Modified zinc silicate – an active rubber filler

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Physico-chemical properties have been characterized for zinc silicates obtained in various conditions in reaction of sodium metasilicate solution with water soluble zinc salt (zinc sulphate or chloride). Attempts have been made to apply the precipitated zinc silicates in rubber mixtures based on butadiene-styrene rubber. Appropriate tests have been conducted. Also, a possibility has been tested of eliminating zinc oxide (an activator in the vulcanization process) from the rubber mixture. Studies have been presented on the modification of zinc silicate surface with silane and titanate coupling agents. The extent of surface modification has been estimated measuring heats of surface immersion and determining chemisorbed carbon on the surface which has originated from coupling agents. The effect of modifying zinc silicate surface has been evaluated by strength tests performed on vulcanizates filled with the modified silicates.

1. Introduction

Until recently, carbon black has constituted an almost exclusive filler of rubber mixtures since vulcanizates containing it exhibit the best physicomechanical properties. However, carbon black colours rubber products black and the respective production uses up valuable petrochemical raw materials. Therefore, silica and silicates obtained synthetically, and natural ones, have recently received increasing attention in rubber production [1, 2]. Among silicate fillers, synthetic zinc silicate ($ZnSiO_3$ + ZnO + SiO_2 + nH_2O) may find a wide application. The synthetic zinc silicate, a white powder, is used mixed with silica and zinc oxide and consists of spherical particles. In the rubber mixtures it acts as an active filler and an activator. Using the filler, one can eliminate zinc oxide and, in part or completely, carbon black from rubber mixtures.

Zinc silicate exhibits significant hydrophilicity, easily wetting with water, adsorbing significant amounts of water, e.g. from air during storage which significantly hampers the introduction of zinc silicate into a rubber mixture.

In order to increase the chemical affinity of zinc silicate with functional groups of polymers and promote hydrophobization of its surface, we have elaborated a method of modifying the silicate using various silane or titanate coupling agents [3-7].

2. Experimental methods
2.1. Materials
Zinc silicates used in the studies were obtained from solutions of sodium metasilicate and water solutions of zinc chloride or sulphate [8]. Conditions of precipitating the silicates are presented in Table I.

The silane coupling agents used in this study were: gamma-Mercaptopropyltrimethoxysilane A-189, beta-Mercaptoethyltriethoxysilane A-1893, gamma-Aminopropyltriethoxysilane A-1100, N-beta-(aminoethyl)-gamma-Aminopropyltrimethoxysilane A-1120, Vinyltri(beta-methoxyethoxysilane) A-172 and gamma-Glycidoxypropyltrimethoxysilane A-187. The titanate

TABLE I List of zinc silicate samples subjected to physico-chemical studies and to surface modification

Sample	Condition for obtaining silicates	Precipitation temperature °C	Alkalinity of solution after carbonation N	Final pH of solution
Z-1	SiO_2 concentration in solution: 5%, metasilicate modulus: 2.5, 5% solution of $ZnSO_4$	75	0.58	8.5
Z-7	SiO_2 concentration in solution: 5%, metasilicate modulus: 2.5, 5% solution of $ZnCl_2$	70	0.51	8.5
Z-14	SiO_2 concentration in soution: 5%, metasilicate modulus: 3.1, 5% solution of $ZnCl_2$	80	0.18	8.0
Z-16	SiO_2 concentration in solution: 5%, metasilicate modulus: 3.9, 5% solution of $ZnCl_2$	75	0.24	8.0

coupling agent in this study was isopropyltriiso-stearoyltitanate KR TTS.

2.2. Procedures and methods

Surface areas of the silicates were determined by the thermal desorption method using nitrogen as an adsorbate [9]. 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 absorption 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].

Particle size was determined in an electron microscope JEM (JEOL, Japan) using a single-stage replica technique.

Samples of zinc silicates were subjected to surface modification in a mixing chamber of our own design [12]. The process was carried out for 1 h. Thus, zinc silicate modification was conducted in the presence of minimum amounts of silane and titanate solution so that silicate particles were wetted only at their surface. The zinc silicates were then dried for 2 h at 110°C. For modification we used 1 to 5 weight parts of silane or titanate coupling agents per 100 weight parts of the silicate [13]. Silane coupling agents were used in methanol:water (4:1 by volume) and in absolute methanol solutions while the titanate coupling agent was dissolved in CCl_4. The reaction of modification with silanes was also catalysed using acids which were introduced to silane–methanol–water and silane–methanol solutions. Fig. 1 presents a scheme of the mixing chamber for surface modification of fillers.

Carbon content on the modified zinc silicate surfaces was determined using the Perkin-Elmer model 240 apparatus for elemental analysis. Efficiency of carbon utilization for silanes and titanates was calculated as a ratio of carbon chemically bound to the surface to the total amount of carbon introduced together with the modifying agent. The amount of chemically bound silane or titanate was estimated in such a way that immediately following modification, the samples were subjected to multiple washes with

TABLE II Rubber compound recipes

Ingredient	Content (parts by weight)	
	Mixture I	Mixture II
Rubber Ker 1500	100	100
Zinc silicate	50	50
Zinc oxide	3	0
Stearin	2	2
Accelerator DM[a]	2.2	2.2
Accelerator M[b]	1.4	1.4
Sulphur	2	2

[a] N, N'-diphenylguanidine
[b] 2-mercaptobenzothiazole

methanol or with carbon tetrachloride for one hour, drying and estimation of carbon content.

The heat of immersion in water (H_i^w) and benzene (H_i^B) were determined by a calorimetric method [14]. Ampoules containing a zinc silicate sample (0.1 g) were carefully evacuated for 6 h at 110°C, sealed under vacuum and then transferred to the calorimeter. Measurements were performed in KRM-type differential calorimeter, described elsewhere [14]. 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.

Zinc silicates were used as rubber mixture components. Two types of mixtures were prepared on the basis of butadiene–styrene rubber Ker 1500 of a composition given in Table II. Particular attention was paid to conditions of obtaining the mixtures to secure identical conditions for all samples. A series of mixtures was prepared, employing a pre-determined technological regime. The mixtures were vulcanized in a hydraulic press with steam heating at 145°C and 15.2 MPa pressure. Vulcanization lasted for 30 min.

3. Results and discussion
3.1. Characterization of the fillers
Chemical composition of studied zinc silicates which were used as fillers of butadiene-styrene rubber are given in Table III.

Table IV presents values of physicochemical parameters of the silicates studied.

Diffraction patterns of studied silicate samples indicate that the silicates are present in an amorphic
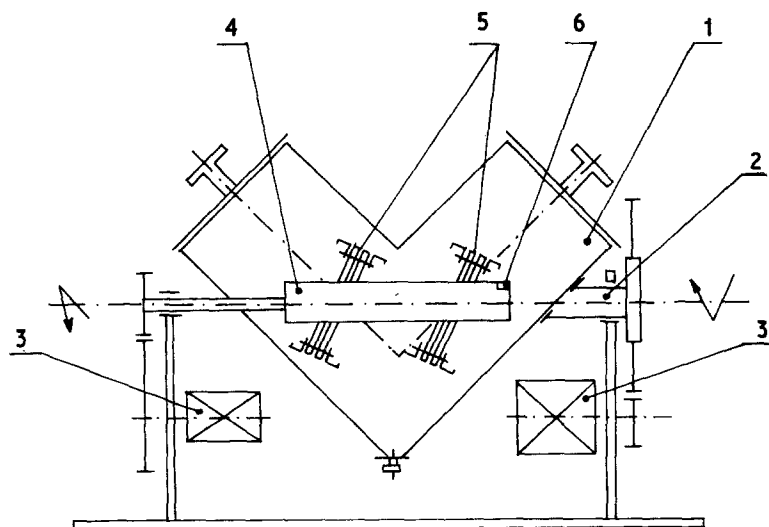
Figure 1 Blender for the modification of zinc silicate in coupling agents solutions: 1. V-shaped container, 2. axis of rotation, 3. motors, 4. dosage arrangement, 5. outputs for modifying solutions, 6. input for modifying solutions.

TABLE III Chemical composition of zinc silicate samples

Sample	ZnO (%)	SiO$_2$ (%)	Moisture (%)	pH of water extract*	Formula
Z-1	30.5	57.4	4.8	9.2	ZnO · 2.5SiO$_2$ · 0.7H$_2$O
Z-7	28.5	54.7	8.4	8.7	ZnO · 2.6SiO$_2$ · 1.3H$_2$O
Z-14	34.6	59.0	7.4	7.6	ZnO · 2.3SiO$_2$ · 0.8H$_2$O
Z-16	31.9	58.9	8.6	7.7	ZnO · 2.5SiO$_2$ · 1.2H$_2$O

*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).

form, as shown by the shape of diffuse lines and by the absence of maxima, typical for crystalline substances.

Results of testing physicochemical parameters have shown that all zinc silicates have exhibited a similar chemical composition as far as zinc oxide and silica contents are considered. The technique of precipitation has exerted an immense effect on properties of the product which has been particularly evident using for precipitation zinc chloride and a solution of sodium metasilicate, module 2.5. The zinc silicate sample denoted Z-7 has shown the most favourable physicochemical parameters (relatively low bulk density — 119.5 g dm^{-3}, high value of specific surface area — 104 m^2 g^{-1} and a good dispersion — 25 nm) which qualifies the preparation as one of a group of medium active fillers. Zinc silicates Z-14 and Z-16 have been only slightly worse than Z-7 silicate; they have also shown a good dispersion (an average particle size of 30 nm), high specific surface area (of 102 to 110 m^2 g^{-1} order) but slightly higher bulk density (130 to 140 g dm^{-3}). Zinc silicate sample Z-1, obtained using zinc sulphate, has exhibited much poorer physicochemical properties: too high bulk density, lower dispersion and lower outer surface. The filler could be regarded as fitting the category of low active fillers.

Values of heats of immersion of modified and unmodified zinc silicates in water (H_i^W) and benzene (H_i^B) are presented in Table V. 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.

Fig. 2 illustrates the variation in the heats of immersion in water H_i^W and benzene H_i^B for silicates (Z-1 and Z-7) treated with 3 wt % of different coupling agents.

As shown in Table V, Z-7 surface modification with silanes or titanate has induced increase in its hydrophobicity, as indicated by increased values of heats of immersion of silicate surface in benzene. The most pronounced increase in hydrophobicity has been noted following modification of Z-7 silicate

with titanate KR TTS, glycidosilane A-187 or mercaptosilane A-189. In parallel experiments, similarly to modification of calcium silicate with aminosilanes, the increase in wettability of silicate Z-7 surface has confirmed both benzene and water [15, 16]. The increase in heats of immersion in water has reflected the ability of adsorbing significant amounts of water by functional amino groups of silanes A-1100 and A-1120.

Surface modification in presence of bis(2-ethylhexylphosphate) acid is more efficient as shown by higher amounts of carbon originating from silanes and chemisorbed on silicate surface as well as higher values of heat of immersion silicate Z-7 surface in benzene. Results of studies on wettability silicate Z-7 surface modified with silane coupling agents in presence of an acidic catalyser (0.01 mole of bis(2-ethylhexylphosphate)acid) are listed in Table VI.

Modification in presence of the acid is more efficient as shown by greater amounts of carbon originating from silane chemisorbed on zinc silicate surface and higher values of heat of immersion the surface in benzene. Earlier work [17] has clarified the mechanism of modifying silicate surface with silanes in the presence of an acidic agent. During modification of zinc silicate with titanate no acid has been added since its negative effect has been noted on the efficiency of titanate chemisorption on the silicate surface.

3.2. Evaluation of the fillers in SBR

Zinc silicate has been used in rubber mixtures as a filler as well as to restrict or eliminate the need of zinc oxide used as an activator of the mixture. Two types of mixture have been examined: in the first one 3 weight parts of ZnO have been applied while in the other no zinc oxide has been applied, maintaining a constant amount of zinc silicate (50 weight parts).

Results of strength testing of the vulcanizates are given in Table VII. Very good strength parameters have been obtained for the mixtures containing no zinc oxide (tensile strength of approximately 14.0 MPa and evidently augmented value of 300% modulus the case of using unmodified silicate Z-7). This indicates that the amount of zinc oxide which coprecipitation with zinc silicate is sufficient for activation of SBR rubber mixtures. The obtained favourable strength parameters shows that mixture preparation is associated with good dispersion of filler (zinc silicate) particles in butadiene-styrene rubber.

Surface modification of zinc silicates has evidently improved strength parameters of vulcanizates. Strength parameters depend upon both kind and amount of coupling agents used. Effect of the amount of coupling

TABLE IV Physicochemical properties of the silicate fillers

Property	Filler			
	Z-1	Z-7	Z-14	Z-16
Bulk density (g dm^{-3})	175.4	119.5	140.9	134.0
Packing density (g dm^{-3})	378.9	308.2	289.5	289.0
Specific surface (m^2 g^{-1})	96	104	102	114
Particle size (nm)	40	25	30	32
Water absorption (g per 100 g)	225	350	315	320
n-butylphthalate absorption (g per 100 g)	249	310	320	360

TABLE V 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 zinc silicate Z-7

Coupling agent in treated silicate (wt %)		Specific surface	Carbon content of the chemisorbed silanes or titanate groups (wt %)			H_i^W J g^{-1}	H_i^B J g^{-1}
			Calculated	Found after modification in methanol–water solution	Found after modification in anhydrous methanol		
–		104.0	–	–	–	22.2	22.8
Mercaptosilane A-189	1		0.184	0.109	0.121	14.2	25.8
	2	103.0	0.374	0.178	0.245	10.9	27.9
	3		0.555	0.280	0.366	9.0	32.1
	5	102.4	0.922	0.393	0.507	6.2	33.9
Mercaptosilane A-1893	1		0.107	0.060	0.069	15.4	24.8
	2	102.5	0.215	0.101	0.129	12.6	26.5
	3		0.321	0.152	0.193	10.2	30.3
	5	102.4	0.536	0.197	0.281	8.2	32.6
Aminosilane A-1100	1		0.163	0.094	0.118	18.9	24.9
	2	103.1	0.325	0.160	0.202	22.4	26.5
	3		0.491	0.257	0.295	25.0	30.2
	5	102.9	0.806	0.442	0.503	27.6	32.6
Aminosilane A-1120	1		0.270	0.138	0.161	21.0	25.1
	2	103.2	0.541	0.282	0.325	23.9	27.3
	3		0.813	0.397	0.567	26.5	31.2
	5	102.8	1.351	0.502	0.742	30.1	33.2
Vinylsilane A-172	1		0.094	0.052	0.065	16.8	25.0
	2	103.8	0.173	0.095	0.120	12.4	26.5
	3		0.261	0.125	0.176	10.0	30.5
	5	103.7	0.432	0.190	0.292	7.1	32.0
Glycidosilane A-187	1		0.305	0.143	0.189	17.2	25.8
	2	102.9	0.610	0.288	0.408	12.9	27.7
	3		0.953	0.415	0.608	10.3	30.3
	5	102.2	1.525	0.569	0.859	7.6	33.6
Titanate* KR TTS	1		0.260	0.155		15.2	26.1
	2	103.5	0.453	0.211		10.7	28.6
	3		0.681	0.264		8.5	31.3
	5	103.6	1.133	0.322		5.0	34.0

*Found after modification in carbon tetrachloride.

agents used to modify silicate Z-7 on physico-mechanical properties of vulcanizates (tensile strength R_T and 300% modulus M_{300}) are presented in Figs 3 and 4.

Studies performed within varying amount of the silanes and titanate have demonstrated that optimum tensile strength and optimum 300% modulus in vulcanizates are reached when 2–3 weight parts of silanes or titanate are used per 100 weight parts of the filler. Any further increase in the amount of coupling agents during modification, e.g. up to 5 weight parts, results in fillers less capable of improving strength parameters and is economically groundless [18]. The most pronounced reinforcing action in the system zinc silicate - rubber Ker 1500 is shown by titanate KR TTS, mercaptosilane A-189 and glycidosilane A-187. Less active in this respect are aminosilanes A-1100 and

A-1120 even if evidently improved strength parameters have been obtained for vulcanizates filled with zinc silicate modified with aminosilane A-1120 (in both types of mixtures). Application of mercaptosilane A-1893 exerts minimal effects on physicomechanical properties of vulcanizates filled with zinc silicate.

Surface of mercaptosilanes-modified zinc silicate is presented in Fig. 5. Clearly the more pronounced effect of silane A-189 on reinforcing of zinc silicate - rubber Ker 1500 vulcanizates may be explained by the longer alkyl chain ($-(CH_2)_3-$) in the silane molecule adsorbed on the silicate surface.

The Mercaptane group bound to the alkyl chain may penetrate rubber molecule more easily due to greater mobility and greater length of such a chain and, therefore, may exert the evident reinforcing
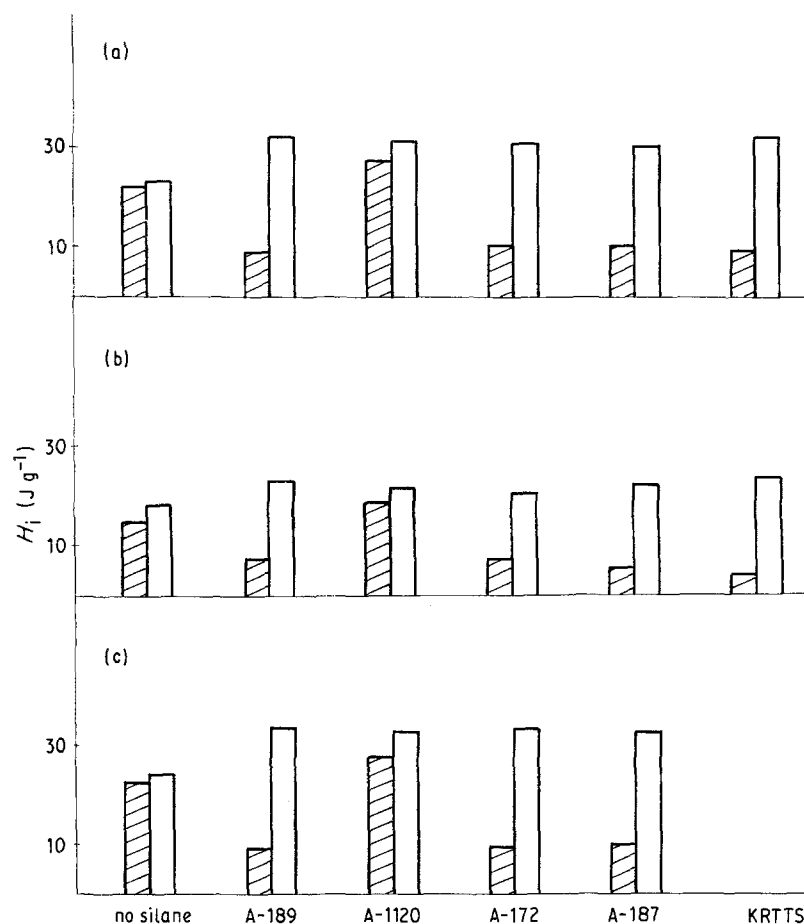
Figure 2 Comparison of heats of immersion in water H_i^W and in benzene H_i^B for different zinc silicate fillers, untreated or treated with 3 wt % silane or titanate coupling agents. (□) = H_i^B, ▨ = H_i^W) (a) Z-7, (b) Z-1, (c) Z-7 + 0.01 mole of bis(2-ethylhexylphosphate) acid per 100 g filler.

effects. In the case of applying silane A-1893, the mobility of the alkyl chain becomes restricted (shortest alkyl chain $-(CH_2)_2$) and the bound mercaptane group can interact at a short range only.

Better strength parameters in the case of using zinc silicate modified with aminosilane A-1120 as compared to that modified with A-1100 reflect the presence of two amine groups in the molecule of A-1120 silane which leads to a higher number of centres on the surface of the silicate which would be capable of interacting with rubber macromolecule.

In the case of zinc silicate modification with titanate KR TTS a monomolecular titanate layer may form on the surface of the silicate, but the presence of silanol groups on the surface may result in condensation of silicate silanol groups with isopropyl groups of titanate. In such a situation, more titanate molecules may be adsorbed on the surface of zinc silicate and, in effect, a higher number of isostearoyl groups may interact with the rubber macromolecule. This would explain the better reinforcing effects of titanate KR TTS in the system zinc silicate - butadiene-styrene

TABLE VI Compilation of heats of immersion in water H_i^W and in benzene H_i^B and carbon contents of the chemisorbed silanes for modified zinc silicate Z-7 in the presence of bis(2-ethylhexylphosphate) acid

Coupling agent in treated silicate (wt %)	Carbon content of the chemisorbed silanes groups (wt %)			H_i^W $J\,g^{-1}$	H_i^B $J\,g^{-1}$
	Calculated	Found after modification in methanol–water solution	Found after modification in anhydrous methanol		
Mercaptosilane					
A-189 1	0.184	0.140	0.152	13.9	26.0
2	0.374	0.219	0.289	10.3	28.4
3	0.555	0.321	0.410	8.6	32.6
5	0.922	0.438	0.643	6.0	32.4
Aminosilane					
A-1120 1	0.270	0.166	0.192	21.9	25.7
2	0.541	0.312	0.409	24.8	27.5
3	0.815	0.423	0.684	27.2	32.4
5	1.351	0.521	0.763	31.5	33.6
Vinylsilane					
A-172 1	0.094	0.068	0.076	15.9	25.4
2	0.173	0.122	0.136	12.0	27.8
3	0.261	0.158	0.201	9.4	32.5
5	0.432	0.235	0.315	6.2	33.6

TABLE VII Physico-mechanical properties of vulcanizates containing the studied zinc silicates unmodified and modified with 3 weight parts of coupling agents (0.01 mole acid was used). Vulcanization time: 30 min.

| Coupling agent in treated silicate	300% modulus M-300 (MPa)	Tensile strength (MPa)	Tension set (%)	Shore hardness (°Sh)	Tearing strength (kN m^{-1})
Mixture I					
Z-1					
No coupling agent	1.6	7.9	25	60	18.3
A-189	3.1	12.7	23	61	20.6
A-1893	2.3	9.8	24	61	19.4
A-1100	2.7	11.2	23	61	20.0
A-1120	2.8	11.5	24	60	19.6
A-172	2.7	12.0	23	61	19.7
A-187	2.7	12.1	22	60	19.9
KR TTS	2.9	11.5	23	61	20.8
Z-7					
No coupling agent	2.7	11.2	32	50	28.2
A-189	4.2	17.5	28	52	31.4
A-1893	3.7	14.4	32	50	29.3
A-1100	3.8	15.2	30	52	29.7
A-1120	4.0	15.4	30	52	30.2
A-172	4.3	16.9	28	52	30.5
A-187	4.1	16.4	31	51	30.0
KR TTS	4.2	16.9	29	52	30.5
Z-14					
No coupling agent	2.1	9.8	26	57	21.7
Z-16					
No coupling agent	2.3	10.3	28	58	23.0
Mixture II					
Z-7					
No coupling agent	4.2	13.7	22	54	28.3
A-189	6.9	20.6	20	56	30.9
A-1893	4.9	15.5	21	55	29.1
A-1100	5.7	16.9	20	56	30.0
A-1120	5.8	17.3	20	56	30.1
A-172	6.0	18.8	20	55	29.9
A-187	5.9	18.3	20	56	29.9
KR TTS	7.1	21.0	20	56	31.1
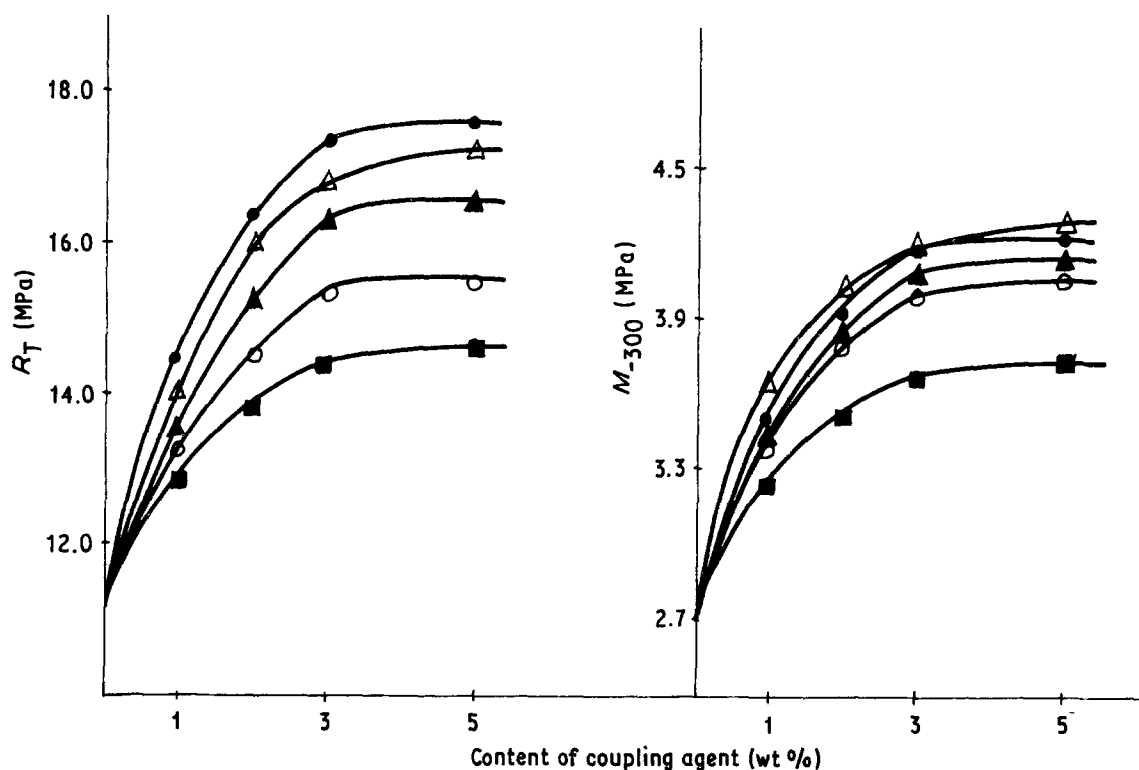
Figure 3 Strength parameters of vulcanizates (mixture I) with Z-7 zinc silicate as a function of coupling agent content (0.01 mole acid was used): (●) A-189, (■) A-1893, (○) A-1120, (△) KR TTS, (▲) A-187.
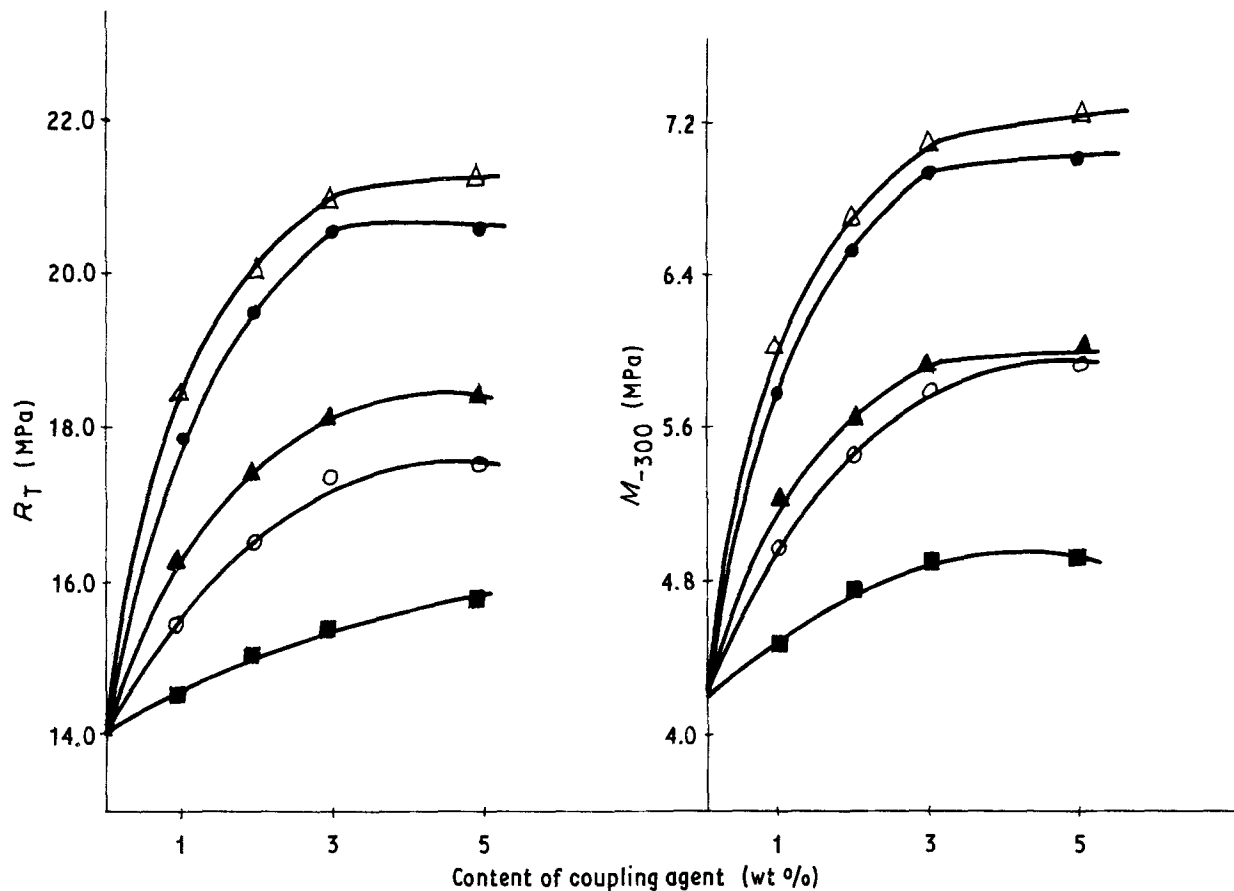
Figure 4 Strength parameters of vulcanizates (mixture II) with Z-7 zinc silicate as a function of coupling agent content (0.01 mole acid was used): (●) A-189, (■) A-1893, (○) A-1120, (△) KR TTS, (▲) A-187.

rubber Ker 1500. Reciprocal interaction of titanate KR TTS with zinc silicate surface is presented schematically in Fig. 6.

4. Conclusions

The studies performed have proven that the amount of coprecipitated zinc oxide present in zinc silicate (e.g. in Z-7 sample) is sufficient to activate a rubber mixture upon vulcanization. Very good strength par-

ameters have been obtained with butadiene-styrene rubber.

Silicate modification with silane or titanate coupling agents improves the wettability of its surface with benzene. The surface of zinc silicate becomes hydrophobic and chemically adsorbed functional groups of silanes or titanate facilitate network rubber formation with the filler during vulcanization. The surface modification of zinc silicate with silane occurs with a
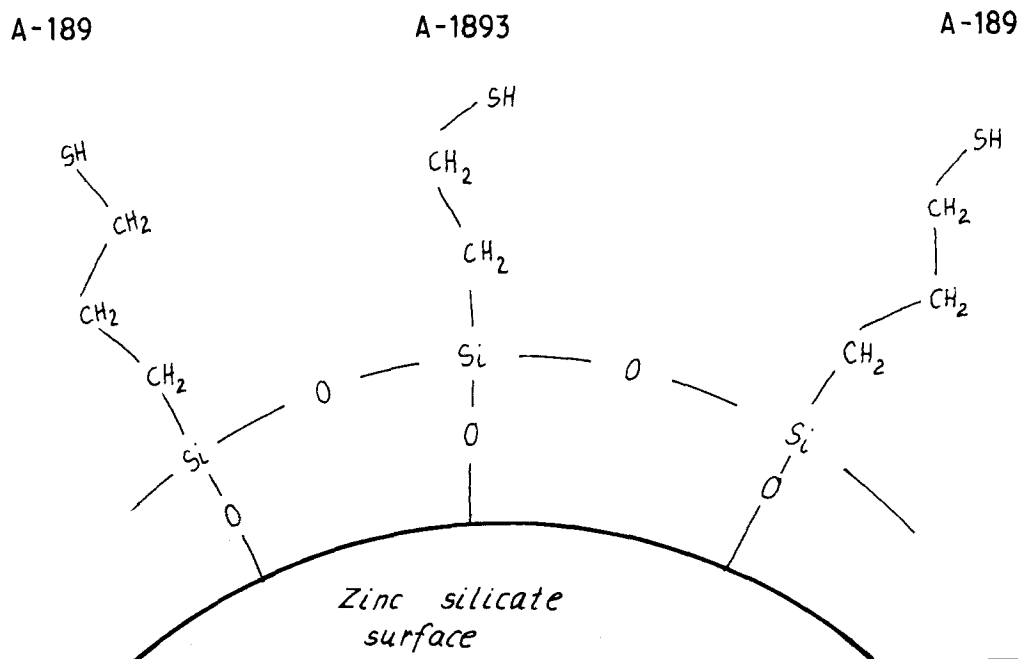

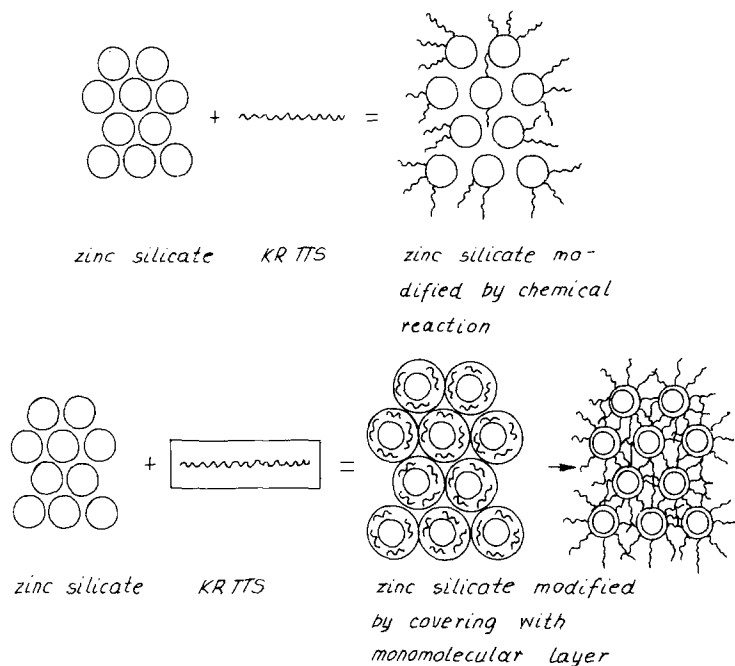*Figure 5* Zinc silicate surface after mercaprosilanes modification.

Figure 6 Interaction of titanate KR TTS and zinc silicate surface.

zinc silicate   KR TTS   zinc silicate modified by chemical reaction

zinc silicate   KR TTS   zinc silicate modified by covering with monomolecular layer

greater yield if anhydrous methanol was used as a solvent of silane. If a methanol–water mixture was used as a solvent, the modification yield decreases, probably as a result of hydrolysis of alkoxysilane. The lower chemisorption of silane on the filler surface is then observed.

Addition of an acidic agent during zinc silicate modification with silane coupling agents promotes an increase in the heat of surface immersion in benzene and in the amount of chemisorbed carbon on the surface.

The optimum content of silane and titanate coupling agents used to modify zinc silicate amounts to 2–3 weight parts per 100 weight parts of the filler.

In vulcanizates of rubber Ker 1500, the best reinforcing effect is exerted by zinc silicate modified with titanate KR TTS, mercaptosilane A-189 and glycidosilane A-187. Less pronounced effects have been noted in cases of zinc silicates modified with aminosilanes A-1100 or A-1120. Zinc silicate modified with mercaptosilane A-1893 only slightly improves strength parameters of vulcanizates as compared to unmodified zinc silicate.

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