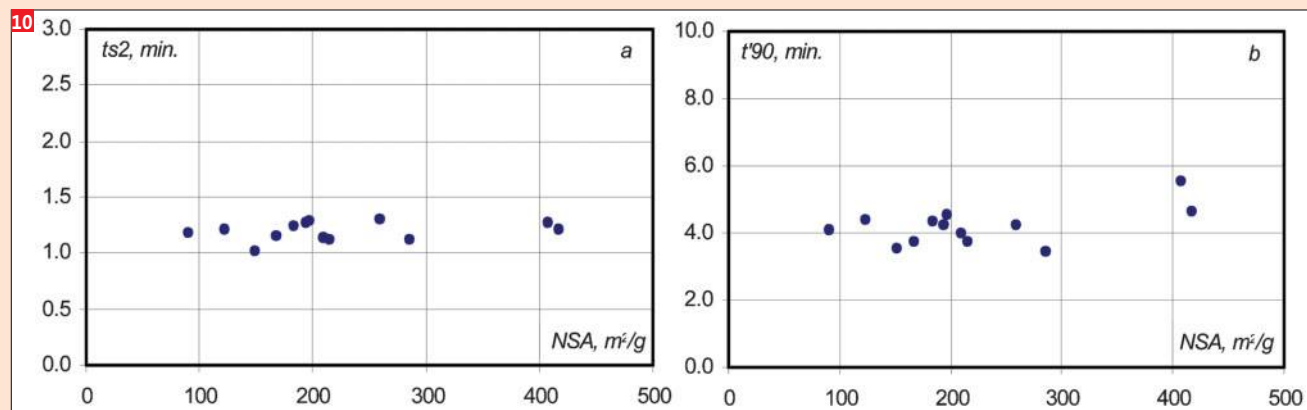**9** Surface roughness of extrudates having similar gloss at 60°.

MS75D 258m²/g, 35 rpm
Gloss @ 60°-11 GU

HS5 286m²/g, 35 rpm
Gloss @ 60°-10 GU

S17D 407m²/g, 45 rpm
Gloss @ 60°-12 GU

for the S17D-filled compound. The conflict in the ratings of the S17D compound between different methods appears to be related to the scale of the surface roughness. The glossmeter can measure surface roughness at the micron scale, whereas visual rating measures larger scale distortions. This effect is illustrated by the images shown in Figure 9. The extrudate of silica S17D is characterized by higher roughness on the micro scale at low extrusion rates, but less distortion at high extrusion rate. The reasons for this unique behavior are not fully understood, but it may be that the particle
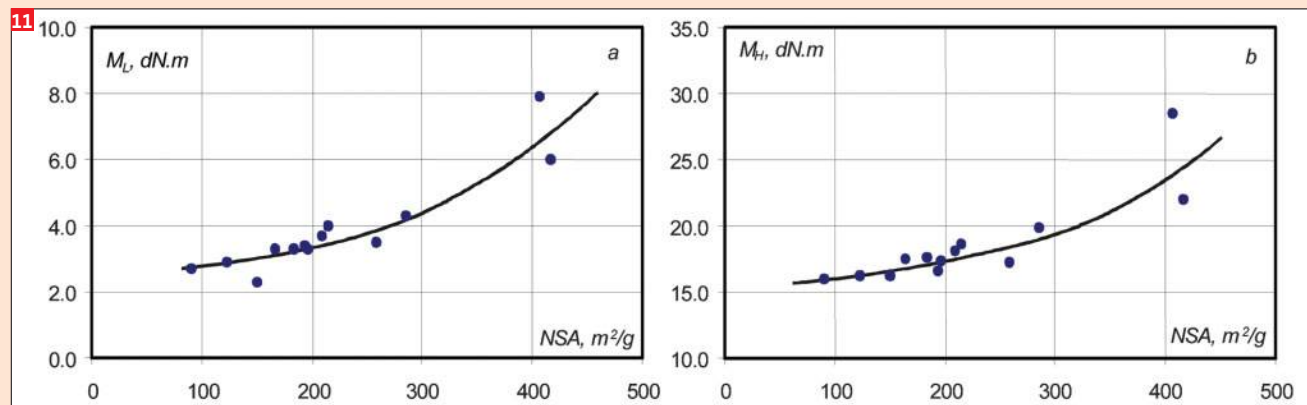
architecture leads to a highly developed filler network. There is evidence presented later in this paper that the S17D compound shows a high degree of filler agglomeration compared to other silicas, but that it seems to be easily broken-down upon strain.

Cure Characteristics

The cure kinetics were measured by an oscillating disk cure meter at 100°C and characterized by *ts2*, the scorch time, and *t'90*, the time to 90 % of the maximum torque developed during cure. The results in Figure 10 show that for the cure system used in this

study, the surface area of the silica does not have a significant effect on cure kinetics. The minimum torque, M_L, and maximum torque, M_H, obtained from the cure curves, both increase with increasing surface area of silica (Fig. 11). The minimum torque is a measure of viscosity at a very low shear rate and the maximum torque is determined by the dynamic modulus at relatively low strain amplitudes. The higher surface area silicas give high compound viscosities due to more adsorbed polymer and more filler networking. The adsorbed polymer on the filler surface can be immobilized and treated as part of filler, increasing filler effective volume. Likewise, filler agglomeration leads to trapped or caged rubber which, at least partially, loses its identity as an elastomer and behaves as filler in terms of stress-strain properties [14]. Similar interpretations can be applied to the effect of silica surface area on maximum torque. In this case, the attachment of polymer chains on the filler surface may serve as additional crosslinks, leading to higher modulus. Compounds containing high surface area fillers, with shorter average inter-particle distances can be expected to have more of these additional effective crosslinks.

10 Effect of silica surface area on (a) scorch time and (b) optimum cure time of compounds at 100°C.

11 Effect of surface area on (a) minimum torque M_L and (b) maximum torque M_H at 100°C.
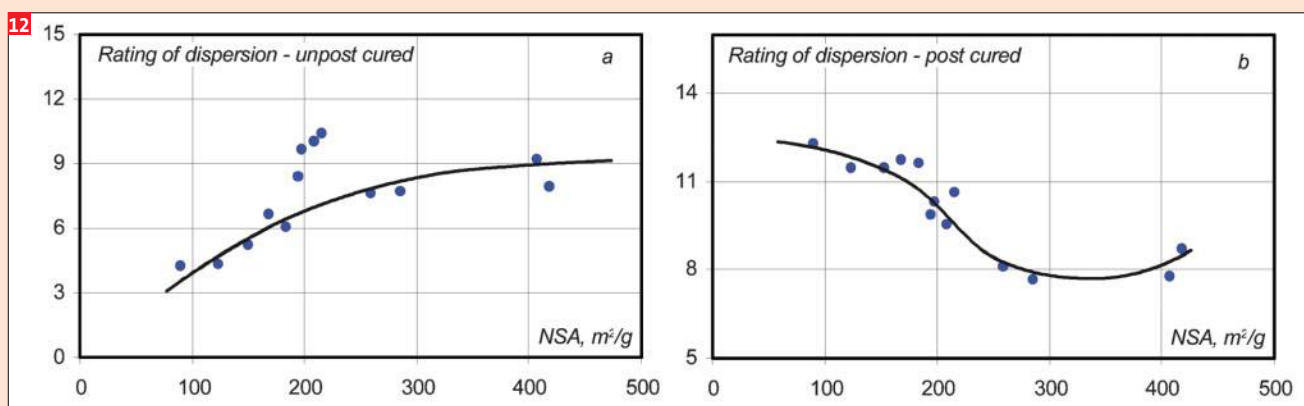
12 DisperGrader rating for unpost-cured (a) and post-cured (b) vulcanizates as a function of silica surface area.

Macro-dispersion of Silica

The macro-dispersions of silica in the vulcanizates were investigated before and after post-cure using a DisperGrader (Fig. 12). For non-postcured samples, there is a trend showing that the rating of fine silica is generally better. However, when the samples were post cured in an oven at 220°C for 2 hours, the trend was reversed. For post-cured vulcanizates, the filler dispersion deteriorates with increasing surface area of the filler up to 250 m²/g, beyond which no further deterioration is observed. This is the trend that was expected based on the generally increasing difficulty of dispersion as surface area increases. In this study, the dispersion difficulty is accentuated by the lower surface concentration of processing aid in the higher surface area silicas.

It was found that the change in rating using the DisperGrader reading upon post-cure is associated with blooming. For the non-post-cured samples with lower surface area silicas, some blooming appeared on the fresh surface in a short period of time after the specimens were cut. This was confirmed by microscopy of the cut surfaces, which showed clusters of crystallites that were not seen on their post-cured counterparts. The blooms are probably due to residuals of the crosslinker and its decomposition products, which volatilize during post-curing. Apparently, the DisperGrader cannot distinguish between the crystals and undispersed filler. Figure 13 shows the differences in Disper-Grader ratings between post-cured and non-postcured samples, which can be considered as an indicator of the degree of blooming. The difference decreases with increasing surface area until about 250 m²/g beyond which it is effectively zero. Blooming is caused by the limited solubility of polar molecules in the relatively non-polar silicone polymer. In the filled rubber system, the low-molecular-

weight polar materials can move to the nearest polymer-filler interface and be adsorbed on the highly polar silica surface, reducing the amount of blooming. As the surface area of silica is increased, the interfacial area per unit volume of vulcanizate increases proportionally, and the degree of surface passivation decreases. Both of these effects would increase the amount of small molecule adsorption and therefore reduce blooming.

Dynamic Elastic Modulus

The change in elastic modulus with strain amplitude at constant frequency (1.7 Hz) and temperature (30°C) shows typical non-linear behavior for all compounds [14]. This phenomenon was first observed in carbon black-filled hydrocarbon rubbers in 1950 by Warring [15] and later it was studied extensively by Payne after whom the effect is often named [16]. It has widely been accepted that the Payne effect is mainly, if not only, related to filler agglomeration in the polymer matrix. As mentioned before, trapped rubber within agglomerates can increase the effective filler volume fraction, increasing modulus of the filled vulcanizates. At moderate and high strains, the agglomerates are, to a certain degree, broken-down and the rubber trapped within the ag-

glomerates is released, lowering modulus. Thus, the Payne effect can serve as a measure of filler agglomeration or micro-dispersion [14]. The dependence of the Payne effect, defined as the difference between G' at strain amplitudes of 0.7 and 98%, on silica surface area (Fig. 14b), shows a general increase in Payne effect with increasing surface area. The higher Payne effect for the high surface area silicas can be explained in terms of a higher degree of agglomeration. This is caused by the shorter inter-aggregate distances as well as by stronger filler-filler interaction due to lower surface treatment levels. For the two silicas with the highest surface areas, the Payne effects are significantly different, indicating more developed filler agglomerates in the S17D-filled vulcanizate compared to EH5. The S17D silica also gives weaker agglomerates, indicated by the more rapid drop in G' with strain. It seems that some mechanism other than those associated with the surface area play a considerable role in filler agglomeration in this case. Further work is required to understand these effects.
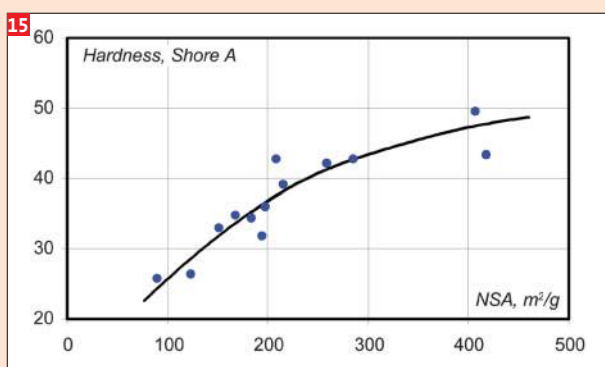
Hardness of the Vulcanizates

The Shore A hardnesses of the filled vulcanizates (Fig. 15), show the expected increase
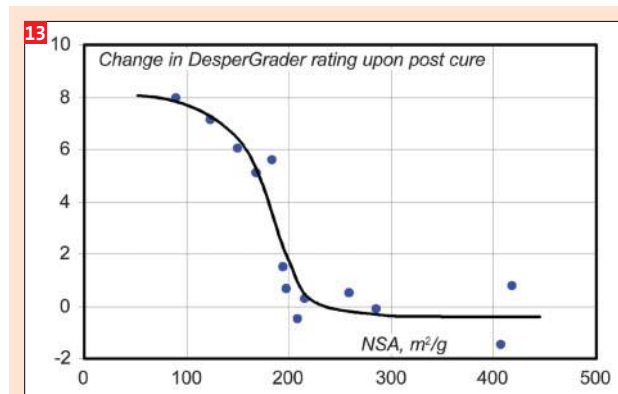
13 Changes in Disper-Grader rating upon post cure as a function of silica surface area
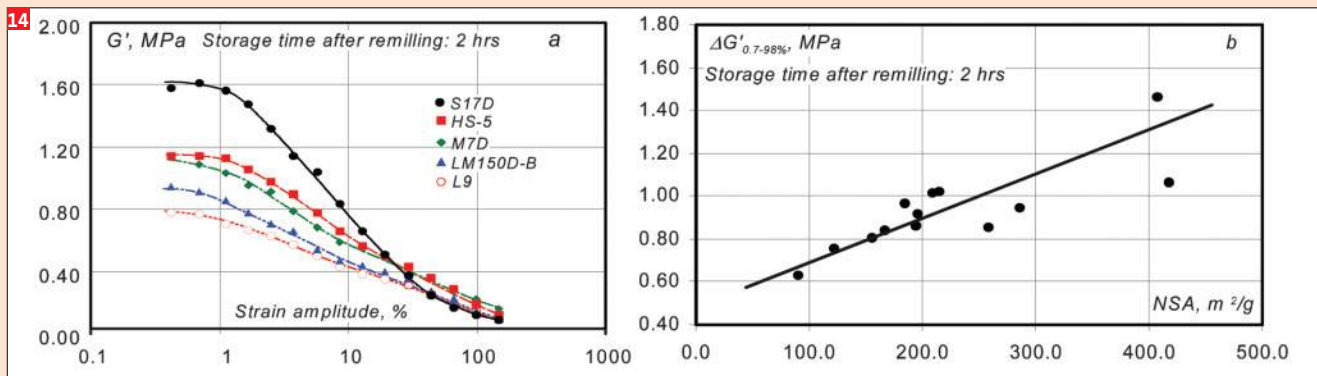
14 (a) Strain dependence of G` at 1.7Hz; (b) Payne effect as a function of silica surface area

15 Hardness of vulcanizates as a function of surface area

in hardness with increasing surface areas of the silica. It has been well established that the hardness of vulcanizates is an expression of their elastic modulus, i.e. their resistance to deformation. Although the deformation by indentation is very complicated, involving deformations in tension, shear and compression in the low strain region, it has been reported that hardness is simply dependent on Young's modulus. [17] The main factors related to fillers which govern the Young's modulus, hence hardness, can be summarized as follows:
- Crosslink density, both chemical and physical in nature, in the polymer matrix;
- Silica loading due to the hydrodynamic effect;
- Silica aggregate morphology leading to the occlusion of polymer in the void volume of aggregates, increasing effective filler volume;
- Adsorption of polymer chains on filler surfaces, resulting in immobilization of chain segments. This, on the one hand, will increase effective volume of the filler slightly. On the other hand, due to the adsorption, the filler particles can serve as a giant multifunctional crosslinks in the crosslinked polymer matrix, increasing the apparent crosslink density, especially at low deformation.

- Filler agglomeration – as the Young's modulus (hence hardness) is measured at very low deformation at which the filler network (agglomerate) is not destroyed significantly upon strain.

The effects of silica surface area on overall crosslink density in the vulcanizates is not clear. However, the high-surface-area silicas would be expected to have a positive effect on hardness due to the effects of adsorption and filler agglomeration.

Tensile Modulus
Tensile stresses at 100 and 300 % elongations (Fig. 16) show that the stress at a given elongation generally increases with increasing surface area of the filler. The factors controlling the Young's modulus also apply to tensile stresses, with the exception that at such high elongation, especially 300 %, the contribution of filler agglomeration has ceased to be important. However, at high strain, the orientation of polymer chains in the original agglomerates along the direction of strain may also easily reach the limitation of finite chain extensibility, giving higher stress at given elongation. In other words, even if the agglomerates are broken-down at high elongation, the more developed multi-attachment of polymer chains in the agglomerates may also contribute to

the higher stress at high deformation, as long as detachment of the polymer chains from filler surface does not occur. In this regard, high surface area silicas will also favor high tensile stress at high elongation based on their highly developed filler network and polymer-filler interactions.

Ultimate Tensile Properties
The surface area dependence of breaking elongation and stress (Fig. 17), measured at constant temperature and strain rate, show that while the elongation at break decreases monotonically with surface area, the effect on tensile strength is more complicated. Breaking stress does not change significantly until 170 m²/g, beyond which it increases sharply to a maximum at around 200 m²/g, followed by a reduction at higher surface area. The lower tensile strength in vulcanizates filled with lower surface area silicas can be attributed to their lower polymer-filler interaction, which in turn, can be related to lower interfacial area between filler and polymer, higher surface coverage with low MW hydroxy-terminated PDMS, and lower surface energies of the fillers. When the vulcanizate is subjected to high tensile stresses, polymer chains may be more easily detached from the surface, thus providing less of a barrier to crack propagation and coalescence. With increasing surface area, both the polymer-filler interaction and the interfacial area between filler and polymer increases. This will significantly reduce the possibility of vacuole formation and favor slippage of chains along the surface to relieve stress concentration [18]. The reduction of the breaking stress at higher surface area is probably caused by poorer dispersion. In this case, the poorly-dispersed filler may furnish flaws that can initiate cracks and then develop into catastrophic failure under lower stresses. The increase in size or concentration of flaws appears to outweigh the effects of finer particle silica beyond about 250 m²/g.
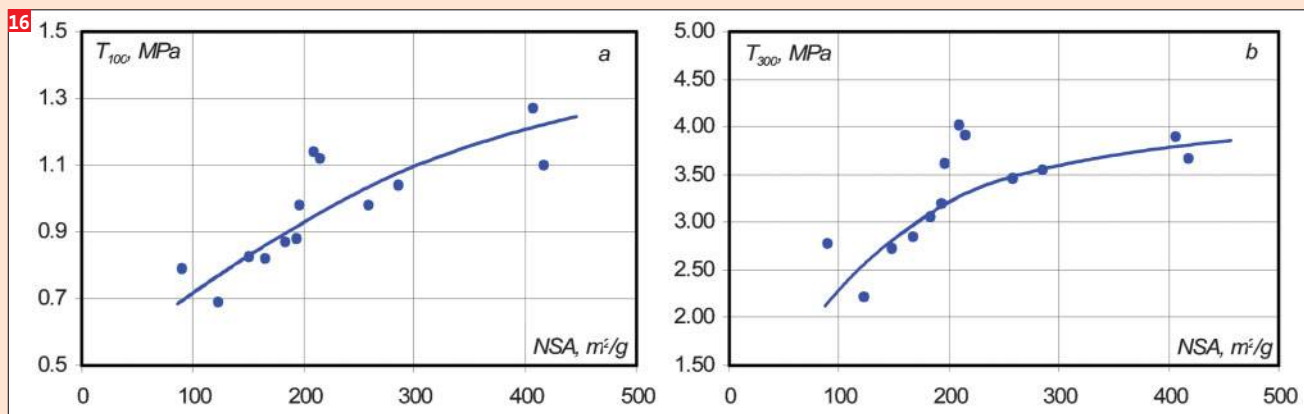
16 Stress at (a) 100 % elongation (T_{100}) and (b) 300 % elongation (T_{300}) as a function of silica surface area
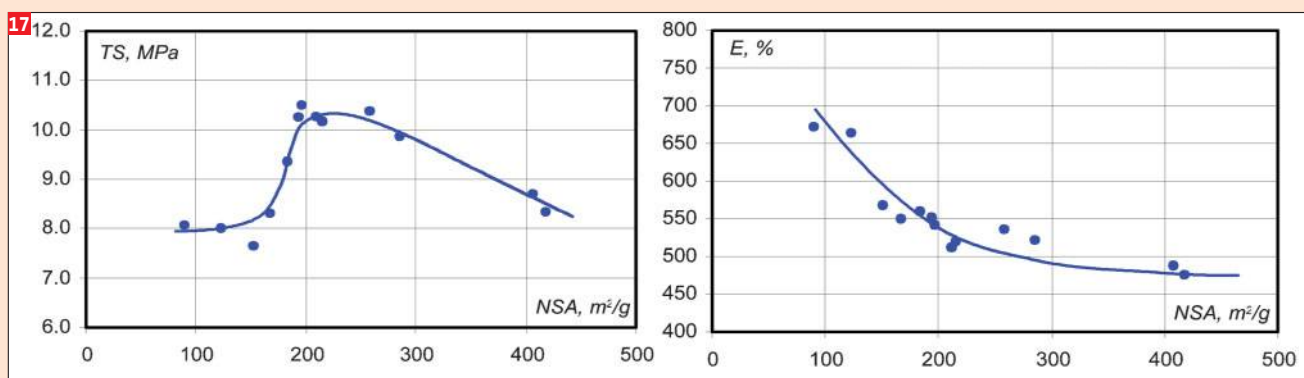
17 (a) Tensile strength and (b) elongation at break as a function of silica surface area

Tear Strength

There is too much scatter in the tear strength results to draw any significant conclusions, although the two higher surface members seem to show lower values (Fig. 18). Generally, it would be expected that trends for effects of filler properties on tear strength would follow those for tensile strength.

Compression Set

The compression set of the samples after aging at 177°C for 22 hours is shown in Figure 19. Clearly there is a trend showing a positive response upon increasing surface area. For the vulcanizates filled with the two low-surface-area silicas, no compression stress remains after aging. Further work is ongoing with the aim of better understanding the mechanisms involved in this system.

Discoloration of Vulcanizates

The phenomenon of discoloration or yellowing of post-cured vulcanizates is generally undesirable. The discoloration of post-cured vulcanizates was rated visually from 1 to 10 with the lower value representing the less discoloration. It was found that the visual rating correlated reasonably well with L^* and a^*, but not with b^*, suggesting that lightness and red-green coloration should be used to assess discoloration. The effect of silica surface area on these parameters (Fig. 20) shows that with increasing surface area, the vulcanizates appear to be darker (lower L^* value), and more red (higher a^*). It has been reported that for precipitated silica filled silicone rubber, the discoloration of silicone rubber is mainly associated with the decomposition of reaction products of organic peroxides. [19] Later, Takahashi et al. proposed a mechanism involving acid-catalyzed decomposition of the dialkyl peroxide to form acetone. This product will, via an aldol condensation/dehydration reaction, form conjugated compounds that may absorb light, leading to discoloration [20]. The involvement of the crosslinker was confirmed by heating blends of silicone polymer, processing aid, and silica at 220°C for 2 hours. This mixture without crosslinker, showed no significant discoloration. It is also interesting to note that there is similarity between the discoloration rating of the compounds and the apparent changes of filler dispersion upon post-cure (Fig. 13). It was concluded that after post-curing, less peroxide residuals would remain in the vulcanizates filled with low surface area silicas than those in the vulcanizates filled with their high surface area counterparts. This may be the reason why lower surface area silica imparts less discoloration to the silicone rubber.

Conclusions

The effects of fumed silica on the processability and vulcanizate properties of silicone rubber have been studied with silicas having specific surface areas from 90 to 420 m^2/g at a fixed loading and with a constant loading of processing aid. It is apparent from the investigation that all rheological properties of the compounds and mechanical properties of vulcanizates are strongly affected by surface area. With increasing surface area, the viscosity of the compounds and the modulus of the vulcanizates increases markedly, the dispersion of the filler, the tear strength and elongation at break are deteriorated, and the compression set is somewhat improved. While the bound rubber and tensile strength
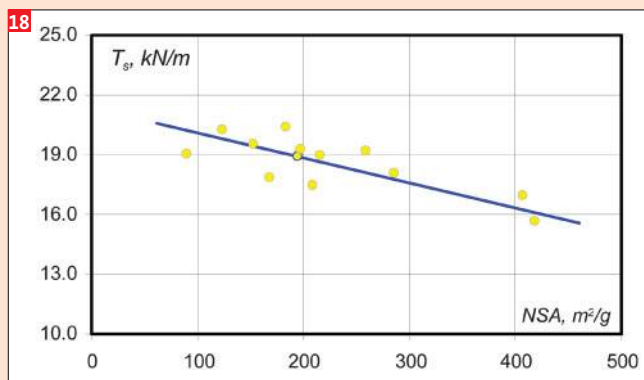
18 Tear strength (T$_s$) as a function of silica surface area
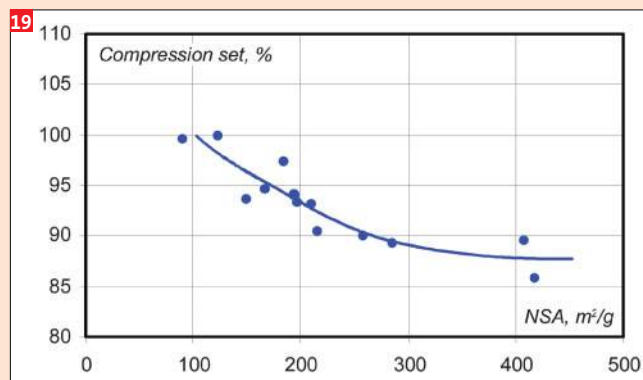
19 Compression set as a function of surface area
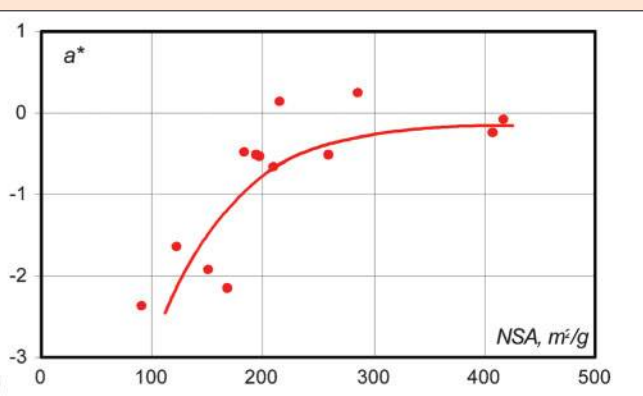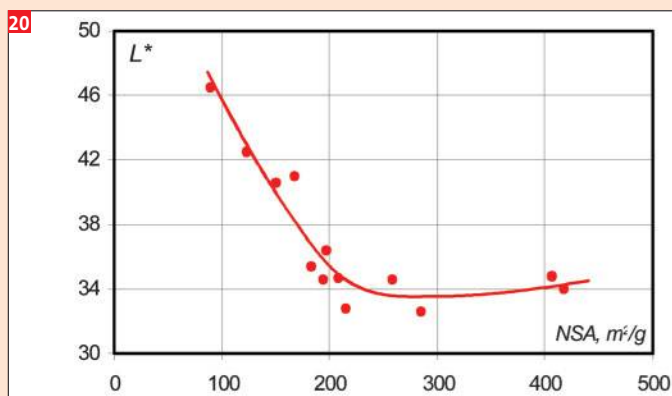
20 L^* and a^* as a function of silica surface area

rise to a maximum at a surface area between 170 and 250 m^2/g, the extrudate appearance is poorer in this area. It was also found that lower surface area silica favors discoloration. All these observations were discussed based on the effects of surface area on the polymer-filler, filler-filler, filler-other small chemical interactions, which influence the compound behaviors via different mechanisms. It should be pointed out that the effect of surface area on the silicone rubber reinforcement reported here may include the effects of other parameters of the silicas, such as structure, surface energies, and degree of surface passivation, which cannot be separated due to their surface area dependence. Further work is required to understand these effects independently.

Acknowledgements

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