Colloid & Polymer Science Colloid Polym Sci 272:1526–1535 (1994)

Model hydrophobing compounds with nitrogen or sulphur atoms in oxyethylene structures, as modifiers of silica filler

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Abstract: Results of studies are presented on effect of new model compounds, applied to modify precipitated silica, on reinforcing of butadiene-styrene rubber vulcanizates filled with modified silica. Precipitated silica applied for the purpose has been obtained according to our own procedure. Estimation of heats of immersion, mainly in benzene, has documented effect of model compounds involving hydrophobization of silica surface.

For comparative reasons, results of strength tests have also been presented on vulcanizates of butadiene-styrene rubber filled with silica modified with a recognized coupling agent-mercaptosilane A-189.

Key words: Silica fillers – coupling agents – oxyethylene compounds – hydrophobization – reinforcing of rubber

1. Introduction

Organofunctional silanes have recently found an increasingly broad application as coupling agents in filler-polymer systems [1–5]. Their unique character relies on the presence in the same molecule of both organic and inorganic functional groups and on the potential to take advantage of each of the characteristic reactivities. The essence of their action involves reciprocal chemical binding of, for example, an inorganic filler (silica, kaolin, etc.) and an organic polymer (butadiene-styrene rubber, polyurethane, etc.). Coupling agents of this type exhibit extensive variability and α, β, and γ-derivatives of silane coupling agents are distinguished [6]. Studies over many years have demonstrated similar durability of α and γ derivatives [7].

In the filler-polymer systems, titanate and borate coupling agents may exhibit similar activity [8–10]. Titanate compounds find an almost universal application: they may serve as modifiers of fillers like chalk or metal oxides which cannot be modified using silane compounds. Elaboration of the techniques used to apply coupling agents to improve resistance parameters in filler-polymer systems did not hamper studies on other agents which might increase mechanical resistance in the systems.

In this work, results of studies are presented on application of specific organic compounds of long chains for modification of filler (particularly precipitated silica) surface. Due to extensive hydrophobization of modified filler surface, they may significantly improve strength parameters of the polymers.

2. Experimental

2.1. Preparation of highly dispersed precipitated silica

Silica was precipitated from sodium metasilicate solution using gaseous carbon dioxide in presence of coagulants. Sodium metasilicate solution was injected at a constant rate to a reactor filled with an appropriate amount of water with dissolved coagulant (calcium nitrate), with intense mixing of the reactive mixture.

CO_2 was fed from a gas tank. Following carbonization, the obtained sediment of silica was left

for 1 h in the mixture and neutralized with diluted hydrochloric acid to approximately pH 6. Upon filtration, the sediment was washed with water (to wash out Cl^- and CO_3^{-2} ions) and it was dried at 150 °C in a spray drier [11].

Optimum conditions for silica precipitation reaction were as follows: temperature: 80–90 °C, module of sodium metasilicate solution: 2.5, SiO_2, content in the carbonated solution: 5% SiO_2, rate of CO_2 injection: 40 $dm^3/h*dm^3$ reactive mixture, content of coagulating agents: 1 to 10 parts of $Ca(NO_3)_2$ per 100 parts of silica contained in the reactive mixture (w/w), final pH of the mixture following neutralization with hydrochloric acid: 6 to 7:

2.2. Compounds used for modification of silica surface

The six model compounds (shown in next page) of the oxyethylene type molecular structure containing nitrogen or sulphur atoms were selected from a broader spectrum of multivalent neutral donor compounds with HLB-values, different ligator atoms (O, N, S) and different number of potential ligator functions.

Some analytical and physicochemical data for these compounds are given in Table 1.

The synthesis of compounds 1–6 include in every case a nucleophilic substitution at a saturated aliphatic carbon atom at elevated temperature between 80° and 130 °C. The working up was done by washing with water, drying the substances by sodium sulfate and fractionating under vacuum.

Compound 1 was so obtained by reaction of a fourfold excess of dibutylamine with triethylene glycol chlorohydrine without a solvent at 120 °C and compound 4 in ethanolic solution by the reaction of an equimolar proportion of octanethiol and sodium hydroxide with the same chorohydrine at 80 °C.

Compound 6 was prepared by the analogous equimolar action of sodium hydroxide, 2-mercaptoethanol and 1-chloro-3,6,9-trioxapentadecane in boiling ethanol.

For the preparation of compound 5 a set of reactions was used. At first hexylbromide was reacted with 2-mercaptoethanol, followed by the reaction with thiourea in a hydrochloric media [15] to obtain the 2-hexylthioethanethiol [16]. The substitution of 1,2-dibromoethane with this compound was the last step.

The syntheses of compounds 2 and 3 were described in [13].

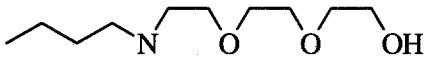
2.3. Evaluation of physico-chemical properties of precipitated silica

Specific area was estimated using a chromatographic technique [19]. The adsorbed amount of nitrogen was calculated from appropriate desorptive peak since it was more symmetrical. Particle size was measured under a microscope using an indirect, one-stage replica technique [20].

Table 1. Physicochemical properties of compounds used for silica modification (a = new compounds described for the first time)

Compound No.	Formula mol. mass	C_{calc} found	H_{calc} found	N_{calc} found	S_{calc} found	B_n °C(Pa)	n_D^{20}	Purity %
1	$(C_4H_9)_2N(CH_2CH_2O)_3H$	64.32	11.95	–	–	117-120(27)	1.4528	99.5
	261.4	64.54	11.80	–	–			
2	$HOCH_2[(CH_2CH_2O)_2C_6H_{13}]_2$	65.20	11.60	3.45	–	175-177(13)	1.4541	99.4
	405.2	65.17	11.63	3.35	–			
3	$C_6H_{13}(OCH_2CH_2)_3N[CH_2CH_2O)_2C_6H_{13}]_2$	66.57	11.60	2.42	–	215-200(7)	1.4525	98.6
	577.3	66.53	11.66	2.30	–			
4[a]	$C_8H_{17}S(CH_2CH_2O)_3H$	60.39	10.86	–	11.51	154-158(0.2)	1.4747	≅99.0
		60.57	10.69	–	–			
5[b]	$C_6H_{13}S(CH_2CH_2S)_3C_6H_{13}$	56.62	10.01	–	33.47	Mp 66-68	–	≅99.0
		56.41	9.96	–	–	from acetone		
6	$C_6H_{13}O(CH_2CH_2O)_2CH_2CH_2CH_2CH_2OH$	57.11	10.27	–	10.89	174-177(120)	1.4740	≅99.0
		57.08	10.05	–	–			

9-butyl-3,6-dioxa-9-azatridecanol [12]



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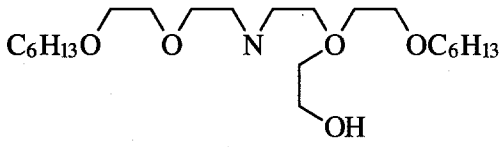
13-(2'-hydroxyethyl)-7,10,16,19-tetraoxa-13-azapentacosane [13,14]



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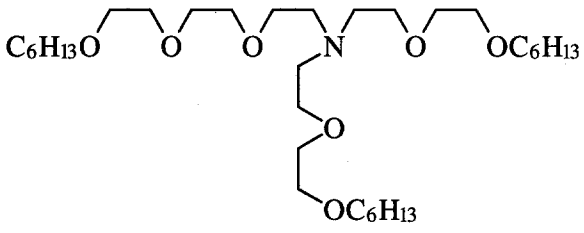
16-(2'-hexyloxyethoxy) ethyl-7,10,13,19,22-pentaoxa-16-azaoctacosane [13,14]



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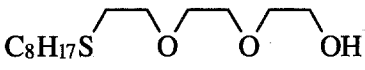
3,6-dioxa-9-thiaheptadecanol [15]



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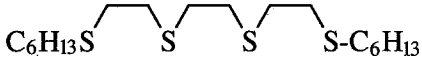
7,10,13,16- tetrathiadocosane [16]



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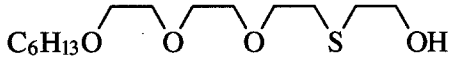
6,9,12-trioxa-3-thiaoctadecanol [17]



6

gamma-mercaptopropyltrimethoxysilane [18]

$SH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si\text{-}(OCH_3)_3$

The objects were filmed in the transmission electron microscope (JEM-7A) Jeolco (Japan). Bulk and packing densities were estimated using an electromagnetic volumeter WE-5.

For a more complete characterization of the fillers, the absorptions of water, dibutyl phthalate and paraffin oil were examined. Value of water absorption was recorded with excess of a single drop of water induced evident liquefaction of the formed paste, while values of phthalate and oil absorptions were recorded when excess of a single drop of the compounds induced a rapid change in paste consistency, causing the paste to adhere to a glass plate.

2.4 Modification of silica surface

Surface modification of precipitated silicas was obtained using organic compounds synthesized as described before and, for comparison, using silane coupling agent, gamma-mercaptopropyltrimethoxy silane A-189 (Union Carbide).

All studied organic compounds, except 7,10,13,16-tetrathiadocosane and gamma-mercaptopropyltrimethoxysilane, were dissolved in methanol while tetrathiadocosane was dissolved in carbon tetrachloride and mercaptosilane in methanol-water solution 4:1 (w/w).

Modification was conducted in a vacuum evaporator, assuring efficient mixing. Amounts of modifying compounds in appropriate solvents (2 parts per 100 parts of modified silica) were adjusted to assure an exclusively uniform wetting of filler's surface in the mixer. After completing a mixing cycle, the solvent was evaporated out and the silica was dried in an oven, at 110 °C [21].

2.5. Determination of heats of immersion of filler surface

Heats of immersion in water (H_i^W) or in benzene (H_i^B) were estimated by the calorimetric technique. In the technique, ampoules were filled with highly dispersed silica, degassed under vacuum for 6 h at 110 °C and, at this stage, heats of immersion were established [22]. The calorimeter permitted to estimate heat effect in conditions approaching adiabatic ones. At first, thermal capacity of the calorimeter was established and, then, heats of immersion were estimated for the examined silica and the tested liquid (water and benzene). In this aim, the ampoule containing accurately weighed out amount of silica was placed in between the jaws of the mill. After crushing of the ampoule, the silica poured down to the container holding with the tested liquid. The observed temperature rise resulted from heat of immersion. It should be mentioned that, in the tests, not the temperature (deg) but rather thermoelectric power STE (mV) was measured.

2.6. Preparation of rubber mixtures and vulcanizates

Unmodified and modified silica fillers were introduced to rubber mixtures, prepared according to standard recipes based on styrene-butadiene rubber Ker 1500 (Chemical Works, Oświęcim). The mixture contained: Ker 1500 rubber-100 parts; zinc oxide-3 parts; stearic acid-2; dibenzothiazole-2.2; *N,N'*-diphenyloguanidine-1.4; silica-50 parts and sulphur-2 parts.

The mixture were vulcanized in the press heated with a steam, with a constant hydraulic pressure of 15 MPa at 143 °C for 20, 30, 40, 50, and 60 min.

The vulcanization optimum was determined using an oscillating disc curemeter (Monsanto rheometer).

3. Results and discussion

3.1. Evaluation of the applied precipitated silicas on grounds of their physicochemical properties

Results of studies on physicochemical properties of silicas, precipitated according to the elaborated procedure in presence of various coagulants, are presented in Table 2.

Silica precipitated in the absence of coagulants exhibits an extensive specific area and relatively large particle size. Microscopic observations have confirmed the above (Fig. 1a) and have permitted to classify the silica as coarse, i.e., granular, gel-like silica. The studies aimed at obtaining highly dispersed sediments and, therefore it proved indispensable to add various amounts of coagulants, e.g., calcium nitrate (1 to 10 parts per 100 parts of SiO_2, w/w in the reaction mixture). At low content of the coagulant, the highly dispersed sediment used to be formed in somewhat lower amounts of

Table 2. Physicochemical properties of precipitated silicas

Amount of coagulant $Ca(NO_3)_2$ w/w%	Specific surface m^2/g	Bulk density g/dm^3	Packing density g/dm^3	Water absorption g/100 g	Dibutyl phthalate absorption g/100 g	Paraffin oil absorption g/100 g	Particle size nm
no coagulant	370.0 (gel)	190	320	400	350	600	150
+ 1 w/w%	220.0	170	265	450	400	700	80
+ 2 w/w %	190.0	140	245	450	400	850	60
+ 3 w/w%	160.0	120	210	500	500	950	40
+ 5 w/w %	125.0	75	110	550	600	1100	25
+ 10 w/w%	105.0	100	145	550	500	1000	35

the gel. Amounts of the latter evidently decreased with increase in amounts of applied coagtulants to 5 weight parts, which clearly also affected the size of formed silica particles (Fig. 1b). Further increase in the amount of the coagulant adversely affected the results: the precipitated silica sediments showed lower specific surface and higher bulk density and the sediments also contained certain amounts of calcium silicate.

The conducted studies on properties of silicas precipitated from sodium metasilicate solutions allowed to; quality for studies the silica precipitated in presence of 5 weight parts of $Ca(NO_3)_2$.

The silica exhibited the most pronounced dispersion (particle size of approx. 25 nm), relatively high specific area (125 m^2/g), low porosity and low bulk density (75g/dm^3), as well as high void volume-high absorption of DBP and oil (absorption of dibutyl phthalate: 600 g per 100 g of paraffin oil – 1100 g per 100 g)

3.2. *Wettability of precipitated silica surface*

Values of heats of immersion on silica surface in water and in benzene are presented in Table 3.

The presented data allow to conclude that modification of silica surface in fact induces significant changes in wettability. The modification has resulted in augmented heats of immersion of the surface in benzene and, in parallel, (with two exceptions), in lowered heats of immersion of the surface in water.

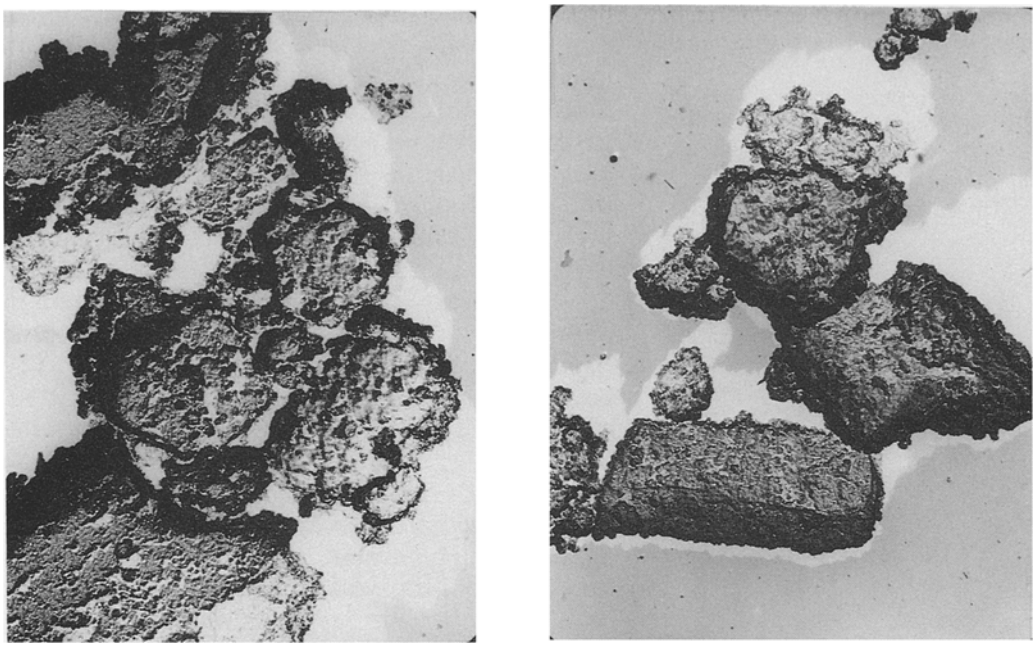
Only in cases of silica modified with substances numbers 4 and 6, has the decrease in heat of immersing in water been insignificant and value of the heat has approached that of unmodified silica surface. Mostly probably, this has reflected the presence of a hydroxyl group in the molecule of the substance which has caused that the surface following modification has been slightly hydrophilic and water molecules used for immersion may interact by hydrogen bonds with the hydroxyl groups. However, such effects were not observed when compounds 1 and 2 were used for modification. They also contain free hydroxyl groups but additionally, basic nitrogen atoms.

Modification with the studied substances has evidently led to hydrophobic transformation of silica surface, pronouncedly affecting strength parameters of vulcanizates containing the fillers. Hydrophobization of silica surface has assisted in increasing chemical affinity of the silica to the filled polymer. Comparing indices of wettability obtained for silica surface modified with synthesized substances and with mercaptosilane A-189, one can note that they approach each other.

In many cases, the values of heats of immersion in benzene for silica surface modified with the new studied substances are higher than the values of heats of immersion in benzene for silica surface modified with the mercaptosilane. The substances contain long alkane groups (C_6H_{13}, C_8H_{17}) which provides them with hydrophobic character. Due to the presence of such hydrophobic groups, silicas modified with the substances show high values of heats of immersion in benzene.

3.3. *Mechanical indices of the obtained vulcanizates of butadiene-styrene rubber*

Values of strength parameters obtained for vulcanizates of the butadiene-styrene rubber Ker 1500 are shown in Table 4.



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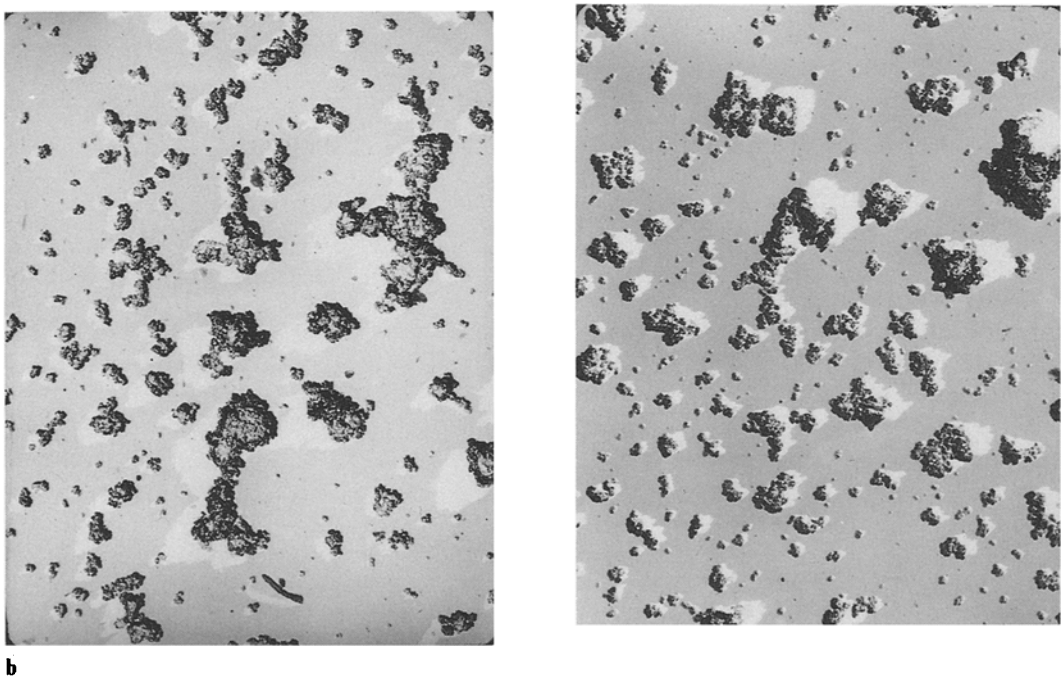

b

Fig. 1. Electromicroscopic images of precipitated silicas a) silica precipitated in the absence of coagulant (magnification 6000x) 1μm = 0.6 cm; b) silica precipitated in the presence of coagulant (5 parts $Ca(NO_3)_2$ per 100 parts of SiO_2 in the reaction mixture) (magnification 6000x) 1μm = 0.6 cm

Data presented in the table demonstrate that addition of modified fillers significantly improves strength parameters of rubber vulcanizates and tensile strength and modules in particular.

In general, one could state that amine derivatives used for modification of silica surface significantly more affect reinforcing of the filled rubber vulcanizates than thiocompounds do.

Table 3. Heats of immersion in water (H_i^W) and in benzene (H_i^B) for untreated silica and silica modified with organic compounds.

Hydrophobing compound		H_i^W J/g	H_i^B J/g
No.	content, w/w %		
no modifier		29.5	29.8
mercaptosilane A-189	1	22.7	35.3
	2	17.5	39.5
1	1	22.8	37.5
	2	17.6	41.0
2	1	22.6	36.9
	2	18.1	40.8
3	1	21.9	37.7
	2	17.2	41.6
4	1	29.2	35.9
	2	27.5	40.2
5	1	22.6	35.2
	2	16.3	39.1
6	1	27.5	37.0
	2	23.2	41.8

Silica modified with amine derivatives and introduced to butadiene-styrene rubber results in a similar strengthening of the vulcanizates as silica modified with highly valued coupling agent, gamma-mercaptopropyltrimethoxy silane A-189. Not all of the amine derivatives used for modification have fulfilled expectations. Silica modified with the compound 3, 16-(2'-hexyloxyethoxy) ethyl-7,10,13,19,22-pentaoxa-16-azaoactacosane, has been least efficient in improving strength parameters of rubber vulcanizates. Both tensile strength and modules increased very little. The greatest increase in strength parameters has resulted from application of silica modified with the compound 1, 9-butyl-3,6-dioxa-9-azatridecanol. In this case, a similar tendency has been observed as that noted with mercaptosilane modified silica: increase in the amount of amine derivative used for silica modification further improves the system of silica-rubber Ker 1500. In the case of using 2 weight parts of the compound 1 tensile strength of vulcanizates filled with the modified silica has amounted to 33.56 MPa (using 2 weight parts of

Table 4. Physicomechanical properties of the vulcanizates based on Ker 1500 rubber, filled with modified silicas (vulcanization time-40 min)

Hydrophobing compound		M-100 MPa	M-200 MPa	M-300 MPa	R_r MPa	E_r %	E_t %
No. content w/w%							
no modifier		4.34	7.82	11.54	14.70	480	12
Amine Derivatives							
1	1	6.08	10.60	16.82	26.50	550	16
	2	6.40	11.40	18.10	33.56	620	25
2	1	6.34	12.12	18.12	30.48	550	23
	2	5.70	10.85	16.83	28.84	600	23
3	1	6.28	11.57	17.40	24.90	525	20
	2	6.04	11.42	17.60	21.75	460	15
Thiocompounds							
4	1	6.28	13.02	20.58	26.52	500	15
	2	3.25	6.18	9.26	22.57	710	23
5	1	5.21	9.45	14.00	21.60	500	19
	2	6.50	11.66	16.14	17.08	400	9
6	1	3.44	10.18	14.36	16.04	450	13
	2	2.84	5.10	7.21	14.66	700	41
Silane coupling agent							
Mercap-	1	5.87	12.01	16.75	25.83	360	18
to silane	2	6.30	14.85	19.26	32.55	360	18
A-189							

silane A-189 the tensile strength has been lowered and amounted to 32.55 MPa). Also, similarly good results have been obtained upon introduction to the rubber Ker 1500 of silica modified with amine derivative 2, 13-(2-hydroxyethyl)-7,10,16,19-tetraoxa-13-azapentacosane. A particularly high module of tensile strength has been obtained upon filling of the system with silica modified with 1 part of the compound.

On the other hand, silica modified with 2 weight parts of compound 2 has proven less efficient in improving strength parameters of vulcanizates. On the grounds of the performed strength testing of vulcanizates filled with silicas modified with amine derivatives, tensile strength and the modules were found augmented most when derivative 1 or 2 were applied. The good results obtained with amine derivatives (No. 1 and 2 in particular) allow to assume that presence of hydroxyl groups in molecules of the compounds may assist in obtaining the most advantageous strength parameters of butadiene-styrene rubber vulcanizates.

Silica modified with thiocompounds, even if they also contain OH groups, has been less efficient in improving strength parameters of butadiene-styrene rubber vulcanizates with the possible exception of silica modified with compound 4, 3,6-dioxa-9-thiaheptadecanol. In Fig. 2

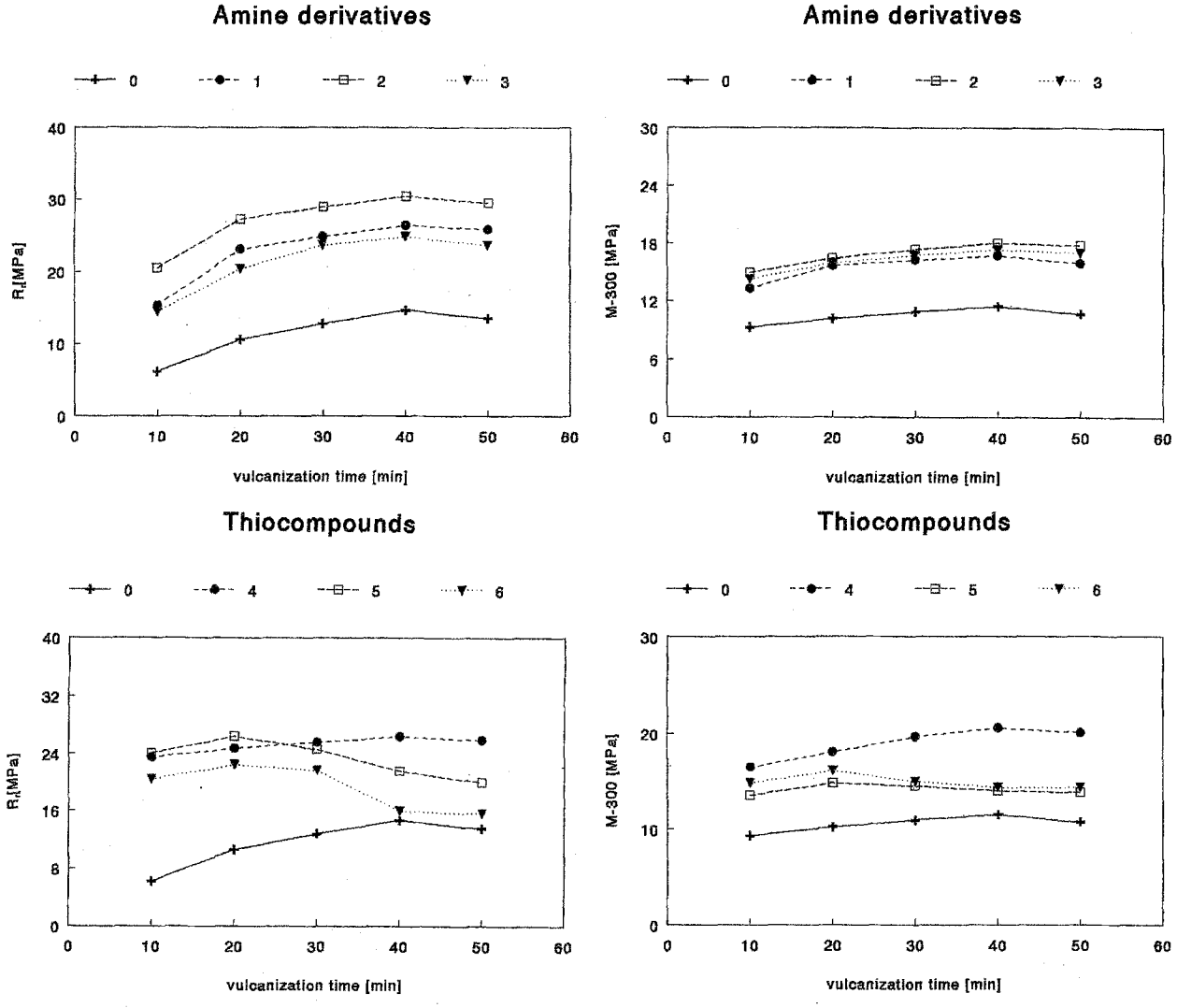

Fig. 2. Dependence of principal strength parameters of butadiene-styrene rubber vulcanizates filled with unmodified and modified silicas upon duration of vulcanization

curves are presented of the dependence of principal strength parameters of butadiene-styrene rubber vulcanizates (module 300 and tensile strength) upon duration of vulcanization, following filling them with silicas modified with amine derivatives with thiocompounds.

As shown in Fig. 2., in the case of using unmodified silica or silica modified with 1 weight part of amine derivatives as fillers of butadiene-styrene rubber, the optimum strength parameters are obtained after 40 min vulcanization. Longer vulcanization results in determination of strength parameters (e.g., after 50 min vulcanization R_r evidently decreased). Similar dependence was obtained for the tensile strength and for the modules. In the case of using thiocompound-modified silicas, similar dependencies in the rubber mixture to those noted in amine compound-modified silicas were observed only for compound 4. Silicas modified with thiocompounds 5 and 6 and introduced to butadiene-styrene rubber improved its strength parameters to a much lower extent after vulcanization lasting 40 min. As is evident from the curves of Fig. 2., maximum values of tensile strength and of module 300 were obtained after much shorter vulcanizations (20–25 min). Most probably, the thiocompounds used to modify silica surface increased the rate of vulcanization with sulphur.

However, silicas modified with 2 weight parts of the compounds have clearly shown worse strength parameters (modules in particular) of vulcanizates, even when compared with system filled with unmodified silica. Following vulcanization, in resistance tests of tensile strength on vulcanizates containing silica modified with all three thiocompounds together, the tested samples underwent deformations and became fragmented into fibers or paddles. It is suggested that in the case of thiocompound modified silicas, times of vulcanization have been erroneously selected and probably the applied thiocompound may accelerate the vulcanization process (they act as vulcanization accelerators). Further studies should be performed on the effect of these thiocompounds on vulcanization rate.

Conclusion

1) Silica precipitated from sodium metasilicate solution with carbon dioxide in presence of 5 weight parts of $Ca(NO_3)_2$ exhibits the most favorable properties (proper dispersion, specific area, and high oil absorption) as a rubber filler.

2) Modification of silica surface with amine derivatives and thiocompound results in its increased hydrophobicity, reflected by an increased heat of immersion of the surface in benzene.

3) Heats of immersion in benzene of the surface of silica modified with new oligoethoxylated tertiary amines and thiocompounds are higher than similar heats of immersion in benzene of the surface of silica modified with mercaptosilane A-189.

4) Filling of butadiene-styrene rubber with silica modified with new model compounds significantly improves strength parameters of vulcanizates, in particular tensile strength and the modules. Amine derivatives used to modify silica surface augment strength of the filled rubber vulcanizates to a greater extent than thiocompounds do.

5) The most advantageous strengthening effect in the silica-butadiene-styrene rubber system has been obtained when introducing to the system silica modified with compound 1, i.e., 9-butyl-3,6,-dioxa-9-azatridecanol. This has provided the system with maximum tensile strength and the best modules.

6) In this respect, clearly weaker effects have been noted when applying thiocompounds to modify silica. The compounds have improved strength parameters of vulcanizates (modules in particular) less evidently but they have affected rate of vulcanization.

7) One weight part of studied oxyethylene compounds was fully sufficient to modify the surface of the precipitated silica, providing, in fact, optimum increase in strength parameters. In the case of silica modified with mercaptosilane application of 2 weight parts of the silane proved more advantageous.

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Received October 19, 1993;
accepted March 24, 1994

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