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Bound Rubber and "Crepe Hardening" in Silicone Rubber

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Synopsis

Some recent results of the research aimed to correlate properties of filled silicone rubber compounds with surface properties of fumed silica fillers are reported. It is shown that the specific interaction between silica surface silanol groups and the siloxane chain of silicone rubber plays the main role in "crepe hardening" and bound rubber formation in compounds. The silanol coverage of silica determines the tightness of polymer–filler network in bound rubber. The experimental data fit Meissner's theory of bound rubber quite well. Remilling of "crepe hardened" compounds was also studied, and the structure of the remilled compounds is proposed. The activation energy of bound rubber formation on mixing was found to be 16.8 kJ/mole; this suggests that physical rather than chemical processes are involved in the interaction between silica and silicone rubber.

INTRODUCTION

The reinforcement of rubbers by fillers depends on several factors: particle size, structure, and filler loading, all determining the polymer–filler contact area available for mutual interaction. The degree of surface interaction activity is the last, but not the least, factor influencing the reinforcement of rubbers. This factor is determined by the physical and chemical nature of both filler surface and elastomer matrix.

This paper is concerned with the problem of determining a correlation between properties of fumed silica fillers and their interaction with silicone rubber. Silicone rubber possesses very poor mechanical properties when unfilled. It must be reinforced by active silica filler for technical application.

"CREPE HARDENING" AND BOUND RUBBER IN SILICONE RUBBER COMPOUNDS

The best reinforcing action of fumed silica in silicone rubber is accompanied by technologically undesirable hardening of uncured compounds on storage. The time-dependent "crepe hardening" accompanied by extensive bound rubber formation is one of the characteristics of the fumed silica–silicone rubber system.

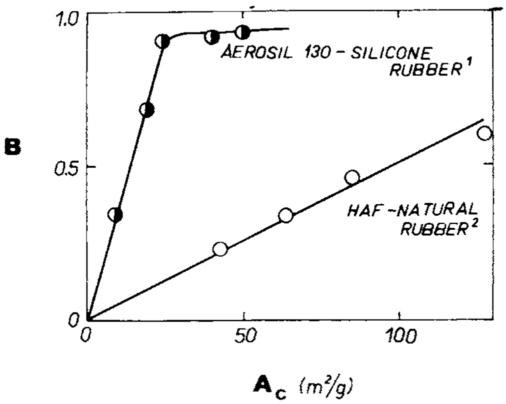

Fig. 1. Bound rubber content B as a function of polymer–filler contact area A_c after prolonged storing (approx. 2000 hr) at 25°C.

The "crepe hardened" compounds crumble when put on a roll mill and become again processable only on prolonged milling.

Figure 1 shows the bound rubber content formed in fumed silica-filled silicone rubber after prolonged storage[1] at 25°C and in natural rubber filled with carbon black[2] as a function of the polymer–filler contact area. The results (Fig. 1) demonstrate that the surface interaction activity of fumed silica is much greater than the activity of carbon black in hydrocarbon rubber. This indicates a much more extensive bonding between silica and silicone rubber.

The enormous surface interaction activity of fumed silica in silicone rubber seems to be responsible for "crepe hardening." The surface activity of silica is determined by its surface chemistry,[3–5] which seems to be a very complex subject.[6–8] However, the main feature of the silica surface is that a great number of strongly protonized[9] silanol (hydroxyl) groups are present, which should be capable of specific interaction with siloxanes.[10,11,12]

Typical groups which can occur on the fumed silica surface[13] are sketched in Figure 2. The presence of silanol groups on the silica surface make the attachment of various other groups possible, and the surface activity of silica can be modified in this way.[13,14]

Our previous work[4,5] on silicone rubber–silica system showed "crepe hardening" as a time- and temperature-dependent process closely connected with bound rubber formation. We have also studied the influence of storing temperature (up to 135°C) on silica surface activity in silicone rubber and evaluated the activation energy of "crepe hardening" and bound rubber formation on storage as being approximately 42 kJ/mole (10 kcal/mole).

EXPERIMENTAL

Compounds were prepared from methylvinylsiloxane rubber Lukopren G 1000, made by VCHZ Synthesia, Kolin, Czechoslovakia, of viscosity-average molecular weight 500,000.

Various silicas differing from each other by their surface nature (Table I), were incorporated in silicone rubber on a laboratory two-roll mill in about 30 min. Properties of these compounds were studied on storage after mixing at various storing temperatures.

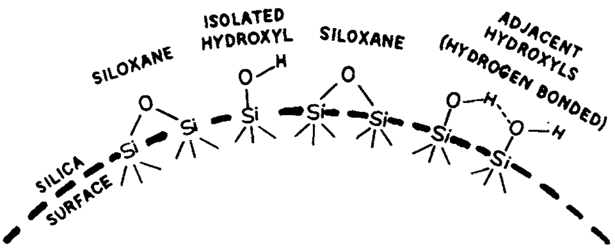

Fig. 2. Chemical groups on the surface of fumed silica.[13]

The plasticity of compounds was measured by the penetrometric method,[15] based on the principle of forcing the conical indentor (weight 135 g, apex angle 30°) into a sheet of the material to be examined for a fixed time of 5 sec. The plasticity values are expressed as a penetration degree (°P), i.e., the indentor penetration of 0.1 mm into the sheet examined at 25°C. Samples stored at higher temperatures were left to cool to room temperature before determining their plasticity.

Bound rubber content and its equilibrium swelling in benzene were determined on samples stored at different temperatures for various periods. Samples of compounds approximately 0.2 g in weight were immersed in benzene (approx. 50 ml) for at least six days with a twice-a-day exchange of fresh solvent. Swollen samples of extracted compounds were weighed, dried first at room temperature and then overnight at 80°C, and weighed again. The bound rubber content *B* is expressed as the percentage of the original silicone rubber found to be insoluble in benzene.

TABLE I
Typical Properties of Silica Filler Used

Filler	Manufacturer	Surface area, m^2/g	Surface treated with	Surface silanol coverage, SiOH/nm^2
Aerosil 130	Degussa	80	untreated	3[a]
Aerosil R 972	Degussa	130	dimethyldichlorosilane	0.75[a]
Aerosil 200	Degussa	200	untreated	3[a]
HDK N 20 S	Wacker-Chemie	200	untreated	1.3[b]
HDK H 20/1	Wacker-Chemie	174	trimethylchlorosilane	0.92[b]
HDK H 20/2	Wacker-Chemie	174	trimethylchlorosilane	0.41[b]
HDK H 20/3	Wacker-Chemie	174	trimethylchlorosilane	0.59[b]

[a] From reference 18.

[b] Calculated from the titration data of Dr. Stohr, Experimental products provided by Dr. Stohr of Wacker-Chemie, Zweigbetrieb Kempten.

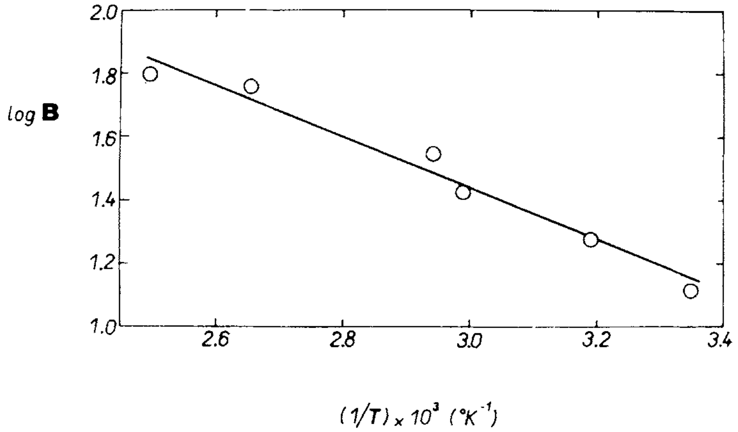

Fig. 3. Logarithm of bound rubber content B as a function of reciprocal absolute temperature of mixing 40 phr of fumed silica into silicone rubber in Plastograph Brabender.

The "crepe hardened" compounds were remilled on a laboratory two-roll mill for the time necessary to obtain processable and homogeneous compounds. The remilled compounds were shelf aged again, and their properties were studied during storage at 25°C.

The Brabender Plastograph was used for mixing compounds at different temperatures. The filler was incorporated into preheated polymer within 10 min, and the mixture was then mixed for an additional 10 min at a given temperature. After mixing in the heated Plastograph chamber, the compound was homogenized on a two-roll mill at room temperature for the next 5 min. The samples for bound rubber determination were then cut off and immersed in benzene for six days with a twice-a-day exchange of solvent.

RESULTS AND DISCUSSION

Activation Energy of "Crepe Hardening" and Bound Rubber Formation

Southwart[16,17] derived from bound rubber data in fumed silica filled silicone rubber an activation energy of approximately 84 kJ/mole (20 kcal/mole) immediately after mixing but of only 42 kJ/mole (10 kcal/mole) in samples after prolonged storage. Therefore, he proposed chemical polymer–filler interaction during the mixing stage and immediately after mixing; prolonged storage might be controlled by diffusion.

To verify this suggestion, we studied bound rubber formation during mixing at different temperatures in silicone rubber containing 40 phr fumed silica having a surface area of 200 m^2/g (Aerosil 200) in a heated chamber of the Brabender Plastograph.

Results of the bound rubber measurements in compounds mixed at a temperature range of 25°–130°C are given in Figure 3, where the logarithm of bound rubber content is plotted against the reciprocal absolute temperature of mixing. The activation energy of bound rubber formation on mixing was calculated from

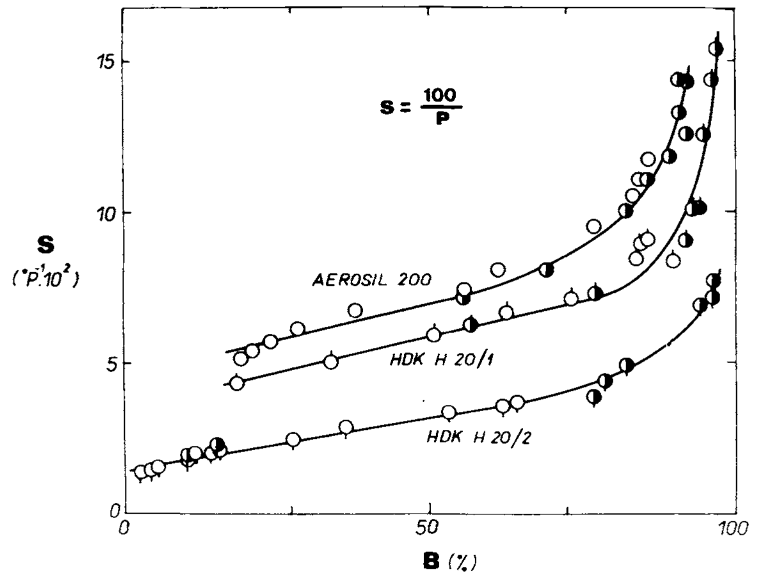

Fig. 4. Stiffness S as a function of bound rubber content B in silicone rubber containing 40 phr of 200 m^2/g type fumed silicas differing in surface treatment. Compounds stored at 25°C (○) and 135°C (◑) after mixing.

the slope as being 16.8 kJ/mole (4 kcal/mole). This value suggests physical rather than chemical interaction and probably hydrogen bonding between surface silanol groups of silica and polysiloxane chains, as proposed by Chahal,[14] Nelson and Ionina,[12] Boonstra et al.,[13] and the authors of this paper.[1,4,5]

The higher value of activation energy of bound rubber formation and "crepe hardening" in silicone rubber filled with fumed silica at longer storing time[1,4,5,16,17] might be taken as evidence for polymer–filler interaction controlled by diffusion except at very short storage time, as proposed by Southwart.[16,17]

But generally, the silica–silicone rubber interaction in unvulcanized compounds appears to be of a physical nature.

Effect of Silica Silanol Coverage on "Crepe Hardening" and Bound Rubber Formation

To investigate the effect of silica silanol inactivation on the behavior of the silica in silicone rubber, compounds filled with silicas differing by degree in their surface modification (Table I) were studied on storage after mixing.

Figure 4 shows stiffness S as a function of bound rubber content B in compounds containing 40 phr of fillers having a comparable surface area of approximately 200 m^2/g. The stiffness S is defined as a reciprocal plasticity P measured penetrometrically. The stiffness should be proportional to the modulus. It is shown in Figure 4 that compound stiffness increases with bound rubber content during storage. The polymer–filler crosslinks are formed in compounds on storage, and the number of the polymer–filler crosslinks increases with increasing bound rubber content forming a pseudovulcanized structure, which is indicated by an increase in stiffness.

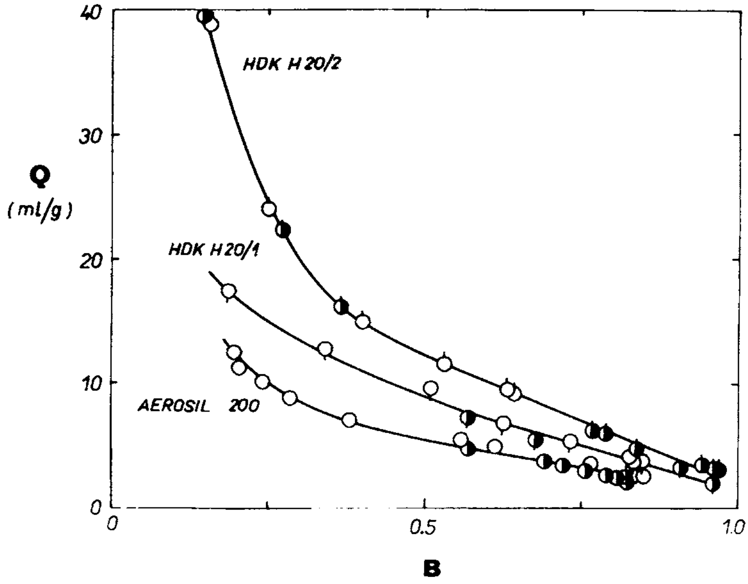

Fig. 5. Bound rubber swell Q as a function of bound rubber content B in silicone rubber containing 40 phr of 200 m^2/g type fumed silicas differing in surface treatment. Compounds stored at 25°C (○) and 135°C (◑) after mixing.

After prolonged storing when the filler surface is practically saturated by the polymer, the content of the insoluble bound rubber can change only slightly. The unreacted free silanol groups might react with polymer chains already bound to the filler surface and cause, in this way, additional crosslinking of bound rubber and tightening of the formed rubber gel. This is manifested by the great increase in hardening at a relatively small change in bound rubber content.

Figure 5 shows the equilibrium swell Q of bound rubber in benzene as a function of bound rubber content B in the same compounds as in Figure 4. These results obtained at a practically constant polymer–filler contact area in compounds suggest a different topological nature of bound rubber gel depending on the surface nature of silica filler. It is clear that the untreated silica surface with high silanol concentration (Aerosil 200) results in a more tightly held network capable of less swelling as compared to the treated silica surface. The lower the silanol concentration, the looser the polymer–filler network is, contributing less to the compound stiffness.

The compound stiffness is plotted in Figure 6 as a function of volume fraction of rubber in the equilibrium swollen bound rubber v_r. There is a linear dependence of compound stiffness on the bound rubber swelling. Therefore, one can see that the compound stiffness is proportional to the crosslink density of bound rubber formed through polymer–filler interaction in the silicone rubber compound on mixing and storing. It seems that the storing temperature has no substantial influence on the bound rubber nature and its contribution to compound stiffness. The results suggest that "crosslink density" of bound rubber is determined by the concentration of free silanols at a constant polymer–filler contact area available.

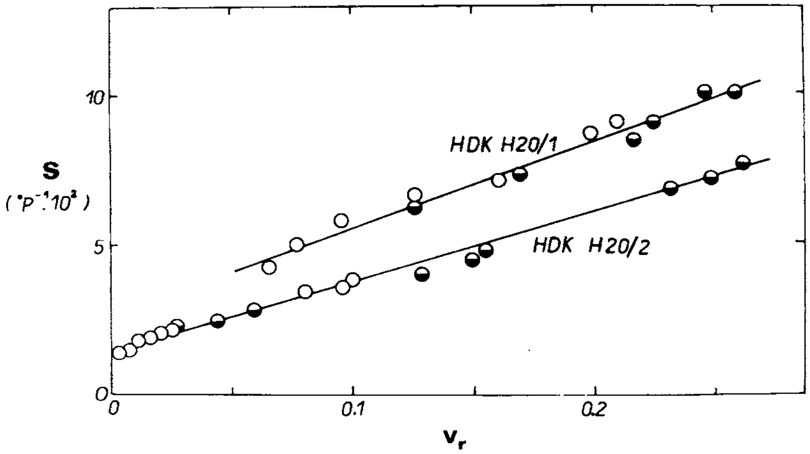

Fig. 6. Stiffness S of silicone rubber compounds containing 40 phr of 200 m^2/g type fumed silicas differing by the level of surface treatment as a function of v_r. Compounds stored at 25°C (○) and 135°C (◒) after mixing.

Correlation with Meissner's Theory of Bound Rubber

Meissner's theory of bound rubber[2] treats the effect as random adsorption of structural units of polymer on reactive sites which are assumed to exist on the surface of filler particles. For the simplest system of filled monodisperse polymer, this theory predicts the linear dependence of "adsorption index" γ on logarithm U (free "unbound" rubber, $U = 1 - B$).

The "adsorption index" γ can be taken as a "crosslinking index" proportional to the crosslink density and also to the modulus G. When one takes the stiffness S as a measure of the modulus, nearly linear dependence of the stiffness on log U can be expected. Our experimental data plotted in Figure 7 fit quite well the predicted linear dependence up to high bound rubber content in compounds containing fillers with different silanol group content. The slope of the experimental dependences of S on $-\log U$ is proportional to the silanol coverage of silica fillers. This indicates again a near correlation between the silica silanol coverage and the "structuring" or "crosslinking" action of the silica in silicone rubber.

Effect of Silanol Coverage and Storage Temperature on Silica Surface Activity

This is also clearly demonstrated by results in Figure 8, where bound rubber content B, stiffness S, and swell Q are plotted as a function of free silanol group concentration in compounds containing 40 phr of fumed silica fillers after one week of storing at 25°C. The surface treatment of silica (see Table I) results in a lower interaction level between elastomer and silica surface.

The remarkable part of the experimental data is the effect of storing temperature on the surface activity measured by bound rubber. In Figure 9, the specific bound rubber content b (steady-state bound rubber content in grams per 100 m^2 of the polymer–filler contact area), defined in our previous work[4,5]

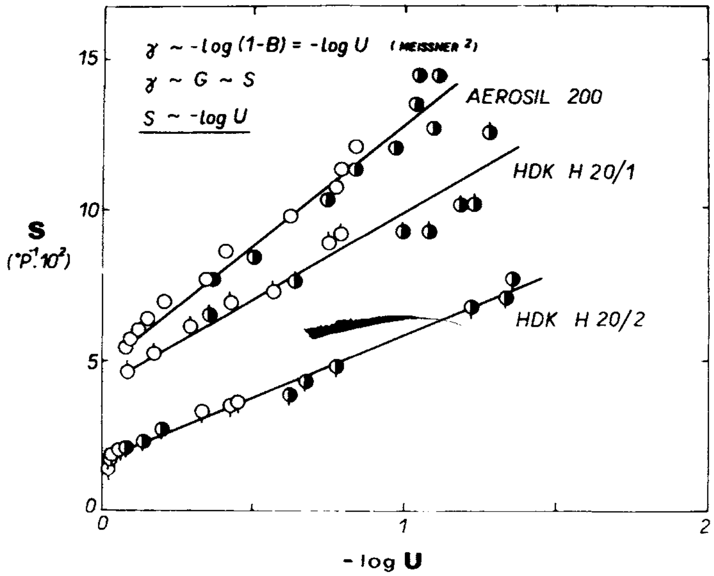

Fig. 7. Stiffness S of compounds containing 40 phr of 200 m^2/g type fumed silicas differing in surface treatment as a function of −log U (unbound rubber). Compounds stored at 25°C (○) and 135°C (◑) after mixing.

as a measure of the filler surface activity, is plotted as a function of silanol coverage in compounds having a polymer–filler contact area of approximately 80 m^2/g. The bound rubber values were measured after 2800 hr of storing at 25°C (lower curve) and 135°C (upper curve).

The silica surface activity is not influenced by the silanol coverage at 135°C, where all the samples show their maximum surface interaction activity. On the other hand, the surface activity of treated silicas at 25°C decreases with decreasing surface silanol concentration. The elevated storing temperature renders the treated silica surface as active as the untreated one, probably because of unreacted free silanol groups remaining on the silica surface after its modification.

The free silanol groups are sterically hindered at a lower temperature, thus not contributing to the interaction with silicone rubber. However, the sterically hindered silanol groups seem to contribute to hydrogen bonding with siloxane groups of polymer at higher temperatures, when the possibility of removing the treating groups by thermal scission is excluded due to the constant activation energy of the bound rubber formation.[1]

The surface interaction activity of untreated silica reaches its maximum value at a storage temperature of 25°C. At higher storage temperatures, this value remains unaffected. This has been ascribed to the increased probability of approaching polymer chains and surface silanol groups necessary for the hydrogen bond formation. Increased mobility and straightening of polysiloxane chains occur at higher temperatures.[1,4,5] The diffusion rate is also higher at higher temperatures. This effect is more pronounced in compounds with small total silanol concentration.

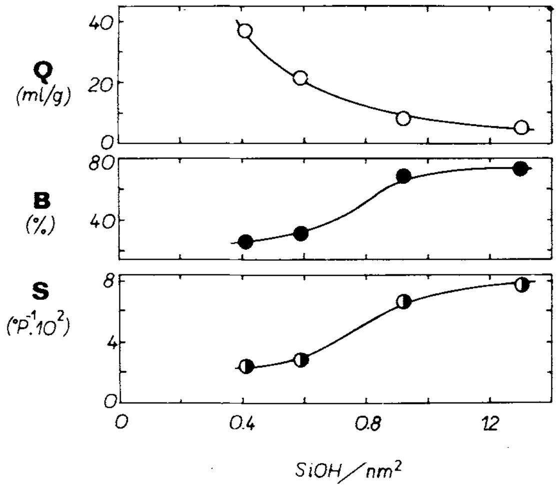

Fig. 8. Stiffness S, bound rubber content B, and its swell Q as a function of silanol coverage in silicone rubber containing 40 phr of 200 m^2/g type fumed silica differing in surface treatment level. Compounds stored one week at 25°C.

Effect of Remilling "Crepe Hardened" Compounds

Very few results have been published on the effect of remilling of "crepe hardened" silicone rubber compounds filled with fumed silica.

Table II lists properties obtained in compounds containing 40 phr of treated and untreated fumed silicas, respectively, after prolonged shelf aging (approx. 1000 hr) at 25° and 135°C followed by remilling the "crepe hardened" compounds on a two-roll mill. The favorable effect of surface modification at 25°C, which vanishes at higher storage temperatures, is again clearly evident. The remilling time of a compound containing treated silica stored at 25°C is reduced to about one half the value for the untreated filler. The heated compounds of silicone rubber with treated silica filler behave in the same way as compounds filled with the untreated material.

The remilling of "crepe hardened" compounds results in a rather dramatic increase in compound plasticity accompanied by a relatively small decrease in bound rubber content (Fig. 10). In Figure 10 are plotted results obtained in compounds with 40 phr of Aerosil 130 and Aerosil R 972 (Table I) during prolonged storing (approx. 1000 hr) at various temperatures after mixing. These results are compared with the data obtained during prolonged storage of remilled compounds at 25°C (the field of points between dotted curves).

The bound rubber gel is much looser in remilled compounds than in compounds after mixing as shown in Figure 11, where the swell Q is plotted as a function of bound rubber content for compounds stored after mixing and remilling, respectively. A crosslinked structure of a continuous polymer–filler network can be assumed in compounds stored after mixing, their structure and tightness depending on the surface silanol concentration. The remilling of "crepe hardened" compounds rearranges the structure of bound rubber gel so that there is no remarkable difference in the character of the gel due to variations in silica surface which has been found in compounds after mixing.

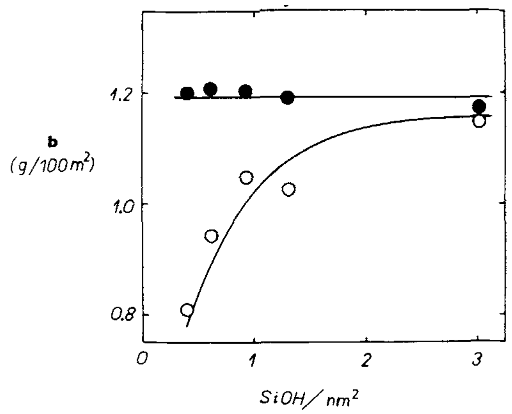

Fig. 9. Specific bound rubber content *b* as a function of silanol coverage of fumed silica and a storing temperature in compounds with polymer–filler contact area of 80 m^2/g polymer, stored for 2800 hr at 25°C (○) (blank points) and (●) 135°C (full points).

The possibility of mechanical destruction of polysiloxane on remilling was verified by the prolonged remilling of the unfilled silicone rubber vulcanizate containing 89% of gel. This vulcanizate was prepared by adding 0.05 phr of 50% paste of dicumyl peroxide in silicone oil (Perkadox PDS-50) to silicone rubber and vulcanizing the mixture at 125°C for 15 min under pressure. The gel content was reduced by milling for 1 hr to 78%, which is nearly the same reduction as occurred in "crepe hardened" filled compounds on remilling (Table II). The behavior on the mill of both systems is very similar, and the gel is macroscopically incoherent, contrary to the coherent gel in compounds and the unfilled vulcanizate before milling.

The authors ascertained from the results that the remilling of "crepe hardened" compounds results in mechanical destruction of polymer–filler bridging. The partially destroyed polymer–filler network, due to polysiloxane mechanical scission, is regenerated on additional storage.

TABLE II

Properties of Compounds Containing 40 phr of Aerosil Fillers After Prolonged Storing Approx. (1000 hr) at Various Temperatures and After Remilling[a]

Filler	Storing temperature, °C	Bound rubber, %	Stiffness, 100/°P	Swelling in benzene, ml/g	Time of remilling, min
Aerosil 130	25	93 (79)	8.3 (2.5)	3.0 (7.6)	50
(untreated)	80	94 (82)	8.3 (2.2)	2.8 (9.5)	60
	135	93 (79)	8.3 (2.2)	2.6 (9.7)	50
Aerosil R 972	25	87 (77)	5.9 (2.1)	4.5 (10.8)	25
(dimethyldi-	80	96 (85)	7.7 (2.0)	2.9 (9.9)	60
chlorosilane treated)	135	97 (79)	9.1 (2.2)	2.6 (9.3)	70
Unfilled vulcanizate[b]	—	89 (78)	—	—	60

[a] The data in brackets are obtained in remilled compounds.

[b] Conditions of vulcanization: 0.05 phr Perkadox PDS 50, 125°C/15 min, under pressure.

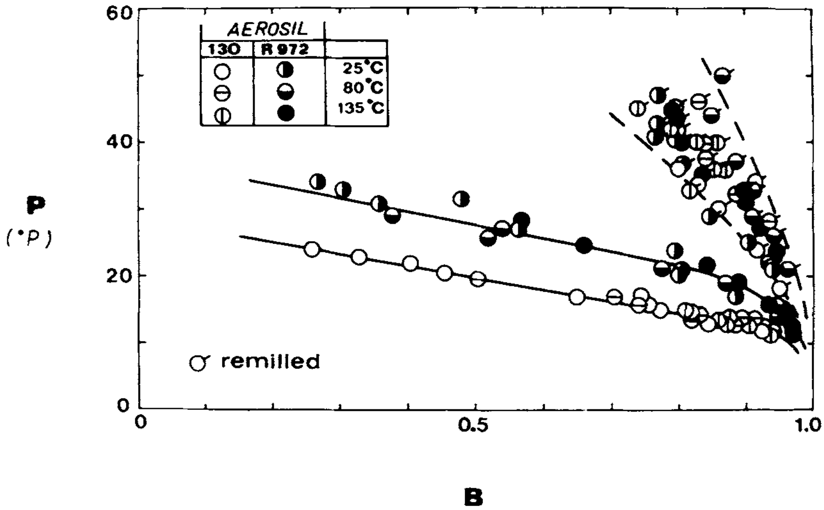

Fig. 10. Penetrometrical plasticity P as a function of bound rubber content B in silicone rubber containing 40 phr of Aerosil 130 (untreated) and Aerosil R 972 (treated) silicas. Compounds stored at various temperatures after mixing, then remilled and stored again at 25°C.

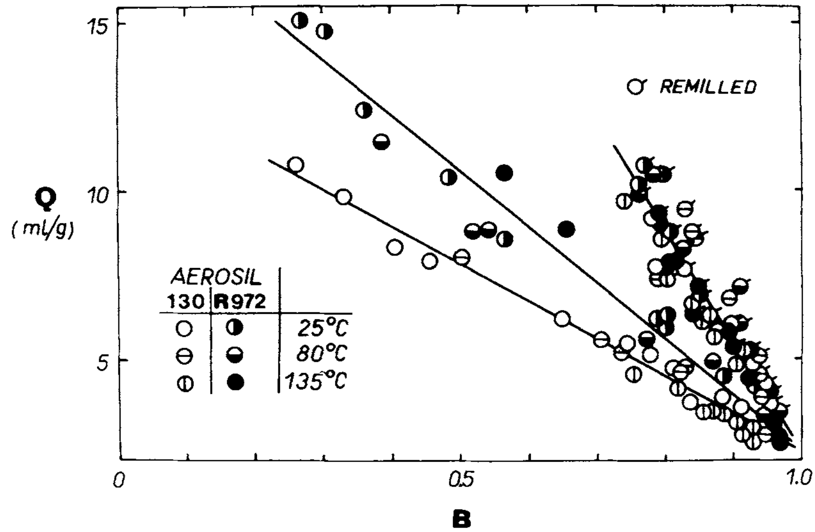

Fig. 11. Bound rubber swell Q as a function of bound rubber content B in silicone rubber containing 40 phr of Aerosil 130 (untreated) and Aerosil R 972 (treated) silicas. Compounds stored at various temperatures after mixing, then remilled and stored again at 25°C.

The structure of remilled compounds seems to consist of incompletely remilled regions, freely connected by polymer chains, the number of which has been decreased by mechanical destruction. These regions cause a relatively high bound rubber content in the remilled compounds, whereas the much reduced stiffness and increased swelling are due to the decreased number of polymer chains connecting the gel regions with each other throughout the compound.

CONCLUSIONS

The interaction between fumed silica, of various surface silanol concentration, and silicone rubber has been investigated. The results indicate that the interaction is much more extensive in comparison with carbon black–organic rubber systems. The specific interaction between silica surface silanol groups and the siloxane chain by hydrogen bonding plays the main role in "crepe hardening" and bound rubber formation in fumed silica filled silicone rubber. The surface treatment decreasing the free silanol coverage results in a more loosely held polymer–filler network, capable of more swelling as compared to the untreated silica.

The experimantal data fit Meissner's theory of bound rubber quite well, suggesting that the filler particles function as polyfunctional crosslinks. The chemical interaction between silica filler and silicone rubber seems to be excluded in "crepe hardening" and bound rubber formation due to the negligible value of the activation energy found on mixing.

The remilling of "crepe hardened" compounds with very high bound rubber content results in a great increase in the compound plasticity and swelling, accompanied by a relatively small change in bound rubber content. This effect is interpreted through the existence of incompletely remilled regions, freely connected by a decreased number of polymer bridgings, due to the mechanical destruction of polysiloxane on remilling. There is no important difference in behavior of remilled compounds during additional storage. The topology of the remilled silica-filled silicone compounds seems not to depend on the surface properties of the silica filler.

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