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Modified calcium silicates as active rubber fillers

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The physicochemical characteristics of calcium silicates obtained from the reaction of sodium metasilicate solution with calcium nitrate are given. Further, studies of the modification of the silicate surface with silane and titanate coupling agents are presented. By wettability measurements and an analysis of the chemically adsorbed carbon arising from the coupling agents, the degree of modification of these surfaces was estimated. The modification of the surface of the silicates with the same agents, but in the presence of acid protons, was also performed with a positive effect. The usefulness of modifications is justified by the results of strength studies of vulcanizates filled with the modified silicates.

1. Introduction

Hydrated calcium silicate is the main representative of those synthesized. It is one among components of silicate fillers, containing also co-precipitated silica and calcium oxide in various proportions [1].

This filler is produced commercially by the precipitation from sodium metasilicate solution when using water solutions of calcium salts (mainly chlorides).

The particle sizes of the precipitate and their activity depend on precipitation parameters like the concentration of reagents, temperature of solutions, stirring intensity and content of accompanying substances [2–4]. An important problem, appearing during the precipitation process, consists in the exclusion of the formation of a gelatinous hydrogel which strongly binds all the water contained in the system, and after drying is characterized by internal porosity and a rigid structure, very difficult to crumble.

The silicates are strongly hydrophilic; they easily become moist and therefore can adsorb large amounts of water on their surfaces, which significantly limits their use as fillers of plasto- and elastomers [5, 6].

Modification has been performed in order to raise the chemical affinity of the filler for the polymer, and particularly to change the hydrophilic character into a hydrophobic or at least partly hydrophobic one [7, 8].

2. Experimental methods

2.1. Materials

Calcium silicates used in the experiments were obtained from sodium metasilicate solution and a water solution of calcium nitrate. Basic conditions for the precipitation of these silicates are shown in Table I.

The silane coupling agents used in this study were as follows: γ-mercaptopropyltrimethoxysilane A-189, γ-aminopropyltriethoxysilane A-1100 and vinyltri-(β-methoxyethoxysilane) A-172. The titanate coupling agent in this study was isopropyltriisostearoyltitanate KR TTS.

2.2. Procedures and methods

Surface areas of the silicates were determined by the thermal desorption method [9] using nitrogen as an adsorbate. Other physical as well as analytical data were determined by commonly employed methods.

In order to fully characterize the fillers studied, the water and n-butylphthalate absorptivity was determined [10].

The crystalline structures of particular preparations were determined by X-rays. Diffraction patterns were obtained with a diffractometer TUR-C-62 (Freiberger, Präzisionmechanik, GDR), provided with a horizontal goniometer HZG [11].

In order to modify 500 g silicate, organosilane and titanate (1 to 10% by weight) were dissolved in the methanol–water mixture (150 cm^3, 4 : 1 by volume) and several drops of acid were added to catalyse the hydrolysis. The process was carried out for 1 h in a mixer of 3.85 dm^3 capacity, provided with a V-shaped blender as described previously [12]. The silicates were then dried for 2 h at 110° C.

The heat of immersion in water (H_i^W) and benzene (H_i^B) were determined by a calorimetric method [13]. Ampoules containing a calcium silicate sample (0.1 g) were carefully evacuated for 6 h at 110° C, sealed under vacuum and then transferred to the calorimeter.

TABLE I Physicochemical studies and the surface modification of samples of calcium silicate

Sample	Conditions for obtaining silicates	Precipitation temperature (° C)	Final pH of solution
K-2	SiO_2 concentration in solution: 3% metasilicate modulus: 2.53, 5% solution of $Ca(NO_3)_2$	60	10
K-10	SiO_2 concentration in solution: 3% metasilicate modulus: 2.53, 10% solution of $Ca:(NO_3)_2$	85	8

TABLE II Chemical and physicochemical properties of the silicate fillers

Property	Filler			
	K-2	K-10	Calsil†	Silene EF‡
Chemical content (%)				
SiO_2	61.0	80.9	70.0	65.0
CaO	20.0	10.1	11.0	20.0
Moisture	3.6	5.0	6.0	5.0
Loss during calcination (%)	12.5	13.5	15.0	14.5
pH of water extract*	10.0	8.5	10.0	9.8
Specific weight ($g\,cm^{-3}$)	1.80	2.12	2.05	2.10
Bulk density ($g\,dm^{-3}$)	175	100	150	160
Packing density ($g\,dm^{-3}$)	300	215	–	–
Water absorptiveness (g per 100 g)	120	210	190	190
n-butylphthalate absorptiveness (g per 100 g)	180	250	230	220
Specific surface ($m^2\,g^{-1}$)	80	78	–	87

*pH was determined for a 4 to 5 g suspension of silicate in 100 cm^3 of water or in a methanol–water solution (1 : 1 by volume).
†Supplied by Fülstoffgesellschaft (GmbH, BRD).
‡Supplied by the Chemical Division, Pittsburg Plate Glass Co. USA.

Measurements were performed in a KRM-type differential calorimeter, described elsewhere [13]. The temperature of the immersion liquid, prior to ampoule breaking, was kept constant at 15 ± 0.001° C. The H_i values were determined at least twice.

The preparation of SBR (butadiene–styrene rubber) blends was carried out on a two-roll mill by the standard procedure. Curing was performed by heating a sheet of the rubber (SBR) under a pressure of 150 kg cm^{-2} at 145° C. The strength properties of the vulcanized rubbers were measured by standard methods.

3. Results and discussion

Table II gives the chemical contents and values of the physicochemical parameters of the silicate fillers studied. There are also for comparison the analogous data on the calcium silicates being produced commercially.

From the diffraction patterns it follows that the silicates studied are amorphous, due to the shape of the diffuse lines and the lack of maxima characteristic of the crystalline forms.

The silicate K-10 has an approximate composition: $CaO \cdot 7SiO_2 \cdot 2H_2O$, which relative to the CaO content is similar to Calsil. The K-2 sample, with less advantageous parameters (increased bulk density, decreased absorptiveness) has the following composition: $CaO \cdot 2.5SiO_2 \cdot 0.5H_2O$. From the physicochemical studies it follows that the calcium silicates have more advantageous properties as fillers the larger the amount of co-precipitated silica they contain (the K-10 sample contains *ca* 80% of SiO_2, and the K-2 sample only 60% of SiO_2).

The heat of immersion values for calcium silicates modified in water (H_i^W) or benzene (H_i^B) are listed in Table III. The table also presents data on the carbon content of the chemisorbed silane or titanate groups on the surface of the studied silicates following their modification. For comparison, the table also shows the carbon content of silane or titanate groups adsorbed on the silicate surface immediately following modification (drying, no multiple washes).

Fig. 1 illustrates the variation in the heats of immersion in water H_i^W and benzene H_i^B for silicates (K-10 and K-2) treated with 3 wt % of the different coupling agents.

As follows from Table III, the modification with silanes and titanate KR TTS causes in each case an increment in the hydrophobicity of the surface, as proved by the increased values of wettability of the silicate surface with benzene. The largest improvement of the surface hydrophobicity is due to mercaptosilane

TABLE III Compilation of heats of immersion in water H_i^W and in benzene H_i^B, carbon contents of the sorbed silanes or titanate groups, and specific surface for modified calcium silicate K-10

Coupling agent in treated silicate (wt %)		Specific surface ($m^2\,g^{-1}$)	Carbon content of the sorbed silanes or titanate groups (wt %)			H_i^W ($J\,g^{-1}$)	H_i^B ($J\,g^{-1}$)
			Calculated	Found after modification	Found following washing (chemisorbed)		
–	–	78.0	–	–	–	19.5	20.7
Mercaptosilane A-189	1		0.184	0.164	0.095	12.9	23.4
	2	77.2	0.374	0.329	0.164	9.8	25.6
	3		0.555	0.505	0.252	8.1	28.9
	5	75.5	0.922	0.825	0.380	5.8	31.4
	10		1.841	1.102	0.425	3.6	34.0
Aminosilane A-1100	1	77.5	0.163	0.150	0.084	16.4	22.5
	3		0.491	0.452	0.248	19.1	26.7
	5	75.8	0.810	0.769	0.425	23.3	30.1
Vinylsilane A-172	1	77.7	0.094	0.088	0.045	14.0	22.4
	3		0.261	0.222	0.128	10.3	27.1
	5	76.0	0.432	0.392	0.182	7.1	30.4
Titanate KR TTS	1		0.260	0.225	0.148	12.2	23.8
	2	77.5	0.453	0.410	0.203	8.7	26.3
	3		0.681	0.621	0.263	7.9	29.4
	5	76.6	1.133	1.054	0.326	4.2	32.5
Mercaptosilane A-189 + 0.01 mole of formic acid per 100 g of filler	1		0.184	0.165	0.120	12.4	24.1
	2	77.5	0.374	0.328	0.211	9.5	26.3
	3		0.555	0.510	0.294	7.7	31.8
	5		0.922	0.825	0.429	5.5	33.5
	10	77.0	1.841	1.112	0.496	3.1	36.0

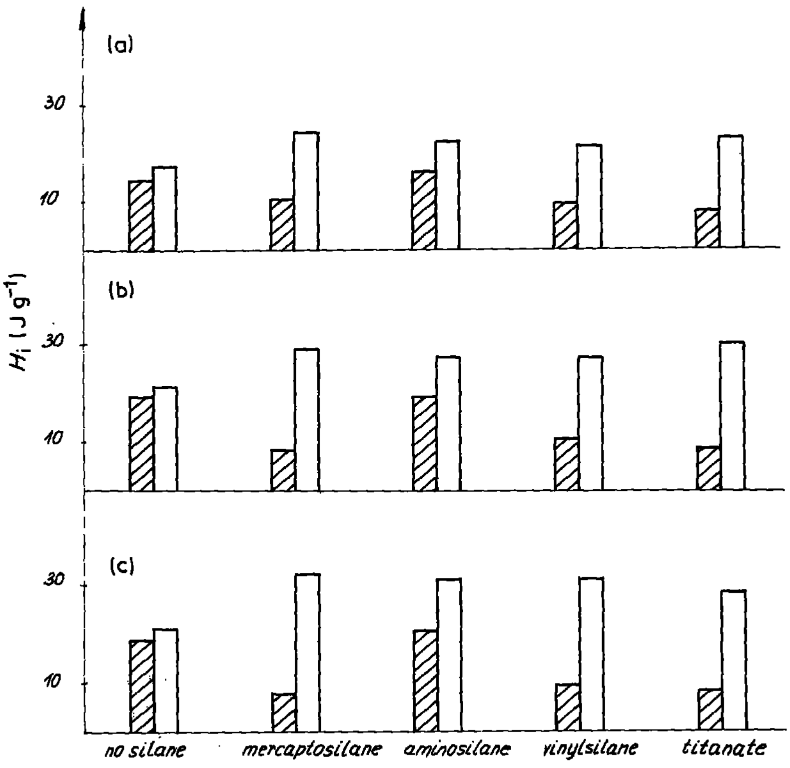
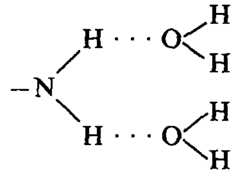


Figure 1 Comparison of heats of immersion in water H_i^W and in benzene H_i^B for different calcium silicate fillers, untreated or treated with 3 wt% silane or titanate coupling agents. □ = H_i^B; ■ = H_i^W. (a) K-2, (b) K-10, (c) K-10 + 0.01 mole formic acid per 100 g filler.

A-189 and titanate KR TTS. Meanwhile, due to aminosilane A-1100 modification one observes an increment of the surface wettability both with benzene and water. Functional amine groups have the ability to absorb a large amount of water, which is the main reason for an enhanced water-wettability. The water sorption can proceed due to the formation of hydrogen bonds between the amine group and water molecule:

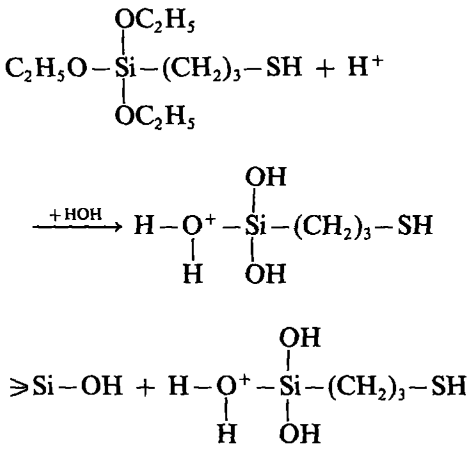


or due to the formation of surface compounds with an ionic character $-NH_3^+-OH^-$.

According to Koenig and Ishida [14–16], the calcium silicate surface modified with e.g. silane A-1100 may be presented as in Fig. 2.

The modification in the presence of formic acid proceeds with a greater yield, as proved by the increased amounts of carbon, arising from silane or titanate, chemisorbed on the silicate surface, and higher values of the heat of immersion of the surface with benzene. The increment in the content of carbon chemisorbed on the surface reaches 10 to 15% relative to the sample modified without any addition of acid.

The possible mechanism of the acid-catalysing reaction is presented below. The mechanism takes into account the role of the proton, originating from the added catalyst, and the possible formation of an electrophilic cation with alcoxysilane. The mechanism also assumes hydrolysis of the silane solution before its deposition on the calcium silicate surface.



$$C_2H_5O-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-(CH_2)_3-SH + H^+$$

$$\xrightarrow{+HOH} H-\underset{H}{O^+}-\overset{OH}{\underset{OH}{Si}}-(CH_2)_3-SH$$

$$\geqslant Si-OH + H-\underset{H}{O^+}-\overset{OH}{\underset{OH}{Si}}-(CH_2)_3-SH$$

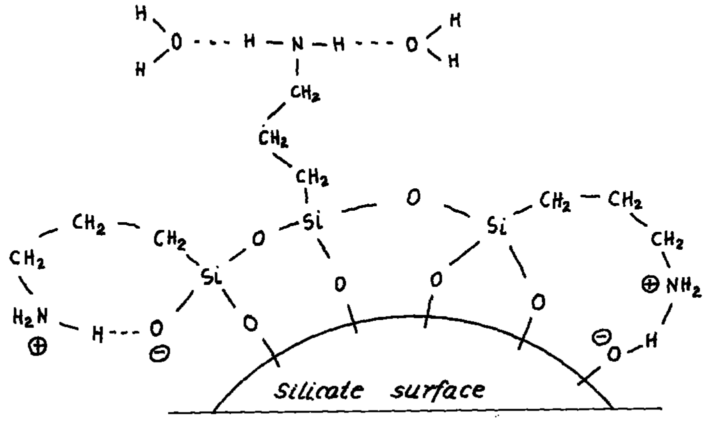


Figure 2 Calcium silicate surface after aminosilane A-1100 modification.

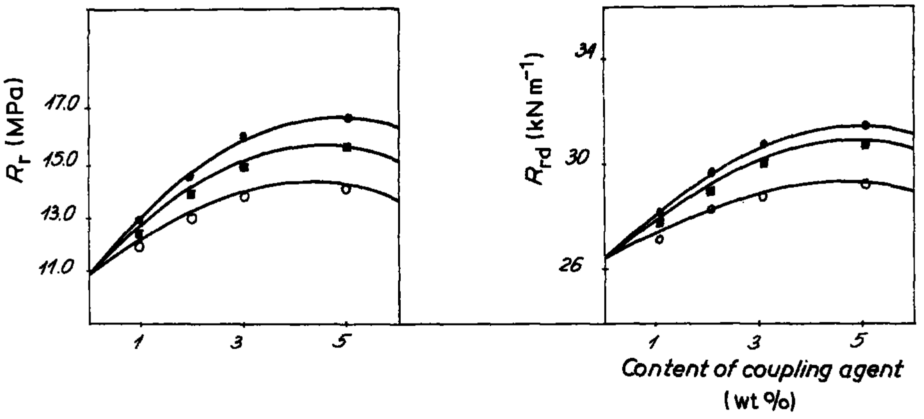
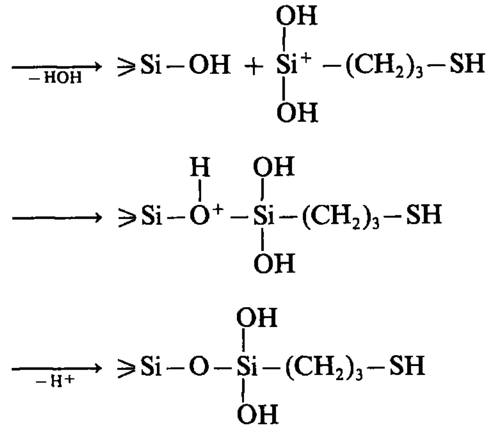


Figure 3 Strength parameters of vulcanizates with K-10 calcium silicate as a function of coupling agent content: (●) A-189, (■) KR TTS, (○) A-172.



$$\xrightarrow[-HOH]{} \geqslant Si-OH + \underset{OH}{\overset{OH}{Si^+}}-(CH_2)_3-SH$$

$$\longrightarrow \geqslant \overset{H}{Si}-O^+-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH$$

$$\xrightarrow[-H^+]{} \geqslant Si-O-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH$$

An addition of formic acid during the surface modification of calcium silicate with KR TTS titanate does not influence or in some cases even decreases the chemisorption of titanate, as proved by the minimum wettability of the silicate surface with benzene (Fig. 1).

In this work, a correlation has been observed between heat of immersion values H_i^B for the silicates examined and the strength properties of the sulphur-cured SBR, filled with these silicates. In Table IV, the results of strength tests are presented for vulcanizates filled with some modified and unmodified silicates.

Fig. 3 displays the relation between the basic strength properties of vulcanizates and the amounts of coupling agent used for silicate modification.

Fig. 4 shows the dependence of the basic strength parameters of vulcanizates filled with various modified and unmodified silicates upon the vulcanization time. Optimum strength on tearing and tensile failure were achieved with 40 min vulcanization.

As follows from the data (Fig. 3 and Table IV), optimum strength properties are obtained for vulcanizates containing silicates modified with A-189 mercaptosilane. In the case of organotitanate KR TTS, the strength properties, despite the most pronounced hydrophobization of the silicate surface, are worse than those obtained with mercaptosilane. This result seems to be due mainly to the lower affinity of isostearoyl groups compared with mercaptane groups of A-189 silane toward the functional groups of SBR rubber, vulcanized with sulphur.

The calcium silicate surface modification with coupling agents applied in amounts greater than 3 parts (wt/wt) leads to a distinctly decreased coverage of the surface with the compounds. Thus, a further increase in the applied silane or titanate amounts is unsuccessful since the hydroxyl groups of the silicate surface have almost completely undergone condensation with alcoxyl groups. An excess of the agents, and silane in particular, at the surface results in the formation of a network of polysiloxanes [17, 18].

4. Conclusions

1. The studies proved that the modification of the surface of calcium silicate with silane and titanate

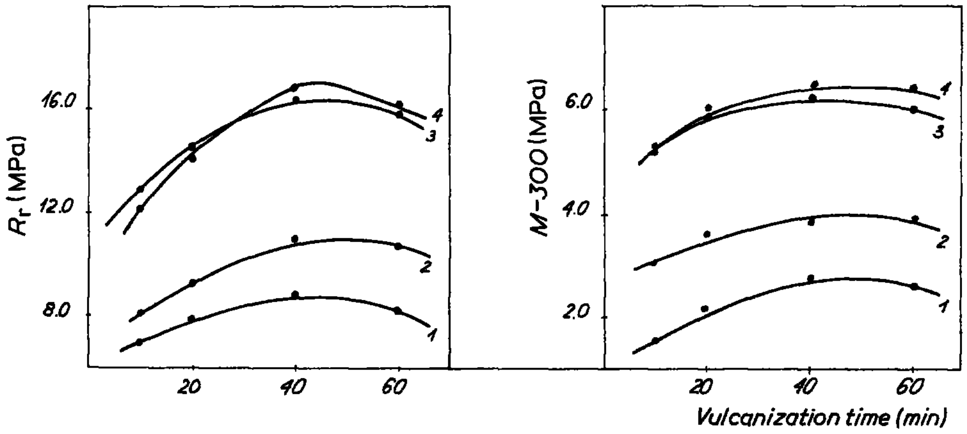


Figure 4 Strength parameters of vulcanizates with calcium silicates modified or unmodified as a function of vulcanization time: (1) K-2, (2) K-10, (3) K-10 + 3% A-189, (4) K-10 + 3% A-189 + 0.01 mole formic acid.

TABLE IV Effects of silane or titanate coupling agents on vulcanizate strength parameters of calcium silicate-loaded SBR (vulcanization time: 40 min)*

Coupling agent in treated silicate (wt %)	Tensile strength, R_r (MPa)	300% modulus, M-300 (MPa)	Tearing strength, R_{rd} (kN m^{-1})	Shore hardness, ^{0}Sh
No filler	0.98	0.60	10.2	28
K-10				
No coupling agent	10.92	3.95	26.5	63
A-189 1	12.98	4.68	28.3	65
A-189 3	16.45	6.25	30.9	65
A-189 5	16.91	6.26	31.6	65
A-189 10	15.50	5.84	30.3	64
KR TTS 3	15.83	5.90	31.5	65
A-189 + 0.01 mole formic acid 3	17.05	6.34	30.7	65
K-2				
No coupling agent	8.79	2.81	21.6	59
A-189 3	12.66	4.19	24.5	61
A-1100 3	11.80	3.90	23.8	60
A-172 3	11.76	3.95	24.0	60
KR TTS 3	12.32	3.88	24.2	61

*Formulation: Ker 1500, 100; ZnO, 3; stearic acid, 2; unmodified or modified calcium silicate, 50; dibenzothiazole disulphide, 2.2; diphenylguanidine, 1.4; sulphur, 2.

coupling agents improves its wettability by benzene. As a result the silicate surface becomes hydrophobic, and the adsorbed functional groups of silanes and titanates facilitate the bonding of the rubber with the filler during vulcanization.

2. The modification of the surface of silicates with silane and titanate coupling agents in the presence of an acid agent improves the surface wettability by benzene relative to the modification performed without an acid proton.

3. An optimum content of silane and titanate coupling agents reaches 2 to 3 parts by weight of the calcium silicate.

4. Within the rubber blends based on SBR rubber, a better reinforcing effect was due to silicates modified with mercaptosilane compared with that due to the titanate-modified silicates.

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