Reinforcement of Siloxane Elastomers by Silicas. Comparison between Fumed and Precipitated Silicas in their Interactions with an Oligomer of Poly(dimethylsiloxane)

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Synopsis

Comparison between fumed and precipitated silicas in their interactions with an oligomer of poly(dimethylsiloxane) showed both materials to exhibit general identical behavior depending on the experimental temperature range. However, the results obtained suggest on the one hand that these interactions are directed more by morphological and structural characteristics than by chemical properties and on the other hand that the distribution of surface silanol groups on precipitated silicas is not the same as on fumed silicas. Both siloxane-modified fillers exhibit high thermal stability.

INTRODUCTION

The study of the interactions between organosiloxanes and silicas was undertaken in order to improve our knowledge of the reinforcement of silicon rubbers by these fillers. Recently, we showed,[1-3] using IR spectroscopy, chromatography, and gravimetry techniques, that the interactions occurring between an oligomer of poly(dimethylsiloxane) (PDMS) and a fumed silica are dependent on the treatment temperature: between 25 and 140°C, the adsorption of octamethylcyclotetrasiloxane (D_4) onto Aerosil 300 (A300) is irreversible due to hydrogen bonding; at temperature close to 150°C, it becomes reversible; finally at temperatures higher than 150°C, chemical interactions take place. Reactional mechanisms were proposed for the grafting processes, and it was shown that the siloxane-modified silicas exhibit high thermal stability.

In this article we will compare, in their interactions with oligomers of PDMS, fumed silicas (previously modified or not by treatment with D_4) to precipitated adsorbents.

EXPERIMENTAL

Reactants

Five silicas were considered in this study: a fumed silica used as model: Aerosil 300 (A300, Degussa)[1,2]; two fumed silicas, A300, previously modified by treatment with D_4: T_1 and T_2; and two precipitated silicas, P_1 and P_2, whose characteristics are close to those of the fumed silicas. It must be pointed out that P_2 was obtained by sodic dissolution of a fumed silica (A200) and precipi-

tation of the ensuing sodium silicate. As a consequence, P_2, from the point of view of chemical purity, is a model precipitated silica. P_1 was obtained from sand and sodium carbonate as raw materials.

Table I lists the characteristics of the five silicas. Octamethylcyclotetrasiloxane used as model for siloxane rubbers was supplied by Rhône Poulenc Industries and used without further purification.

All chemicals used were reagent grade and were purified by standard procedures.

Gas-Phase Chromatography, IR Spectroscopy, and Gravimetry

All equipment, devices and experimental procedures used were described previously.[1,3]

Study of the adsorption of water by the different silicas was performed by gravimetry, according to the method devised by Dannenberg and Opie.[4] In this technique, the amount of water adsorbed under controlled atmosphere by a known quantity of silica previously degassed by heating at 130°C was followed until samples of constant weight were obtained. Saturated aqueous solutions of mineral salts were used for the obtention of the controlled atmospheres (Table II). Moreover, it was ascertained that the results were independent of the amount of adsorbent used.

RESULTS AND DISCUSSION

As shown previously,[1–3] the interactions which take place between PDMS oligomers (D_4) and A300 are dependent on the experimental temperature range. Particularly three temperature domains were defined: $T < 140°C$, $T \sim 150°C$, and $T > 150°C$. In this study, precipitated silicas will be compared to A300 and modified fumed silicas in these three temperature ranges. The characterization

TABLE I
Characteristics of the Silicas[a]

	A300	T_1	T_2	P_1	P_2
Surface N_2 (BET), m^2/g	310[b]	268	270	285	234
Surface CTAB, m^2/g	—			232	210
Water takeup, % w/w (RH: 64%, at 23°C)	5.5[b]	0.3		4.8	2.3
pH	3.6–4.3[b]			6.9	4.7
Na, ppm	0			980	105
Al_2O_3, ppm	<500[b]			2000	150
CaO, ppm				200	60
MgO, ppm					<15
D_4, % w/w	0	8.7	9.9	0	0

	A300		T_1	T_2	P_1		P_2	
	a	na	a	na	a	na	a	na
$OH_f/100\ \text{Å}^2$	1.7	1.25	0.5	0.05	1.3	1.7	1.5	1.6
$OH_{ass}/100\ \text{Å}^2$	1.6	1.1	1.55	0.25	1.6	0.8	1.2	0.6
$OH_{total}/100\ \text{Å}^2$	3.3	2.35	2.05	0.3	2.9	2.5	2.7	2.2

[a] a: Agglomerated; na: nonagglomerated.
[b] Degussa specification.

TABLE II
Partial Water Pressures

Solute	P/P_0
H_2SO_4 $d = 1.7$	0.032
H_2SO_4 $d = 1.6$	0.085
LiCl	0.15
$CaCl_2$	0.325
KNO_2	0.45
$Na_2Cr_2O_7$	0.52
NaBr	0.58
NH_4Cl	0.795
KBr	0.84
Na_2HPO_4	0.95

of the materials obtained after modification of the filler by grafting and their properties will be considered.

Comparison of Precipitated Silicas with Fumed Silicas in their Interactions with PDMS Oligomers at Temperatures Lower than 140°C

The adsorption of D_4 on precipitated or modified fumed silicas is irreversible at temperatures lower than 140°C, and the amount of adsorbed material is strongly dependent on temperature. There is indeed (Fig. 1) a continuous decrease in the amount of adsorbed D_4 when temperature is increased from 25 to 140°C. To interpret this behavior, D_4–silica interactions associated with different levels of energy are postulated. The existence of surface free OH groups (OH_f) with hindered accessibility would account for this behavior. Therefore, the ensuing hydrogen bonds would be of various strength, the stronger bonds breaking at higher temperatures.

Since up to 140°C precipitated silicas behave similarly to A300, P_1 and P_2, like A300, have on their surface enough free silanol groups to allow a monolayer of D_4 to be held through hydrogen bonding (1 molecule/100 Å²).

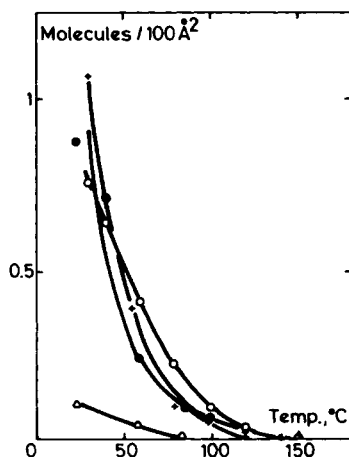Contrary to the other fillers, T_1 adsorbs only a small amount of D_4 (at 25°C,

Fig. 1. Amount of adsorbed D_4 vs. temperature: (O) A300; (●) P_1; (+) P_2; (△) T_1.

one tenth of that of A300). Such a behavior underlines the predominant role played by free silanol groups in this process. Indeed, T_1 which, as a consequence of its treatment, has fewer free OH groups available, will not allow the total coverage of its surface by a hydrogen-bonded monolayer of D_4. It is, however, worth noting that in this particular case, the adsorption process is reversible as soon as the temperature reaches 100°C, while A300, P_1, and P_2 exhibit a similar behavior only above 140°C.

Comparison of Precipitated Silicas with Fumed Silicas in their Interactions with PDMS Oligomers at Temperatures Close to 150°C

As seen before, above 140°C adsorption of D_4 onto silicas becomes reversible. Thus, adsorption isotherms can be plotted by means of gas-phase chromatography techniques. Since for each silica, isotherms are of the type II, which means strong adsorbate–adsorbent interactions, the BET equation can be appplied. Therefore, a_0 (amount of siloxane necessary to the completion of a monolayer on the surface of the filler) and as a consequence σ (surface area of the adsorbed D_4 molecule) could be calculated. Results obtained are presented in Table III together with the constant c, which determines the shape of the adsorption isotherms, and ΔE (average heat of adsorption for the completion of a monolayer). It appears that the σ values obtained for P_1 and P_2 are close to that obtained for A300 and are in agreement with values deduced from Fox et al.[5] and Hurd.[6] On the other hand, T_1 yields apparent σ values much higher than the other adsorbents. However, this modified silica exhibits isotherms close to type III, hence application of the BET equation is problematic. From Table III it appears that the adsorbents can be classified into three groups: fumed silica, which exhibits the highest c and ΔE values; precipitated silicas, with intermediate values; and treated A300, with low ΔE and c.

From two isotherms determined at close temperatures it is possible, using Clapeyron's equation, to calculate the isosteric heat of adsorption, ΔH_a. Figure 2 gives, for each sample, the variation of ΔH_a with covering ratio θ. The four curves have the same general trend. As shown for A300,[1-3] P_1 and P_2 have high ΔH_a at small covering ratios. When θ increases, ΔH_a decreases rapidly and is heading toward a first plateau for $0.6 < \theta < 2$. For $\theta > 2$, a new decrease is observed and the curves are heading toward a second plateau corresponding to $\Delta H_a \sim 12$ kcal/mole, close to the heat of liquefaction of D_4. T_1 exhibits a slightly different behavior, with only one plateau at $\Delta H_a = 16$ kcal/mole.

In Table IV, we report ΔH_a at $\theta = 0.1$ for each silica, as well as the net heat of adsorption related to the first plateau, $\Delta H_{net\ 1}$, to the second plateau, $\Delta H_{net\ 2}$, and to the heat of liquefaction of D_4, $\Delta H_{net\ L}$.

As already underlined, the adsorbents can be classified into three groups:

TABLE III
Values for σ, c, and ΔE of Adsorbed D_4

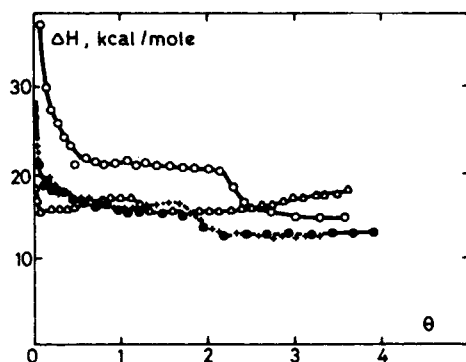| Silica	σ, Å^2	c	ΔE, cal/mole
A300	100	20.1–18.7	2500
P_1	102	13.2–12.2	2160
P_2	114	10.3–11.5	1925
T_1	282	4.3–4.5	1250

Fig. 2. Heats of adsorption vs. covering ratios: (O) A300; (●) P_1; (+) P_2; (△) T_1.

fumed silica with clearly higher heats of adsorption, precipitated silicas exhibiting identical behavior with intermediate values, and modified fumed silica with lower heats of adsorption.

These results suggest that the interactions between D_4 and silicas are directed more by morphological and structural characteristics (determined by the mode of obtention of the adsorbents) than by chemical properties. Indeed, the main difference between P_1 and P_2 results from their sodium and aluminum contents (Table I). Since these two silicas exhibit the same behavior toward D_4, it appears that these metallic impurities do not play any part in the adsorption process. Finally, modification of A300 by chemisorbed D_4 contributes to a strong decrease in the interactions between the PDMS oligomer and the filler. This is in agreement with the conclusions drawn from the study of the irreversible adsorption processes.

The occurrence of two plateaus on the ΔH_a vs. θ curves could be due to a rearrangement of the D_4 adsorbed layer. Indeed, the surface area covered by a molecule of D_4 whose plane is parallel to the surface of the filler is[1,2,5,6] 100 Å^2 but becomes 50 Å^2 when its plane is perpendicular to the adsorbent. Thus, it could be envisioned that at low relative pressures the adsorbed D_4 molecules are lying "flat." But when P/P_0 increases, their configuration could change in order to get the plane of the molecule perpendicular to the surface of the adsorbent. Therefore, more D_4 molecules could be adsorbed under the same configuration. With a covered surface area of 50 Å^2 per molecule, this new layer of adsorbed material will be completed for an apparent covering ratio of 2. It is difficult to check such hypothesis with the available experimental techniques, but it is worth noting that a similar kind of molecular rearrangement has been postulated by Eirich.[7]

TABLE IV
Isosteric and Net Heat of Adsorption of D_4 on the Silicas

Silica	$(\Delta H_a)_{\theta=0.1}$, kcal/mole	$\Delta H_{net\ 1}$,[a] kcal/mole	$\Delta H_{net\ 2}$,[a] kcal/mole	$\Delta H_{net\ L}$,[a] kcal/mole
A300	32	11	17	20
P_1	21	6	8	9
P_2	21	5	8	9
T_1	16	—	0	4

[a] $\Delta H_{net} = (\Delta H_a)_{\theta=0.1} - (\Delta H_a)_{plateau}$.

TABLE V
Spreading Pressure of D_4 on the Silicas

Silica	π_e mJ/m^2 at 153°C
A300	28.2
P_1	29.7
P_2	25.4
T_1	8.9

This change of configuration should, however, be associated with an important decrease in the filler surface energy following adsorption, i.e., with its spreading pressure π_e. Application of the Gibbs relationship to the four samples yields the values of the spreading pressures reported in Table V.

It appears on the one hand that the pretreatment of A300 by D_4 contributes to a strong decrease in the corresponding spreading pressure and thus confirms the low surface energy of a pretreated filler. On the other hand, the values measured for A300, P_1, and P_2 are nearly identical and therefore do not reflect the differences previously noted between these three silicas. This could be due to the large size of the D_4 molecule, which requires only a small number of grafting points or of active sites for specific interactions. Hence, a leveling of possible differences seems plausible.

The adsorbents used as supports in the chromatography columns were submitted to elemental and IR spectroscopy analyses. The results obtained with A300, P_1, and P_2 gave evidence of the occurrence of a chemisorption of the organosiloxane onto the surface of the fillers (Table VI). However, the amount of D_4 molecules chemically held on the silica surfaces are small and nearly identical whatever the adsorbent.

Since at 150°C a beginning of chemisorption is observed, this process was examined at higher temperatures.

Comparison of Precipitated Silicas with Fumed Silicas in their Interactions with PDMS Oligomers at Temperatures Higher than 150°C

The chemisorption kinetics of D_4 onto A300, P_1, and P_2 were established at 250°C by gravimetry, using the same agglomerated silicas as those investigated by gas chromatography. Since the hydrothermal treatment selected to agglomerate the adsorbents is associated with a modification of the surface hydroxyl groups content of the fillers (Table I), the influence of this treatment upon the previous results was examined by studying the chemical interactions occurring between a nonagglomerated silica ($P_{1\,na}$) and D_4.

Figure 3 relates the number of molecules of D_4 chemically held on the surface

TABLE VI
Elemental Analysis of Silicas after Treatment with D_4 at 150°C

Silica	D_4 molecule grafted/100 Å^2	
	Elemental analysis	IR spectroscopy
A300	0.12	0.12
P_1	0.11	0.11
P_2	0.11	—
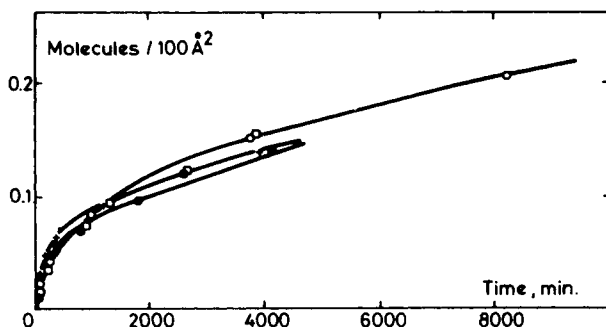
Fig. 3. Amount of adsorbed D_4 vs. reaction time: (O) $A300_a$; (●) $P_{1\,a}$; (+) $P_{2\,a}$; (□) $P_{1\,na}$.

of A300, P_1, P_2, and $P_{1\,na}$ to the time of reaction. Differences between the three adsorbents are slight. This is in agreement with previous conclusions according to which the effect of the metallic impurities of precipitated silicas is negligible. However, the reactivity of the different adsorbents toward D_4 increases with their OH_f content (Table VII). Therefore, they can be classified as follows: A300 $> P_{1\,na} > P_2 > P_1$.

IR spectroscopy allows the calculation of the number of surface free OH groups that have reacted for one molecule of D_4 chemically held on the surface of the filler and supports a reactional mechanism identical to the one postulated for A300.[2,3] It is, however, worth underlining that the ratio of reacted OH_f/D_4, which should depend on the number of available surface free OH groups, is not satisfied in the case of P_2 (Table VIII). This result suggests a distribution of the silanol groups on the surface of precipitated silicas different to that of the fumed silica. Such observations are consistent with conclusions of Basset et al.[8] and Van Roosmalen et al.[9] who showed that, concerning silanol groups, fumed and silica gel or precipitated silica surfaces are not identical.

In order to confirm our assumption and try to differentiate fumed from precipitated silica surfaces, we compared their reactivity toward water.

TABLE VII
Number of Free Silanols and D_4 Molecules per Unit Surface Area After 66 Hr of Treatment

Silica	$OH_f/100\ Å^2$	Molecule $D_4/100$ $Å^2$ after 66 hr of reaction
A300	1.7	0.155
P_{1na}	1.7	0.155
P_{2a}	1.5	0.14
P_{1a}	1.3	0.135

TABLE VIII
Number of Free Silanols and D_4 Molecules per Unit Surface Area

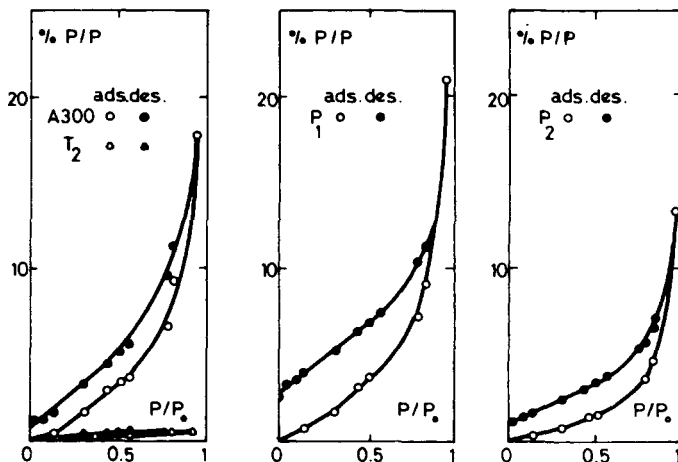| Silica	$OH_f/100\ Å^2$	OH_f/D_4
A300	1.7	2.7
P_1	1.3	2.2
P_2	1.5	3.4

Fig. 4. Adsorption–desorption isotherms of water on nonagglomerated A300, T_2, P_1, and P_2.

Comparison of Precipitated Silicas with Fumed Silicas in their Interactions with Water

This study was performed by gravimetry on both agglomerated and non-agglomerated A300, P_1, P_2, and T_2. When the adsorption of water was studied on nonagglomerated dehydrated silicas, all the adsorbents except T_2 showed irreversible processes (Fig. 4). Such hysteretic behavior is associated with chemical reactions taking place between water and the surface functional groups of silica, implying particularly a reopening of the siloxane bridges.[10] As for the very weak affinity exhibited by T_2 toward water and illustrated by the obtaining of type III isotherms, it is the consequence of the substitution of its surface hydroxyl groups by dimethylsiloxy grafts.

On the other hand, the adsorption of water onto agglomerated A300, P_1, and P_2 is reversible (Fig. 5). Such behavior suggests that complete rehydration of the adsorbents remains possible after the agglomerating hydrothermal treatment.
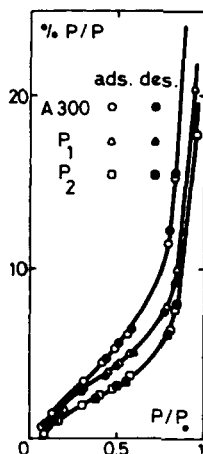

Fig. 5. Adsorption–desorption isotherms of water on agglomerated A300, P_1, and P_2.

TABLE IX
Values for c, ΔE, and σ of Adsorbed Water

Silica	c	ΔE, cal/mole	σ, Å^2
A300	3.1	6.6	25
P_1	10.0	1340	27
P_2	7.2	1150	34
T_2	<1	<0	—

The isotherms recorded then are of type II. Therefore, the BET equation can be applied, and c, σ, and ΔE can be calculated. The values obtained for the surface area of the adsorbed molecule of water (Table IX) are in agreement with previous observations.[11,12] The results reported in this table allow a classification of the silicas according to their affinity toward water: $P_1 > P_2 \gg A300 \gg T_2$.

The outstanding affinity of the precipitated silicas is unexpected. Owing to its total silanol content (Table I), which is assumed to be related to the hydrophylic behavior of a filler, A300 should indeed exhibit stronger interactions with H_2O than the other adsorbents.

The interpretation of these experimental results requires precipitated and fumed silica surfaces to have different distributions of their silanol groups. These differences should be reflected by the surface energies of the adsorbents, i.e., by their spreading pressure π_e, which has both dispersive and polar components. The part played by the latter should be particularly important as a consequence of the hydrothermal treatment to which the adsorbents are submitted.

Therefore, assuming that the dispersive component is unaffected by agglomeration, π_e could be connected with the hydroxyl content of the silicas. Results presented in Table X show that for all fillers except A300, this assumption is valid. The different behavior of the fumed silica is obviously connected with the distribution of the silanol groups on its surface.

Such assumptions are in agreement with Basset et al.[8] and Van Roosmalen et al.,[9] who showed that geminal silanediol is found in higher quantity on precipitated than on fumed silica surfaces. The latter authors moreover showed[13] that the rehydrations of dehydrated precipitated silicas and fumed silicas proceed according to different mechanisms. They particularly suggested the physisorption of molecular water on precipitated silica to take place chiefly through hydrogen-bonded silanol pairs.

We have shown that precipitated silicas react efficiently with PDMS oligomers, thus yielding grafted materials, while on the other hand they exhibit in these interactions different behavior than fumed silicas. In order to know if these differences depend on their thermal stability, the grafted silicas were tested under various atmospheres.

TABLE X
Spreading Pressure of Water on the Silicas

Silica	π_e mJ/m^2 at 20°C
A300$_a$	57.0
$P_{1\ a}$	56.9
$P_{2\ a}$	38.7
T_2	4.3

Comparison of Modified Precipitated Silicas with Fumed Silicas in their Thermal Behavior

The study was performed by following the variation of the IR spectral line of the CH_3 group in the temperature range of 150–600°C either under vacuum or at the vapor pressure of water at 20°C. Modified precipitated silicas exhibit a general thermal behavior identical to that of modified A300.[2,3] Particularly, two temperature domains have to be considered: 150–500°C and 500–600°C.

Modified P_1 and P_2 heated for $\frac{1}{2}$ hr under vacuum to 600°C or under controlled atmosphere to 500°C exhibit only slight modification of their CH_3 line intensity. But at temperatures higher than 500°C, in the presence of water, a $\frac{1}{2}$-hr treatment is followed by a significant decrease in the amount of grafted material. Table XI provides not only the observed weight loss of D_4 under the various experimental conditions but also the amount of OH_f groups regenerated per molecule of D_4 eliminated (OH_f/D_4). From this table, the fillers can be classified according to the thermal stability of the grafted D_4: (1) under vacuum, $150 < T < 600°C$: $P_1 > A300 > P_2$; (2) in the presence of water, $150 < T < 600°C$: $P_1 = P_2 = A300$; (3) in the presence of water, $500 < T < 600°C$: $A300 > P_1 > P_2$.

Considering the amount of free OH groups regenerated per molecule of D_4 eliminated under controlled atmosphere, A300 and precipitated silicas have completely different behavior. It is moreover worth noting that with P_1 and P_2, in the presence of H_2O, all OH_f which have reacted during the grafting process are regenerated. As previously stressed, a difference in the distribution of the silanol groups on the surface of precipitated silicas could account for this result. Nevertheless, P_1 and P_2, like A300,[2,3] have outstanding thermal stability under vacuum and even under controlled atmosphere at temperatures lower than 500°C.

CONCLUSIONS

The study of silica–siloxane interactions by means of IR spectroscopy, gravimetry, and chromatography has shown precipitated silicas to exhibit a general behavior identical to that of fumed silicas. Particularly whatever the adsorbents, their interactions with D_4 can be classified according to three temperature ranges and therefore three processes: $T < 140°$, irreversible adsorption; $T \sim 150°C$, reversible adsorption; $T > 150°C$, chemisorption.

TABLE XI
Thermal Stability of D_4-Modified Silicas

Silica	Experimental conditions	Weight loss upon heating[a]		Reappearance of OH_f OH_f/D_4
		$150 < T < 500$	$500 < T < 600$	
A300	vacuum	7	11	—
	H_2O	9	21	0.17
P_1	vacuum	0	0	—
	H_2O	6	41	2.3
P_2	vacuum	8	20	—
	H_2O	8	39	2.7

[a] % D_4 eliminated.

While at 150°C interactions between D_4 and both precipitated and fumed silicas are reversible, the latter yield higher heats of adsorption. With the two studied precipitated silicas, smaller and nearly identical heats of adsorption are obtained. These observations suggest that interactions between PDMS oligomers and silicas are governed more by morphological and structural characteristics than by chemical properties. Metallic impurities of precipitated silicas do not play a significant role in the adsorption process.

The analysis of the chemisorption processes occurring above 150°C suggests a distribution of the silanol groups on the surface of precipitated silicas different to that of fumed silicas, confirmed by the study of H_2O dehydrated filler interactions.

Investigation of thermal properties of the siloxane-modified silicas showed the precipitated adsorbents to exhibit an outstanding thermal stability. Under controlled atmosphere they are, however, more sensitive to the effect of high temperature than are fumed silicas.

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