

NH₃-Modified Swelling of Silica-Filled Silicone Rubber*

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Synopsis

The NH₃-modified swelling method was used for fume silica-filled silicone rubber compounds and vulcanizates. The method provides an estimation of the polymer-filler interaction in the system. Bound rubber reduction due to the modified swelling is shown to be dependent on the silica surface silanol content in the compound. The swelling behavior of silica-filled vulcanizates was also studied in an NH₃ atmosphere. The fraction of polymer-filler attachments in the vulcanizates was found not to depend on the particle size of silica and its surface modification, depending only on the total polymer-filler contact area in the system. No relation was found between bound rubber content in a compound and swelling of a filled vulcanizate of the same composition. The strong rubber-to-filler adherence found in toluene changed to nonadherence under NH₃-modified swelling conditions. The NH₃-induced cleavage of silica-silicone rubber attachments was found to be nearly completely reversible. In the silica-filled silicone rubber vulcanizates, the fraction of polymer-filler attachments due to polymer-filler interaction represents a substantial contribution to the total number of network chains.

INTRODUCTION

During the past decades important progress has been made in the understanding of reinforcement of elastomers by carbon black,¹ but no comparable advances have been achieved for reinforcement by silica. Fume silica is generally used as a reinforcing agent in silicone rubber technology.

It is recognized that there is a pronounced interaction between silicone rubber and fume silica, which is manifested by crepe hardening and bound rubber formation on storage after mixing.²⁻⁵ However, complete agreement on the exact nature of the polymer-filler interfacial bonding is lacking.

In the case of the silicone rubber-silica system, it is accepted that the chemical nature of the filler surface is an important factor in determining its behavior in rubber. The silanol groups on the fume silica surface can react by hydrogen bonding with the few residual terminal hydroxyl groups on the polymer chains as well as with the oxygen atoms in the polysiloxane macromolecule.^{3,5,6} In addition, physical adsorption of polymer molecules on the solid surface may occur. The silica particles can be bonded together by hydrogen bonds to form aggregates and filler-filler network.

The interfacial processes in a silicone rubber compound result in formation of a network consisting of filler particles or aggregates connected by means of elastomer attachments. The "filler-crosslinked" silicone rubber cannot be completely dissolved in solvents.

Only a part of the polymer in the filled compound can be dissolved, the other

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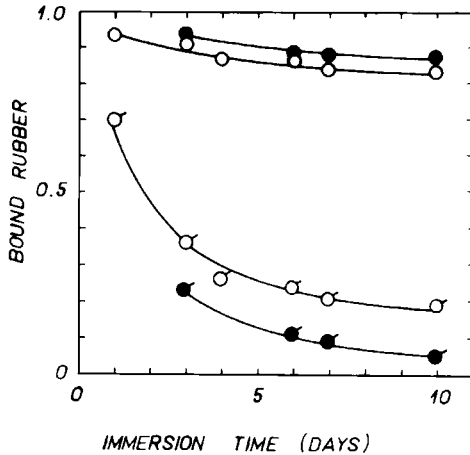


Fig. 1. Bound rubber content as function of immersion time in toluene under conventional (O) and NH_3 -modified (O) conditions. Silicone rubber compounds filled with Aerosil 130/80 (O) and Aerosil 200 (●) were stored for 2 years at room temperature after mixing.

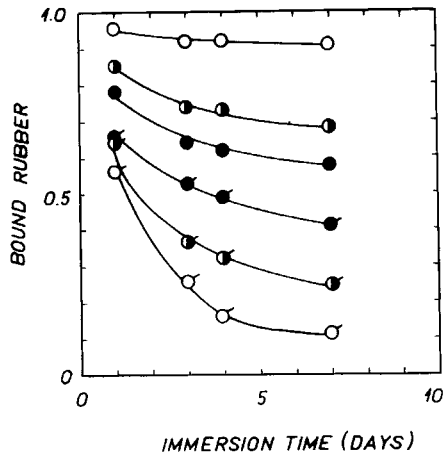


Fig. 2. Bound rubber content as function of immersion time in toluene under conventional (O) and NH_3 -modified (O) conditions. Silicone rubber compounds filled with HDK N 20 (O), HDK H 20-1 (●), and HDK H 2000 (●) were stored for 2 years at room temperature after mixing.

part is insolubilized by the adsorption on the filler surface and/or the "filler crosslinking".⁷ It is proposed by Southwart⁴ that the so-called filler gel consists of the adsorbed rubber and the interparticular rubber. The adsorbed polymer molecules are attached to one filler particle at one or more points; the interparticular macromolecules are bound to two or more filler particles, thus forming a three-dimensional network.

The difficulty in attempting to use bound rubber determinations to investigate filled rubber systems is an impossibility of distinguishing the particular structures and attachments involved. The same problem arises when studying the swelling behavior of filled vulcanizates. These are very complicated systems in which we can assume some structures due to polymer-filler interaction (polymer-filler attachments, filler-polymer-filler crosslinks), and filler-filler interaction (filler aggregation, filler network), along with the structures resulting from vulcanizing processes (polymer-polymer crosslinks).

The present work had been initiated by the paper of Polmanteer and Lentz⁸ dealing with the effect of silica structure on properties of silicone rubber vulcanizates. The method based on swelling the vulcanizates in toluene under an NH₃ atmosphere was described. The procedure was designed to chemically break polymer–filler bonds and should provide a possibility to distinguish the polymer–filler and polymer–polymer attachments.

The work to be described in this paper was designed to allow separation of polymer–filler interaction effects and chemical crosslinking effects in silicone rubber vulcanizates loaded with fume silica. The effects of various factors influencing the polymer–filler interaction level have been evaluated in connection with swelling of the vulcanizates. The influence of the NH₃ atmosphere on the bound rubber determination in silicone rubber filled with fume silica has also been studied.

The study was undertaken to judge the capability of the Polmanteer–Lentz method for investigating the structure of the filled silicone rubber systems.

EXPERIMENTAL

The experiments in the study were carried out with various fume silicas in a commercial poly(methylvinylsiloxane) elastomer Lukopren G 1000, produced by VCHZ Synthesia, Kolín, Czechoslovakia, of viscosity-average molecular weight 500,000. The silicas differing from each other by their surface area and/or surface nature, as shown in Table I, were incorporated in the silicone rubber on a laboratory two-roll mill within approximately 30 min at room temperature.

The compounds, “shelf aged” for 7 days after mixing were vulcanized, after remilling on a two-roll mill for the time necessary to obtain processible and homogeneous materials, by means of 1.2 phr 50% bis-2,4-dichlorobenzoyl peroxide in silicone oil (Perkadox PDS 50, product of Noury & Van der Lande N.V., Holland). The catalyzed compounds were cured under pressure for 20 min at

TABLE I
Typical Properties of Fume Silica Fillers Used

Filler ^a	Surface area BET, m ² /g	Silanol coverage, SiOH/nm ²	Surface treatment
Aerosil 130	130 ^c	3 ^c	none
Aerosil 130/80	80 ^b	3 ^c	none
Aerosil 200	200 ^c	3 ^c	none
Aerosil 300	300 ^c	3 ^c	none
HDK N 20	168 ^d	2.7 ^d	none
HDK N 20 S	186 ^d	1.8 ^d	none
HDK H 20-1 ^e	174 ^d	1.03 ^d	trimethylchlorosilane
HDK H 20-2 ^e	174 ^d	0.66 ^d	trimethylchlorosilane
HDK H 20-3 ^e	174 ^d	0.47 ^d	trimethylchlorosilane
HDK H 2000	182 ^d	0.35 ^d	trimethylchlorosilane

^a Aerosil is the trade name of fume silica produced by Degussa, W. Germany; HDK is the trademark of fume silica produced by Wacker-Chemie GmbH, W. Germany.

^b Own measurement.

^c Product leaflet data.

^d Experimental data provided by Dr. Stohr of Wacker-Chemie GmbH, Zweigbetrieb Kempten, W. Germany.

^e Experimental products provided by Dr. Stohr of Wacker-Chemie GmbH, Zweigbetrieb Kempten, W. Germany.

125°C (short cure) followed with some samples by additional heating for 4 hr at 160°C plus 16 hr at 200°C in a circulating air oven (oven cure).

Bound rubber content was determined in unvulcanized compounds in toluene (100 ml) at room temperature in samples of weight 0.2–0.3 g. Immersion times of the determination were 1, 3, 4, 6, 7 and 10 days.

The weighed samples of vulcanizates (approximately 0.2 g) were swollen in toluene at room temperature for 72 hr with refreshing the solvent after every 24 hr. For samples of the thickness used in this study (2 mm), these swelling conditions were sufficient to reach equilibrium swell. The swollen samples were weighed immediately after swelling and after drying overnight at 80°C. From the swelling data values of the volume fraction of rubber in the equilibrium swollen vulcanizate (v_r) were calculated.

The modified swelling procedure in the NH_3 atmosphere was used both for the bound rubber determination and for the vulcanizate swelling. The compound or vulcanizate sample in a tared filter crucible with a porous glass bottom was placed in a beaker filled with 100 ml toluene. The open beakers were put into the desiccator and arranged round the vessel containing concentrated NH_4OH . The ammonia was exchanged for a fresh one after each opening of the desiccator.

The swelling procedure was carried out at room temperature for 1, 3, 4, 6, 7, and 10 days for determining the bound rubber content. The highly swollen and inconsistent samples of bound rubber were weighed after drying in the tared filter crucibles.

RESULTS AND DISCUSSION

Bound Rubber Determination

The series of bound rubber determination in “crepe-hardened” silicone rubber compounds was carried out in samples containing 30 phr fume silica after storing the mixed compounds two years at room temperature. The silica fillers used differ from each other in specific surface area and/or surface nature, viz., silanol group concentration. In compounds stored or “shelf aged” for such a long time we can assume the equilibrium value of bound rubber content.

The data presented in Figure 1 show the kinetics of dissolving the “crepe-hardened” silicone compounds in toluene and in toluene under NH_3 atmosphere. The fillers used differ in their surface area. The influence of the ammonia atmosphere on bound rubber content is clearly evident from Figure 1. Silicone polymer in the filled compounds dissolves much more efficiently in toluene under NH_3 atmosphere than in the same solvent during the conventional swelling procedure.

Figure 2 shows equivalent curves for the series of fume silicas with the same particle size differing in their surface nature (see Table I). The influence of NH_3 atmosphere on the dissolving efficiency is again evident.

Bound Rubber Reduction

From results displayed in Figures 1 and 2 it is also obvious that the difference between bound rubber content determined conventionally and over NH_4OH is not constant in compounds with the same filler concentration. It seems that

there is quite a characteristic polymer fraction in the particular compound which can be dissolved by toluene in ammonia atmosphere. It appeared useful to express this fraction as a bound rubber decrement ΔB :

$$\Delta B = \frac{B_{\text{tol}} - B_{\text{NH}_3}}{B_{\text{tol}}} \quad (1)$$

where B_{tol} is bound rubber content determined in toluene and B_{NH_3} is bound rubber content determined in toluene under ammonia atmosphere. The bound rubber decrement ΔB expresses what fraction of silicone rubber in bound rubber determined by the conventional way in toluene can be additionally dissolved by immersion in toluene over ammonia.

In Figures 3 and 4 are plotted the bound rubber decrement values as function of the immersion time in toluene. When comparing fume silicas with different surface areas such as Aerosil 130 and 200, we can see that the bound rubber decrement depends on the particle size of the filler after any time of immersion.

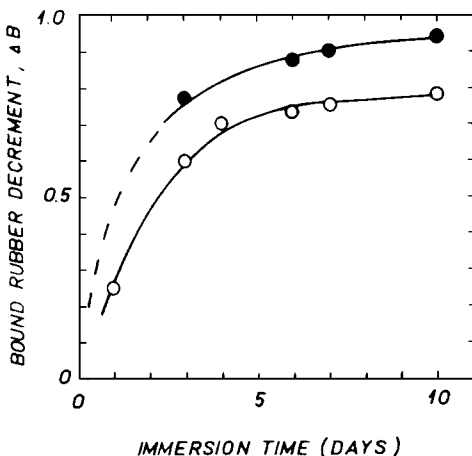


Fig. 3. Bound rubber decrement due to NH_3 -modified swelling as function of immersion time in toluene. Silicone rubber compounds as in Fig. 1.

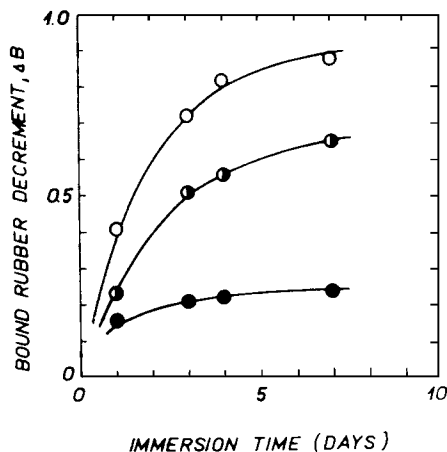


Fig. 4. Bound rubber decrement due to NH_3 -modified swelling as function of immersion time in toluene. Silicone rubber compounds as in Fig. 2.

The decrement increases for the particular compound with the immersion time, and after some time it reaches the equilibrium value.

Influence of Trimethylsiloxy Surface Treatment of Silica

Data presented in Figure 4 were determined in compounds loaded with the same concentration of fume silicas differing from each other by their silanol surface coverage (see Table I). A series of HDK fume silicas N 20, H 20-1, and H 2000 provided a possibility to study the effect of silanol inactivation on bound rubber determination under NH_3 atmosphere. The HDK H 20-1 and H 2000 fillers are surface-treated silicas with increasing conversion of silanol groups into trimethylsiloxy groups. The HDK N 20 silica is an untreated filler with the greatest silanol coverage within the series.

It is remarkable that the bound rubber decrement increases with increase in silanol coverage of silica. In other words, the additional dissolving of bound rubber in the ammonia atmosphere becomes greater at higher levels of silica surface silanol coverage. The bound rubber content determined in toluene by the conventional way increases in the same direction. On the other hand the bound rubber content determined in toluene over ammonia decreases with the growing silanol coverage. In the system with higher silica silanol content, more polymer may be bound to the filler surface through hydrogen bonds, as indicated by the enhanced bound rubber in toluene, and therefore more polymer-filler hydrogen bonds may be cleaved by the NH_3 -modified swelling.

This is clear from Figure 5, where bound rubber content determined by both swelling procedures and bound rubber decrement as function of silanol group concentration in 1 g silicone rubber are presented. The immersion time at room temperature was 7 days, and the silanol concentration was calculated from the data given in Table I according to the following formula:

$$c_{\text{SiOH}} = \text{ALC} \times 10^{-7}/6.024 \text{ (mol/g)} \quad (2)$$

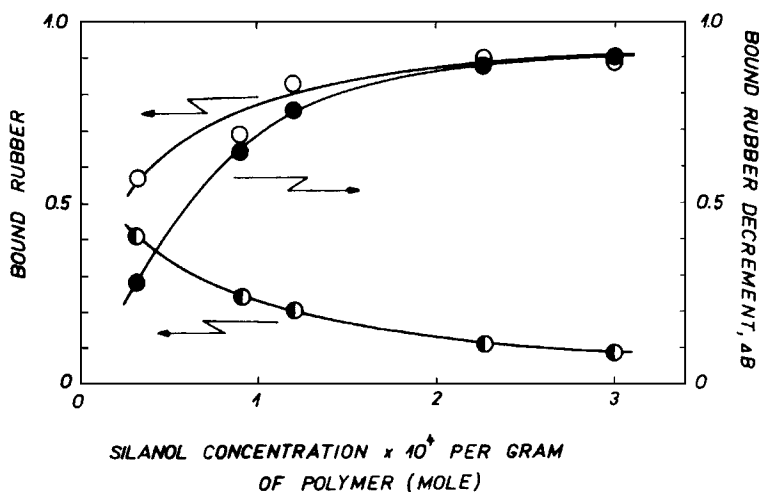


Fig. 5. Bound rubber content in toluene (\circ), in toluene over NH_4OH (\circ), and bound rubber decrement due to NH_3 -modified swelling (\bullet) as function of silica silanol concentration in silicone rubber compounds filled with 30 phr of various fume silicas (from left side: Aerosil 130/80, Aerosil 200, HDK N 20, HDK H 20-1 and HDK H 2000). Immersion time in toluene was 7 days at room temperature.

where A is specific surface area of silica (m^2/g), L is loading of silica in the compound (phr), C is surface silanol coverage of silica (SiOH/nm^2), and c_{SiOH} is silanol concentration in 1 g rubber (mol/g).

The dependence of bound rubber decrement on silanol concentration in a compound supports the concept of selective cleavage of polysiloxane-silica hydrogen bonds, the number of which is proportional to the silanol concentration in the fume silica-filled silicone rubber compound.^{3,5} The bound rubber decrement provided a measure for the SiOH-induced hydrogen attachments between silica surface and silicone elastomer.

An Explanation of the Bound Rubber Data

Three types of polymer molecules in silica loaded silicone rubber can be differentiated by the conventional and NH_3 -modified swelling procedures in toluene, viz., (1) polymer fraction dissolved in toluene during normal immersion conditions, (2) polymer fraction dissolved in toluene under ammonia atmosphere; this fraction is insoluble under normal toluene swelling; and (3) permanently insoluble polymer fraction. The situation is schematically summarized in Figure 6.

A polymer portion dissolved in toluene under normal swelling conditions, the unbound rubber, can be considered as not being attached to filler surface. When held by the filler surface anyhow, only weak "single contact" adsorptive polymer-filler bonds could be assumed in the soluble rubber fraction.

The polymer fraction extracted by toluene during NH_3 -modified swelling procedure seems to be the polymer attached to silica surface by the hydrogen bonds between free silanol groups on the filler surface and siloxane bonds of the elastomer.

The third part of the polymer is permanently attached to the silica surface. The permanently insoluble polymer fraction was found to be greater in compounds loaded with trimethylsiloxy-treated silicas, as shown in Figures 2 and 5. As the trimethylsiloxy treatment level increases and the silanol concentration in a compound decreases, the insoluble fraction of rubber in NH_3 -modified environment increases.

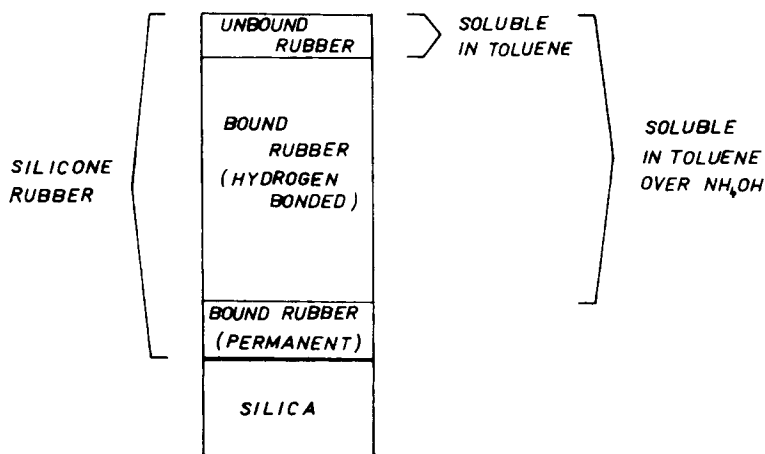


Fig. 6. Composition of bound rubber as determined in toluene under conventional and NH_3 -modified conditions.

The increase in the insoluble polymer fraction could result from the NH_3 -induced trimethylsiloxy group cleavage, as proposed by Polmanteer and Lentz.⁸ On sites of cleavage the polymer chains could be covalently bonded to the silica surface. In compounds loaded with the unmodified silica, the insoluble fraction of the polymer is much lower, which would lend support to the concept of NH_3 -induced cleavage of the modifying trimethylsiloxy groups on the silica surface. Therefore, the occurrence of the NH_3 -induced covalent bonds between the surface of treated silicas and silicone elastomer seems to be one factor contributing to the permanently bonded rubber.

It is also possible that even in samples with the unmodified silica a small number of covalent bonds occur, especially in the case of poly(dimethylsiloxane) obtained by KOH-catalyzed polycondensation, which may hold some remaining, not properly deactivated terminal $-\text{OK}$ groups reactable with silica silanols by covalent bonding.

The occurrence of permanently bonded rubber on the filler surface could be also readily explained by the multicontact physical adsorption of polymer molecules onto the solid surface, as proposed by Frisch, Simha, and Eirich.⁹

Therefore, we must assume both the covalent and multicontact adsorptive polymer-filler attachments in the permanently insoluble polymer portion.

Vulcanizate Swelling

To prove the selectivity of NH_3 -modified swelling environment for bond cleavage at the polymer-filler interface, an unfilled silicone control vulcanizate was swollen in both swelling environments. A decrease of 2% in the value of the volume fraction of the swollen rubber in the unfilled vulcanizate, v_{r0} , was found in the NH_3 modified procedure both in short cured samples ($v_{r0}^{\text{tol}} = 0.1485$, $v_{r0}^{\text{NH}_3} = 0.1454$) and in oven-cured vulcanizates ($v_{r0}^{\text{tol}} = 0.1742$, $v_{r0}^{\text{NH}_3} = 0.1707$).

The results also proved the stability of the chemically introduced polymer-polymer bonds in the vulcanizate under NH_3 -modified swelling conditions.

Influence of Silica Loading

The first thing to investigate in filled vulcanizates was the effect of fume silica loading on swelling in toluene under conventional and NH_3 -modified conditions. Our data show that there is a considerable decrease in the value of the volume fraction of the swollen rubber gel in the filled vulcanizate, v_r . The relative increase in swelling in toluene over ammonia was expressed as a network chain decrement Δv_r :

$$\Delta v_r = \frac{v_r^{\text{tol}} - v_r^{\text{NH}_3}}{v_r^{\text{tol}}} \quad (3)$$

The network chain decrement Δv_r is proportional to the fraction of total network chains resulting from effective polymer-filler attachments. We had decided not to recalculate our swelling data from v_r values to crosslink density values according to Flory and Rehner's theory because the proper quantitative relation for the swollen filled systems between v_r and crosslink density is still lacking. The v_r values can provide the same conclusions as to the effect of NH_3 -modified swelling in filled vulcanizates.

The data presented in Figure 7 show that the decrease in v_r due to NH_3 -modified environment is higher at higher levels of loading in Aerosil 130-filled silicone rubber vulcanizates. Thus, the network chain decrement increases with silica loading. The data in Figure 7 provide also the evaluation of the effect of the additional oven cure on the fraction of polymer-filler attachments.

As the loading with fume silica in silicone rubber vulcanizates increases, the relative number of breakable polymer-filler attachments increases. This fact leads again to the concept of the selective cleavage of silica-silicone rubber bonds in NH_3 -modified swelling environments. If the hypothesis is correct that the two swelling procedures can differentiate between polymer-polymer crosslinks and polymer-filler attachments, it seems from our results that the fraction of polymer-filler attachments in the total network crosslinks is growing during oven curing of the fume silica-filled silicone rubber vulcanizates. In other words, the increase in the total network chains due to the oven cure results not only from the growing number of polymer-polymer crosslinks but also from the formation of polymer-filler attachments. The authors feel that these attachments are resulting from SiOH -induced hydrogen bonding between silica surface and polysiloxane molecules. The formation of the polymer-filler bonds in the fume silica-filled silicone rubber compounds is accelerated by heating with an activation energy of 42 kJ/mol.^{2,5}

Rubber-Filler Adherence

The other remarkable point is that the $v_r^{\text{NH}_3}$ values of filled vulcanizates are lower than in the unfilled control. That fact points to the dewetting of the silica filler by the NH_3 -modified environments.

To test the filler-elastomer adherence, we have used the Kraus theory¹⁰ for the swelling of filled elastomers in solvents. The theory is based on the assumption that the swelling is zero at the filler surface and increases progressively at increasing distance from the interface until its normal value is reached. When the relationship between v_{r0}/v_r and $\phi/(1 - \phi)$, in which v_r is the volume fraction

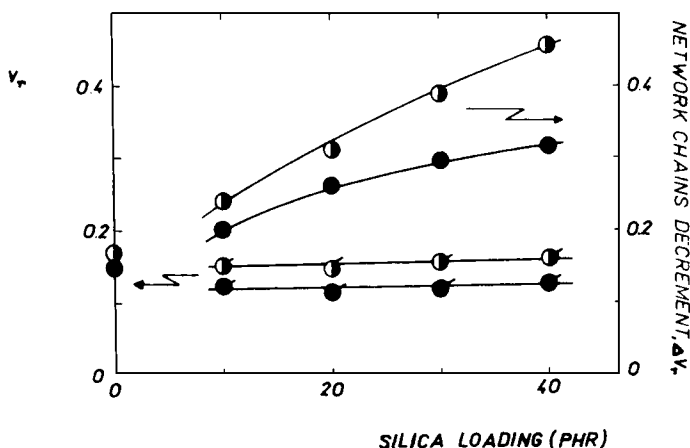


Fig. 7. Network chain decrement due to NH_3 -modified swelling (●) and $v_r^{\text{NH}_3}$ (○) as function of silica loading in short-cured (●) and oven-cured (○) silicone rubber vulcanizates filled with Aerosil 130.

of rubber in the gel of the swollen filled vulcanizate, v_{r0} is the volume fraction of the swollen unfilled control, and ϕ is the volume fraction of the filler in the vulcanizate before swelling, is plotted, the lines either with a negative slope for filler-polymer adherence or with a positive slope for nonadherence, both starting from $v_{r0}/v_r = 1$ at $\phi/(1 - \phi) = 0$, are results of the Kraus theory.

The evaluation of the adherence between fume silica and silicone rubber in toluene and in toluene over ammonia is given in Figure 8. The data of Figure 8 indicate a strong adherence between silica and silicone rubber matrix in toluene swelling. The NH_3 -modified environment leads to dewetting and vacuole formation. The strong nonadherence at lower filler concentration changes to the weak adherence at higher concentrations.

This shows that for the NH_3 -modified swelling there are two opposing factors. At low loadings, the dominant factor is nonadhesion, but at higher loadings the filler network is assumed to form through filler-filler interaction thus imposing a potent swelling restriction.

The oven-cured vulcanizates show a much better filler-elastomer adherence than the short-cured samples under both swelling conditions. The increase of the adherence corresponds to the increased number of polymer-filler attachments as indicated by results in Figure 7.

Influence of Total Contact Area

The swelling data of vulcanizates compounded with different silicas for the equal polymer-filler contact area in 1 g rubber are presented in Table II. The interface contact area is calculated by multiplying the specific surface area of the filler by its content in 1 g elastomer.

The results show that the relative decrease in v_r due to the NH_3 -modified swelling does not depend on the particle size of the filler but is only a function of the total contact area between the silica surface and the rubber matrix. This

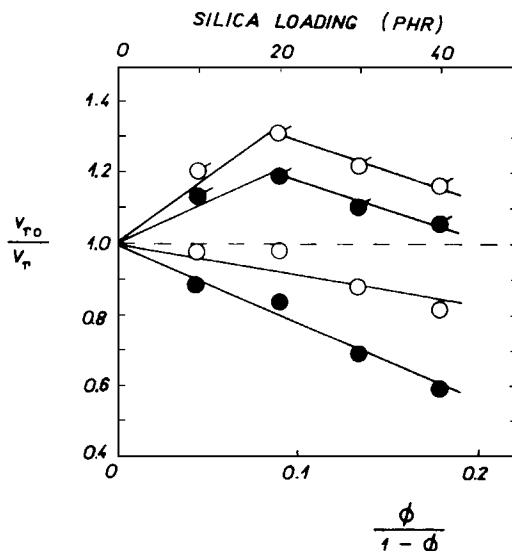


Fig. 8. Swelling in toluene under conventional (O) and NH_3 -modified (O) conditions for short-cured (O) and oven-cured (\bullet) silicone rubber vulcanizates filled with Aerosil 130.

TABLE II
Swelling of Fume Silica-Filled Vulcanizates (Oven Cured) with Constant Polymer-Filler Contact Area ($52 \text{ m}^2/\text{g}$)

Filler	Loading, phr	ν_r^{tol}	$\nu_r^{\text{NH}_3}$	$\Delta\nu_r$
Aerosil 130	40	0.296	0.162	0.453
Aerosil 200	26	0.254	0.141	0.445
Aerosil 300	17	0.238	0.130	0.454

is valid for silicas with equal silanol coverage such as fume silicas presented in Table II. The effect of surface treatment of the silica will be described later in this paper.

The particle size of the filler influences the swelling behavior in both swelling environments used, so that ν_r^{tol} and $\nu_r^{\text{NH}_3}$ values decrease with increasing surface area at the constant contact area in the system. The low loading of silica with higher surface area results in higher toluene swelling in both environments than does the higher loading of the lower surface area filler.

This may be attributed to the smaller contact area with fillers with high BET surface area. The BET area which is taken to adjust loadings to constant contact area is accessible to the small N_2 molecules but not completely to the polymer macromolecules. The difference between the BET area and the effective area in contact with polymer matrix is increasing with increasing specific surface area of the filler.

Nevertheless, the fraction of polymer-filler bonds, as reflected by the network chain decrement $\Delta\nu_r$, remains unaffected by changing loading and particle size of the silica.

The dependence of the network chain decrement $\Delta\nu_r$ on the polymer-filler contact area in samples loaded with various unmodified silicas is plotted in Figure

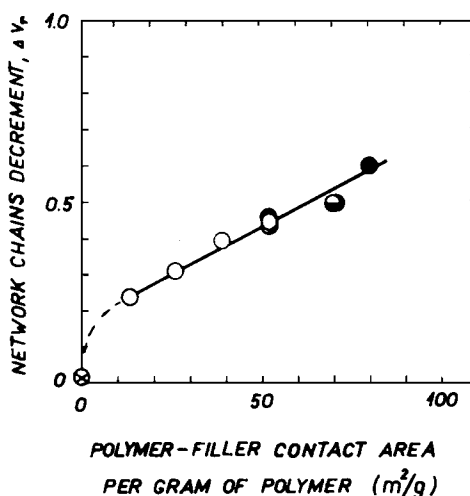


Fig. 9. Network chain decrement due to NH_3 -modified swelling as function of polymer-filler contact area in silicone rubber vulcanizates filled with Aerosil 130 (○), Aerosil 200 (●), Aerosil 300 (○), HDK N 20 S (●), and HDK H 20-3 (●).

9. We can conclude that the fraction of polymer–filler bonds in silica-loaded silicone rubber vulcanizates is determined by the polymer–filler contact area at equal surface silanol coverage.

Influence of Bound Rubber Content

The same relation is valid in the unvulcanized silicone rubber compounds.⁵ Therefore, we tried to find whether some relation between the bound rubber content and the fraction of polymer–filler attachments in the vulcanizate exists. Measurements were made with the silicone rubber compound containing 40 phr Aerosil 130 with changing bound rubber content due to prolonged “shelf aging” at room temperature after mixing. The bound rubber content was determined in toluene during storage of the compound after mixing. At the time of bound rubber determination, the vulcanizates were cured without remilling the compound, thus providing a series of vulcanizates prepared from one compound with increasing bound rubber content. Only the compound “shelf aged” for 1000 hr was remilled before curing. Swelling behavior of the vulcanizates is summarized in Table III, along with the bound rubber data of the compound.

The results show that swelling of vulcanizates does not depend on the bound rubber content due to polymer–filler interaction in the unvulcanized compound. Crosslink density both in toluene and in toluene over ammonia remains unchanged as the “shelf aging” of the compound proceeds. The remilling of the compound results in decreased values of both v_r^{tol} and $v_r^{\text{NH}_3}$ while the fraction of polymer–filler bonds remains unaffected.

Influence of Trimethylsiloxy Surface Treatment of Silica

Swelling data obtained with silicone rubber vulcanizates loaded with the trimethylsiloxy surface-treated silicas having the same surface area and different silanol coverage are presented in Table IV. The data in Table IV were used for estimating the influence of silica surface modification on swelling behavior of the filled silicone vulcanizates in the conventional and NH_3 -modified swelling environments.

It is evident that a reduction in the crosslink density occurs in both swelling environments with increasing degree of surface treatment. There is a continuous increase in crosslink density with an increase in silanol group concentration. The

TABLE III
Swelling of Vulcanizates (Oven-Cured) Prepared from the Compound Containing 40 phr of Aerosil 130 after Various Time of “Shelf Aging”

Shelf aging, hr	B, ^a %	v_r^{tol}	$v_r^{\text{NH}_3}$	Δv_r
2 ^b	27.1	0.329	0.179	0.456
24 ^b	47.3	0.332	0.177	0.467
48 ^b	56.2	0.331	0.180	0.456
216 ^b	76.4	0.327	0.181	0.446
1000 ^b	80.5	0.331	0.182	0.450
1000 ^c	65.9	0.277	0.149	0.462

^a Bound rubber content determined in the compound before curing.

^b Vulcanizates prepared without remilling the compound.

^c Vulcanizates prepared with remilling the compound before curing.

TABLE IV
Swelling of Vulcanizates Filled with 40 phr Silicas with Different Level of Trimethylsiloxy Treatment (Oven Cured Vulcanizates)

Filler	Silanol coverage, SiOH/nm ²	ν_r^{tol}	$\nu_r^{\text{NH}_3}$	$\Delta\nu_r$
HDK N 20 S	1.8	0.376	0.193	0.487
HDK H 20-1	1.03	0.352	0.179	0.492
HDK H 20-2	0.66	0.322	0.164	0.491
HDK H 20-3	0.47	0.312	0.159	0.490

relative difference in swelling between the conventional and NH₃-modified swelling environments expressed as the network chain decrement $\Delta\nu_r$ shows no change, while the silanol coverage of silica is changed by trimethylsiloxy treatment.

Thus, the situation in the vulcanizate seems to be quite different from that found in the unvulcanized compounds. A number of polymer–filler attachments in the compound, as estimated by NH₃-modified swelling in toluene, depends on the silica silanol concentration in the system. In the vulcanizate, on the other hand, it seems to depend only on the polymer–filler contact area, thus not being dependent on the silanol coverage of silica. We have recently obtained similar results in silicone rubber vulcanizates loaded with fume silica modified by the addition of alkoxy silanes into the compound during mixing.¹¹

The cleavage of trimethylsiloxy surface groups on the silica was reported in silicone rubber vulcanizates.⁸ In this study, the increase of bound rubber content in compounds loaded with trimethylsiloxy surface-treated fume silica has been explained through the NH₃-induced cleavage followed by the additional covalent bonding of silicone rubber onto the silica surface. Our present results given in Table IV do not lend support to the concept of the trimethylsiloxy group cleavage in filled silicone rubber vulcanizates containing surface-treated silica.

Reversibility of Polymer–Filler Bonding

The data in Table V provide insight into what happens after exposure of fume silica-filled silicone rubber vulcanizates to the NH₃-modified swelling environment followed by drying. The decreased value of ν_r obtained by swelling the vulcanizate in the NH₃-modified swelling environment increases after drying the sample and swelling it conventionally in toluene up to nearly the same value of ν_r that is obtained by normal swelling procedure in an original sample. The

TABLE V
Values of ν_r Measured by Successive Swelling of Fume Silica-Filled Vulcanizates with Different Level of Trimethylsiloxy Treatment (Oven-Cured Vulcanizates)

Swelling procedure ^a	HDK N 20 S	HDK H 20-3
Toluene	0.376	0.312
Toluene + toluene	0.369	0.304
NH ₃	0.193	0.159
NH ₃ + toluene	0.344	0.301
NH ₃ + toluene + NH ₃	0.216	0.165

^a Each swelling step was followed by drying for 72 hr, toluene = swelling in toluene under conventional conditions for 72 hr; NH₃ = swelling in toluene over NH₄OH for 72 hr.

next swelling step in the modified environment provides a ν_r value quite the same as in the first NH_3 -modified swelling of the sample. The process of NH_3 -induced cleavage of polymer–filler bonds seems to be rather reversible on drying.

The authors feel that the NH_3 -modified swelling environment can selectively cleave fume silica–silicone rubber attachments in vulcanizates, which are present there because of hydrogen bonding between silica silanols and polysiloxane polymer chains. The polymer–filler bonds interrupted by the modified swelling can nearly completely recover during drying and be cleaved again by the subsequent swelling in the modified environment.

The additional swelling in toluene of toluene-swollen and dried samples has practically no effect on the value of ν_r . The surface treatment of silica by trimethylsiloxy groups does not influence the reversibility of polymer–filler bonding in silicone rubber vulcanizates on swelling in NH_3 -modified environment.

CONCLUSIONS

The results of the present study lend support to the concept of hydrogen bonding between fume silica and silicone rubber matrix not only in unvulcanized compounds but also in vulcanizates. Polymer–filler attachments in the fume silica-filled vulcanizates markedly contribute to the total swelling restriction due to crosslinking in the vulcanizate. The NH_3 -modified swelling procedure provides a possibility of estimating the fraction of total swelling restricting attachments resulting from polymer–filler interaction.

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