

Original Contributions

Modification estimate of kaolin, chalk, and precipitated calcium carbonate as plastomer and elastomer fillers

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Abstract: Investigation into possible modifications of surfaces of white fillers such as Kornica chalk, precipitated calcium carbonate and KOG Kaolin. The surfaces of these fillers were modified with a variety of proadhesive compounds in different amounts. Optimum proadhesive compound was determined for each kind of filler. The modified fillers were tested in rubber mixtures based on butadiene-styrene rubber and in polyurethanes.

Key words: Surface modification of fillers – kaolins – chalks – precipitated calcium carbonates – plastomers – elastomers

Introduction

Chalks, kaolins, and synthetically obtained calcium carbonates must meet some definite parameters which decide about their applicability for a given technology [1–2]. It is necessary therefore to learn of all their physico-chemical parameters, such as specific surface area, dispersion degree, wettability with polar and non-polar reagents, surface absorbing, surface structure, etc.

Kaolin and carbonate fillers, both synthetic and natural, reveal some chemical affinity to different polymers to which they are introduced in order to improve physico-mechanical parameters of the latter. The fillers are hydrophilic, which limits their chemical affinity to polymers [3.] This is the reason why the issue of surface modification is so important, and further— the selection of proper modifying substances [4], and their application mode seems so crucial. As far as the former element-modifying substances are concerned— many types of surface active substances [5–6], fatty acids and their derivatives [7–9], silane coupling agents [10–13], titanate coupling agents [14–15] and other metallorganic compounds made on the basis of zirconium-organic compounds and metallocenes [16] may be applied to this effect.

Though for improvement of strength parameters of the filler-polymer system, proadhesive compounds have been widely applied and the technology of their application has been mastered, search for other compounds that could improve the parameters even further has been carried out. It appeared that specific organic oxyethylated compounds with long chains may serve the purpose equally well. It seems that due to a relatively strong hydrophobization, in particular of the surfaces of chalk fillers, their modification with the above compounds may lead to a considerable improvement of strength parameters of polymers.

Experimental

1. Materials

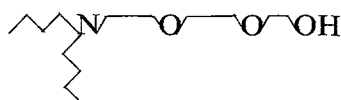
In the studies, three types of fillers of intermediate activity have been applied: KOG kaolin from the deposit in Surmin deposit Bolestawiec, precipitated calcium carbonate [17,18], and natural chalk from the Kornica deposit. Chemical composition and the basic physico-chemical properties affecting the quality of fillers are compiled in Table 1.

Table 1. Chemical composition and physico-chemical properties of white fillers.

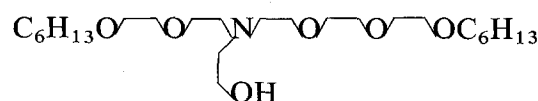
Parameter	Kornica chalk	Precipitated calcium carbonate	Kaolin KOG
CaCO ₃ [%]	97.0	99.9	—
SiO ₂ [%]	—	—	48.52
Al ₂ O ₃ [%]	—	—	37.31
CaO [%]	0.112	0.02	0.33
Fe ₂ O ₃ [%]	0.037	—	1.50
H ₂ O [%]	0.10	0.15	1.0
pH of water dispersion	7.8	7.7	6.0
specific weight [g/cm ³]	2.68	2.6	2.6
flow-off point [cm ³ /log]	2.10	18.1	—
specific surface area [m ² /g]	10.5	16.2	12.6
bulk density [g/dm ³]	640	275	280
packing density [g/dm ³]	1240	320	570
average particle size [μm]	1	0.08–0.40	0.6
whiteness [%]	80	90.1	—
water absorption [g/100 g]	—	—	60
paraffin oil absorption [g/100 g]	—	—	72

For surface modification of fillers of intermediate activity, the following groups of pro-adhesive compounds have been used:

- fatty acids, both saturated and unsaturated, and their derivatives (stearic acid, calcium and magnesium stearates, oleinic acid, tall oil, sorbic acid);
 - surface-active compounds, like cation-active (tetrabutylammonium or ethyltrimethylammonium chloride), anion-active (sodium dodecyl sulfate, sodium glutamate), and non-ionic (polyglycols-polyethylene glycol);
 - proadhesive agents from the group of “coupling agents”: silane coupling agents
- A-172 Vinyltri (β-methoxyethoxy) silane
A-1100 γ-aminopropyltriethoxysilane
A-1120 N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane
A-189 γ-mercaptopropyltrimethoxysilane
A-1893 β-mercaptoethyltriethoxysilane
A-174 γ-methacryloxypropyltrimethoxysilane
A-187 γ-glycidoxypropyltrimethoxysilane titanate coupling agent
KR TTS isopropyl, triisostearoiltitanate organic polyethylene compounds
9-butyl-3, 6-dioxa-9-azatridecanol (compound I)



13-(2-hydroxyethyl)-7, 10, 16, 19-tetraoxa-13-azapentacosane (compound II)



2. Procedure and methods

For fillers surface modification, 0, 5–3.0 weight parts of proadhesive compounds per 100 weight parts of filler dissolved in appropriate solvents were used. Fatty acids their water insoluble salts were transferred to a water-phase via emulsion made in the presence of potassium hydroxide. For example stearic acid and calcium or magnesium stearates were first immersed in ethyl alcohol, then emulsified in water upon potassium hydroxide addition. Oleinic acid, tall oil, and sorbic acid were prepared under the same conditions.

Ionic and nonionic surfactants were prepared by dissolving them in water. Silane coupling agents were dissolved in a mixture of water-methyl alcohol (5:1), titanate coupling agent and polyoxyethylene organic compounds in carbon tetrachloride. The issue at stake here is a proper selection of the amount of the modified compound with respect to the amount of the filler (for plasto- and elastomers). It was assumed that modification should be carried out exclusively via

surface chalk immersion till a homogeneously wetted mass is obtained.

The modification was conducted at a semi-industrial scale, in a mix equipped with a modifying factor feeder [20].

About 1000 g of filler are subjected to modification. For this amount of filler about 300 cm³ of appropriate modifying agents at a required concentration are prepared. After the modification is over, the filler is removed from the mixer, and only then the excess of solvent is removed by drying the product in a flow of hot air at the temperature of 110 °C for 3 h.

Some physical properties may serve as a measure of changes in the filler induced by modification. In our experiment, we have taken into consideration the following parameters:

- bulk and packing densities
- flow-off point and the heat of immersion of filler surface in water and benzene.

Bulk and packing densities were estimated using the electromagnetic volumeter WE-5.

The flow-off point—which represents the lowest amount of water which when shaken with 10 g of chalk and precipitated calcium carbonate results in dense, detaching fragments of slurry flowing off a cylinder inclined at 15°—was estimated according to the norm [21].

Surface modification of fillers significantly affected hydrophobic/hydrophilic properties of the surface. The estimate took advantage of the differences, measuring the heat of immersion of filler surface in water (measure of hydrophilic character) and in benzene (measure of hydrophobic character). The heats of immersion were estimated in the differential calorimeter of the KRM type [22].

All the above determinations were carried out after additional drying of the samples till a constant value of water content below 0, 05% was reached.

To determine the modification effect, an analysis was performed using electron microscopy. To this effect, a method of one-stage replica was applied [23]. Transmission electron microscope JEM 7A (Japan) was used for this purpose. Acceleration voltage of 80 V was applied.

The specific surface area of samples prior to and after filler modification was determined by employing the chromatographic method [24].

Rubber mixtures were prepared on rolling mills. The following mixture composition was accepted: Ker 1500 rubber — 100 percents (wt/wt); ZnO — 5 percent (wt/wt); stearic acid — 1 percent (wt/wt); filler — 50 percent (wt/wt); mercaptobenzotiazole bisulphide — 1, 5 percents (wt/wt); mercaptobenzotiazole — 0, 5 percents (wt/wt); sulphur — 2 percents (wt/wt). In order to determine the vulcanization optimum was prepared using oscillation rheometer (Monstanto) [7]. The mixtures were vulcanized in a press at a pressure of 15 MPa at 143 °C. Duration of vulcanization was 10 to 60 min. Following vulcanization, the principal strength parameters of the obtained vulcanizates parameters were estimated.

For synthesis of polyurethanes, 1,4-diazocyanotoluene/Izocyn T-80, isocyanate groups content 42%/, polyoxypropylene glycol (Rokopol 2002, mean molecular weight 2000) and polyoxypropylene triol (Rokopol 330, mean molecular weight 3600) were used.

Phenylmercuric oleate (Bayer, Germany) was applied as a catalyst. Conditions and the procedure of synthesis were described in a previous publication [25].

3. Discussion of results

If the heats of immersion of the filler surfaces under study were measured in a differential calorimeter of the KRM type, then it was possible to perform these estimations by a dynamic method under conditions close to adiabatic ones, both for polar (water) and non-polar (benzene) liquids. This method permits the estimation of surface modification of carbonate and kaolin fillers, i.e. increase or decrease in either hydrophilicity or hydrophobicity.

Tables 2 to 4 list the values of heats of immersion in water (H_i^W) and benzene (H_i^B) of surfaces of the fillers under investigation and the calculated values of hydrophobization degree (N).

This degree was calculated from the ratio:

$$N = 100 (mH_i^B - nH_i^B) / mH_i^B [\%]$$

where:

mH_i^B — heat of immersion in benzene of surface of modified filler [J/g]

nH_i^B — heat of immersion in benzene of specific of unmodified filler [J/g]

Table 2. Heats of immersion of Kornica Chalk

Type of proadhesive compound	Amount [weight parts]	H_i^W [J/g]	H_i^B [J/g]	h_i^W [J/m ²]	h_i^B [J/m ²]	Degree of hydro- phobization [%]
no proadhesive compound	—	5.40	5.95	0.51	0.56	—
stearic acid	1	4.90	6.90	0.46	0.66	13.8
	2	4.41	7.45	0.42	0.71	20.1
	3	3.96	8.12	0.38	0.77	26.7
magnesium stearate	1	4.90	6.98	0.46	0.66	14.8
	2	4.90	7.54	0.47	0.72	21.1
	3	3.92	8.31	0.37	0.79	28.4
calcium stearate	1	4.92	6.95	0.47	0.66	14.4
	2	4.55	7.50	0.43	0.71	20.7
	3	3.95	8.30	0.38	0.79	28.3
oleinic acid	1	4.80	6.98	0.46	0.66	14.8
	2	4.90	7.55	0.47	0.72	21.2
	3	3.82	8.20	0.36	0.78	27.4
sorbic acid	1	6.02	6.90	0.57	0.60	5.6
	2	6.48	6.52	0.62	0.68	8.7
	3	6.90	6.87	0.66	0.65	13.4
tall oil	1	4.14	7.02	0.39	0.67	15.2
	2	3.85	7.70	0.37	0.73	22.7
	3	3.65	8.30	0.35	0.79	28.3
tetrabutylammonium chloride	1	4.80	7.12	0.46	0.68	16.4
	2	4.31	7.80	0.41	0.74	23.7
	3	3.85	8.52	0.37	0.81	30.2
sodium dodecylsulphate	1	5.21	6.30	0.50	0.60	5.6
	2	4.97	6.75	0.47	0.64	11.9
	3	4.70	7.25	0.45	0.69	17.9
sodium glutamate	1	6.10	6.45	0.58	0.61	7.8
	2	6.61	6.90	0.63	0.66	13.8
	3	6.94	7.50	0.66	0.71	20.7
polyoxyethyleneglycol (PG 4000)	1	6.00	6.45	0.57	0.60	6.3
	2	6.50	6.60	0.62	0.63	9.8
	3	7.01	6.94	0.67	0.66	14.3
mercaptosilane A 189	1	5.20	6.25	0.50	0.60	4.8
	2	4.95	6.48	0.47	0.62	8.2
	3	4.80	6.79	0.46	0.65	12.4
aminosilane A-1100	1	5.90	6.15	0.56	0.59	3.3
	2	6.37	6.30	0.61	0.60	5.6
	3	6.67	6.52	0.64	0.62	8.7
isostearyl titanate KRTTS	1	4.70	7.25	0.45	0.69	17.9
	2	4.15	8.11	0.40	0.77	26.6
	3	3.60	8.96	0.34	0.85	33.3
organic compound I	1	4.77	7.20	0.45	0.69	17.4
	2	4.22	8.00	0.40	0.76	25.6
	3	3.80	8.65	0.36	0.82	31.2
organic compound II	1	4.78	7.18	0.46	0.68	17.1
	2	4.25	7.95	0.40	0.76	25.2
	3	3.82	8.60	0.36	0.82	30.11

These Tables give also values of specific heats of immersion (h_i^W , h_i^B) (heat of immersion relative to the specific surface area of fillers).

Heats of immersion in water H_i^W of all the studied fillers, i.e. Kornica chalk, precipitated

CaCO_3 and kaolin, treated with most of the proadhesive compounds decrease proportionally to the increase in the amount of the added proadhesive compounds. Only in the case of surface modification of the fillers with sorbic acid, sodium

Table 3. Heats of immersion of precipitated calcium carbonates.

Type of proadhesive compound	Amount [weight parts]	H_i^W [J/g]	H_i^B [J/g]	h_i^W [J/m ²]	h_i^B [J/m ²]	Degree of hydro- phobization [%]
no proadhesive compound	—	7.00	7.05	0.50	0.50	—
stearic acid	1	6.60	8.42	0.41	0.52	16.3
	2	6.05	9.00	0.37	0.56	21.7
	3	5.70	9.38	0.35	0.58	24.8
magnesium stearate	1	6.50	8.55	0.40	0.53	17.5
	2	6.02	8.82	0.37	0.54	20.1
	3	5.70	9.46	0.35	0.58	25.5
calcium stearate	1	6.55	8.50	0.40	0.52	17.1
	2	6.00	8.82	0.37	0.54	20.1
	3	5.67	9.46	0.35	0.58	25.0
oleinic acid	1	6.50	8.50	0.40	0.52	17.1
	2	5.92	9.15	0.43	0.56	23.0
	3	5.55	9.60	0.34	0.59	26.6
tall oil	1	6.42	8.61	0.40	0.53	18.1
	2	5.90	9.00	0.36	0.56	21.7
	3	5.71	9.65	0.34	0.60	26.9
tetrabutylammonium chloride	1	6.45	8.30	0.46	0.51	15.1
	2	5.90	9.11	0.42	0.65	22.6
	3	5.71	9.48	0.35	0.59	25.6
sodium dodecylsulphate	1	6.52	8.15	0.97	0.58	13.5
	2	6.01	9.00	0.43	0.64	21.7
	3	5.80	9.20	0.36	0.57	23.4
sodium glutamate	1	6.45	8.32	0.40	0.51	15.3
	2	5.90	9.23	0.36	0.57	23.6
	3	5.21	9.40	0.32	0.58	25.0
polyoxyethyleneglycol (PG 10000)	1	7.25	7.35	0.52	0.53	4.1
	2	8.02	7.70	0.57	0.55	8.4
	3	8.30	7.90	0.51	0.49	10.8
mercaptosilane A 189	1	7.14	7.24	0.44	0.45	2.6
	2	7.30	7.39	0.52	0.53	4.6
	3	7.52	7.60	0.46	0.47	7.2
aminosilane A-1100	1	7.21	7.30	0.45	0.45	3.4
	2	8.12	7.30	0.50	0.45	3.4
	3	8.49	7.77	0.52	0.48	9.3
isostearoil titanate KRTTS	1	6.05	7.92	0.37	0.49	11.1
	2	5.12	9.95	0.32	0.61	29.1
	3	4.70	11.03	0.29	0.68	36.1
organic compound I	1	6.50	8.52	0.40	0.53	17.3
	2	5.50	9.40	0.34	0.58	25.0
	3	5.11	10.48	0.32	0.65	32.7
organic compound II	1	6.53	8.60	0.40	0.53	18.0
	2	5.65	9.32	0.35	0.58	24.4
	3	5.22	10.15	0.32	0.63	30.5

glutamate, polyoxyethylene glycols, and aminosilanes, a slow increase in the value of H_i^W is observed, depending on the amount of proadhesive compound. Heats of immersion in benzene, on the other hand, of surfaces of fillers modified with all types of proadhesive compounds increase,

yet they also depend on the amount of these compounds used.

Increase in the heats of immersion in benzene of filler surfaces – observed after modification – indicates increase in hydrophobization of their surfaces. The highest hydrophobization degree was

Table 4. Heats of immersion of KOG kaolins

Type of proadhesive compound	Amount [weight parts]	H_i^W [J/g]	H_i^B [J/g]	h_i^W [J/m ²]	h_i^B [J/m ²]	Degree of hydro- phobization [%]
no proadhesive compound	—	9.8	10.1	0.78	0.80	—
stearic acid	1	9.00	10.75	0.71	0.85	6.0
	2	8.75	11.12	0.69	0.88	9.2
	3	8.20	11.43	0.65	0.91	11.2
calcium stearate	1	8.95	10.68	0.71	0.85	5.1
	2	8.80	11.01	0.70	0.87	8.3
	3	8.40	11.35	0.67	0.90	11.0
tetrabutylammonium chloride	1	8.02	12.44	0.64	0.99	18.8
	2	7.11	13.69	0.56	1.09	26.2
	3	5.95	14.08	0.47	1.12	28.3
sodium dodecylsulphate	1	9.01	11.25	0.72	0.89	10.2
	2	8.15	11.80	0.65	0.94	14.4
	3	7.45	12.45	0.59	0.99	18.9
polyoxyethylene glycol (PG 10 000)	1	10.35	11.25	0.82	0.82	10.2
	2	11.25	11.94	0.89	0.95	15.4
	3	11.88	12.44	0.94	0.99	18.9
mercaptosilane A-189	1	7.5	12.8	0.60	1.02	21.1
	2	6.4	14.0	0.51	1.11	27.8
	3	5.0	14.9	0.40	1.18	32.2
aminosilane A-1100	1	10.7	11.5	0.85	0.91	12.2
	2	11.9	12.4	0.94	0.98	18.5
	3	13.1	13.6	1.04	1.08	25.7
aminosilane A-1120	1	10.9	11.64	0.87	0.92	13.2
	2	11.95	12.52	0.95	0.99	19.3
	3	13.38	13.81	1.06	1.10	26.9
vinylsilane A-172	1	8.7	11.7	0.69	0.93	13.7
	2	7.3	12.6	0.58	1.00	19.8
	3	6.6	13.7	0.52	1.09	26.3
mercaptosilane A 1893	1	7.72	12.58	0.61	1.00	19.7
	2	6.82	13.71	0.54	1.09	26.3
	3	5.21	14.39	0.41	1.14	29.8
methacryloxysilane A-174	1	8.85	11.95	0.70	0.95	15.9
	2	7.36	13.01	0.58	1.03	22.4
	3	6.52	14.05	0.52	1.12	28.1
glycidoxysilane A-187	1	8.62	11.78	0.68	0.93	14.3
	2	7.15	12.75	0.57	1.01	20.8
	3	6.48	13.80	0.51	1.10	26.8
isostearyl titanate KRTTS	1	6.9	13.65	0.55	1.08	26.0
	2	5.82	14.82	0.46	1.18	31.8
	3	4.39	15.76	0.35	0.25	35.9
organic compound I	1	7.42	13.11	0.59	1.04	22.9
	2	6.25	14.26	0.50	1.13	29.2
	3	4.88	15.20	0.13	1.21	33.6
organic compound II	1	7.35	13.00	0.58	1.03	22.3
	2	6.22	14.05	0.49	1.12	28.1
	3	4.70	14.95	0.37	1.19	32.4

reported for Kornica chalk modified with isostearyl titanate KRTTS, organic polyoxyethylene compounds, fatty acids and their derivatives, as well as for sodium glutamate.

For precipitated calcium carbonate, similar values of surface hydrophobization degree were achieved when analogous proadhesive compounds were used, whereas for kaolins the highest

hydrophobization degree (Table 4) was reached when they were modified by isostearoil titanate (KRTTS), silane proadhesive compounds, organic polyoxyethylene compounds, and by cationic surface active compounds. Their hydrophobization degree is significantly affected by the amount of proadhesive agents, and for 3 weight parts of titanate KRTTS used for modification of all three types of fillers – it is equal to 35–36%.

The performed studies provided evidence that fatty acids and their derivatives considerably improve hydrophobization of carbonate fillers, while to a much lesser degree – of kaolin surfaces. This may be explained by means of a model which illustrates the influence of stearic acid and fatty acid derivatives on surface configuration of modified chalk (Fig. 1).

Increase in the values of strength parameters of rubber vulcanizates as well as of polyurethanes brought about by fatty acids or their derivatives is related to a decrease or increase in polymer matrix density at the surface of solid calcium carbonate in solid state. On the basis of studies on the density of polymer matrix [26, 27], a model describing configuration of polymer chains fragments on chalk surfaces of different modification degree was developed. In the case of unmodified chalk characterized by high surface energy (Fig. 1a), development of rubber or polyurethane chains on chalks surface takes place till these

chains meet other developing chains of these polymers. Due to the above, strong adhesive powers between the chalk surface and chain segments of proper polymer are activated. The remaining chain segments are tangled with other rubber or polyurethane chains, therefore, the number of polymer particles directly linked with the surface of chalk is rather small. As a result, the degree of packing density of polymer in the transition layer is low, even lower than for the filled polymer. Modification with appropriate fatty acid or its derivative causes some changes in surface energy of the filler, as part of surface active centers undergo modification (Fig. 1b) This involves rearrangement of polymer chains near the chalk surface: the developing segments of polymer chains come across an obstacle in the form of aliphatic chains deriving from fatty acids which are placed perpendicularly to the surface. As a result, segments of polymer chains close to the chalk surface assume a clear orientation, which leads to an increase in the packing degree of the transition layer. In this case, the number of polymers in direct contact with chalk surface is the highest.

As follows from Fig. 1c, the result of any further increase of the modifying agent, e.g. above 5 weight parts, is that most of centers active on chalk surface are substituted by aliphatic chains of fatty acids. In consequence, orientation of polymer chain segments near chalk surface is less clear and the packing degree in the transition layer decreases. Then we face a situation which resembles a case when unmodified filler was used in the system with polymer – i.e. on chalk surface entanglement of polymer chains is observed. Chalk surface may react, for example, with stearic acid according to the above mechanism:

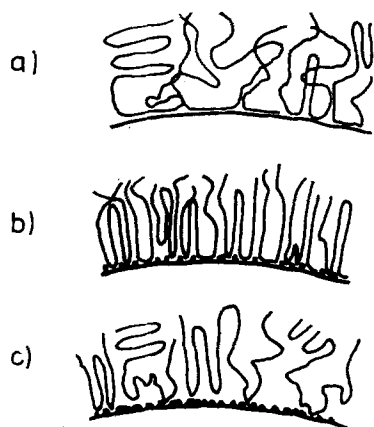
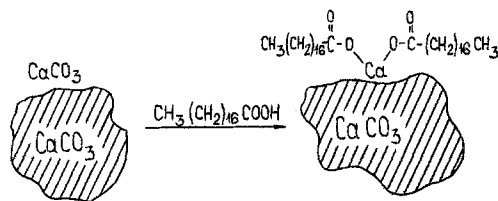


Fig. 1. Configuration of polymer chains fragments on the surface of chalk and precipitated calcium carbonate which are a) unmodified b) partly modified (ca 1–2 weight parts of the proadhesive compound per 100 weight parts of the filler) c) modified to a large extent



Chalk surface modification with stearic acid brings also good results, because it decreases anisotropy of its particles and at the same time increases its specific surface area. All these three factors contribute to the fact that the modified

chalk clearly improves the strength parameters of butadiene-styrene rubber vulcanizates.

In the case of surface modification of kaolin with fatty acids and their derivatives an opposite phenomenon is observed, as the unmodified kaolin has many bound silanol and aluminol group which remain inactive against hydrophobic groups of fatty acids. This is the reason why the hydrophobization degree of kaolin surface after its modification even with 3 weight parts of stearic acid or calcium stearate changes only slightly.

A similar mechanism is observed for the interaction of the surfaces of carbonate surface fillers with sodium glutamate and sodium dodecylsulphate. On these surfaces, according to the above mechanism, various groups will be formed as in the case of stearic acid.

Titanate coupling agents may react both with fillers containing on their surface bonded hydroxyl groups (e.g. silanol or aluminol groups in kaolins) and with fillers which do not contain these groups (e.g. chalk). Fig. 2 illustrates a mechanism of mutual interaction between titanate coupling agents and fillers with or without hydroxyl groups.

As it was proved by the studies on heats of immersion of fillers surfaces (Tables 2–4), the silane coupling agents do not react at all or hardly react with chalk fillers, but they react very well with kaolin surfaces. Bonded silanol or aluminol groups present on the surface of kaolin can condense with hydrolyzed alkoxy molecules of silane coupling agents, while because of an absence of such groups on the surface of chalk fillers, a similar condensation cannot take place.

It should be also mentioned that silane coupling agents contain in one molecule three alkoxy groups capable of condensation with surface hydroxyl group of the filler, while titanate coupling agents possess only one such group. Therefore the titanate may both interact with a filler containing bonded hydroxyl groups and to form on the surface of fillers which do not contain bonded hydroxyl groups – homogenous monomolecular layers of titanate. In view of the above we can say that silane coupling agents practically have no value in surface modification of chalk.

Silane coupling agents on the surface of kaolin interact according to the following scheme (Fig. 3) This Figure illustrates also the interaction mechanism of a functional group of a coupling agents

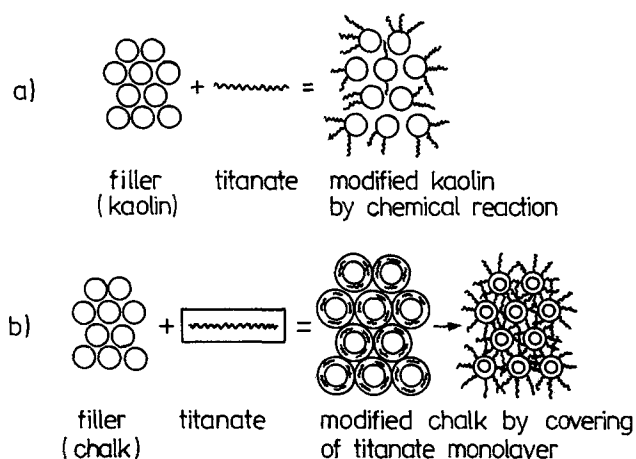


Fig. 2. Interaction between the titanate proadhesive agents and the following fillers a) active filler (kaolin) b) inert filler (precipitated calcium carbonate or natural chalk)

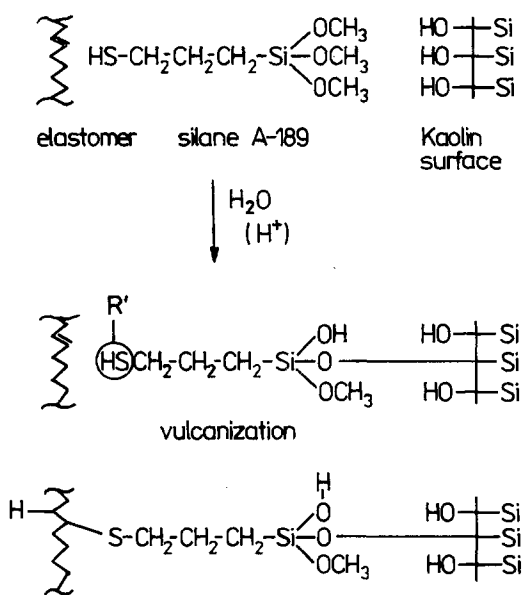


Fig. 3. The probable reaction mechanism in the system-kaolin filler/elastomer with γ -mercaptopropyltrimethoxysilane

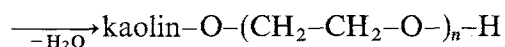
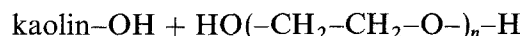
absorbed on kaolin with a chain of polymer (rubber or polyurethane).

Surface active compounds have been found more useful in the kaolin-polymer system than in the chalk-polymer one. In the former case, i.e. for kaolin and non-ionic surface-active compounds, a mixed absorption has been observed. First, these compounds undergo surface chemisorption on kaolin surface, then physical absorption takes

place via interaction between the organic part of the particle of the surface-active compound chemisorbed on kaolin and the molecules of this compound present in water. In the latter case, on the other hand, i.e. on kaolin, due to the absence of surface-active hydroxyl groups, chemical interaction with functional groups of surface-active compounds is practically not possible. Instead, physical adsorption induced by the presence of weak dispersion forces between active centers of chalk surface and the organic part of the surface-active compound particle is observed.

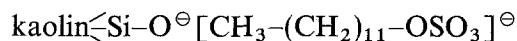
During the adsorption of surface-active compounds, a silanol group (probably the aluminol one too) may act as proton acceptor or donor – in either case any interaction results in decrease in the number of silanol groups (or aluminol). This decrease in the number of bonded hydroxyl groups provides evidence of chemical reaction of exchange between silanol group and R_4NX (cation surface-active compound), which leads to exchange of hydrogen for the R_4N^+ cation accompanied by formation of insoluble $\dots Si-ONR_4$ product. At the same time, acidification of aqueous phase following HX formation is also observed.

For example, on kaolin surface following its modification with tetrabutylammonium chloride, the following compounds are yielded: Non-ionic surface-active compounds may be adsorbed on kaolin surface in the same way as the cation surface-active compound as a result of chemical reaction between bonded hydroxyl groups of kaolin surface and hydroxide groups of a particle of polyethylene glycol.



Adsorption of cation and non-ionic surface-active compounds on surfaces, in particular, of kaolin brings about a significant hydrophobization of these surfaces, which is reflected by increase in the heats of immersion of surfaces in benzene. The directly adsorbed complexes of surface-active compounds help to improve strength parameters of vulcanizate of butadiene-styrene rubber (Table 5) filled with modified kaolins. The interaction of anionic surface-active compound with kaolin surface takes place at the expense of

the Van der Waals forces. Adsorption observed, for instance, for sodium dodecylsulphate, takes the following course:



– where the negative-charged groups repel each other, thus limiting the effect of dispersion forces. This accounts for the weak adsorption of anionic surface compounds on the surface of kaolin. Yet, anionic compounds prove useful in chalk modification, for the sulphate ion is capable of esterification on chalk surface according to the same mechanism as in the case of chalk modification with sorbic acid or sodium glutamate. As a result, chalk surface undergoes hydrophobization, and thus modified chalk better improves the physico-chemical parameters of rubber chinks.

Fig. 4 shows what effect the amount of proadhesive substances used for modification of the studied fillers has on the basic strength parameters of butadiene-styrene rubber vulcanizates. All the application studies performed in rubber proved that surface modification of all fillers by a wide range of proadhesive and hydrophobizing compounds results in a marked improvement of strength parameters of the vulcanizates. As follows from the measurements conducted for various amounts of modifying compounds, the best strength parameters – i.e. tensile strength and modules $M_{100} \dots 300$ (Table 5 and Fig. 4) – were obtained for vulcanizates containing filler modified by 2–3 weight parts of these compounds against 100 weight parts of the fillers. In particular, the most favorable appeared the titanate proadhesive compound KRTTS as it contributes to the improvement of strength parameters of vulcanizates filled with all kinds of fillers. Thus KRTTS turns to be a perfect bridge between the polymer system and inorganic filler (both chalk, precipitated CaCO_3 , and kaolin).

For the chalk-butadiene-styrene rubber system, practically no effect on the increase in the reinforcing has been recorded for silane-coupling agent, which however, significantly contributes to the strengthening of the kaolin-butadiene-styrene rubber system. In the latter case, also chalk and precipitated CaCO_3 modified with 2–3 weight parts of fatty acids or their derivatives may appear of good advantage for the properties of vulcanizates, especially stearic acid or stearates. However, the improvement of strength parameters

Table 5. Physico-mechanical properties of rubber Ker 1500 vulcanizates filled with unmodified and modified fillers (for modification used 2 wt./wt. proadhesive compounds)

Type of sample	Modulus M-300 [MPa]	Tensile strength Rr [MPa]	Elongation Er [%]	Tension set Et [%]	Hardness H [°Sh]	Optimum vulcanization time [min]
Kornica chalk						
unmodified	1.8	4.2	800	34	55	50
modified with stearic acid	2.4	8.6	900	30	60	50
magnesium stearate	2.5	8.6	900	32	60	50
calcium stearate	2.6	8.8	860	32	60	50
oleinic acid	2.8	8.9	940	30	60	50
sorbic acid	2.0	6.2	840	34	58	50
tall oil	2.8	9.6	800	28	60	50
tetrabutylammonium chloride	2.7	9.2	800	28	60	50
sodium dodecylsulphate	1.9	5.7	1000	32	56	48
sodium glutamate	2.3	8.8	9000	30	60	50
polyoxyethylene glycol (PG 4000)	1.7	5.1	1040	36	58	50
mercaptopilane A-189	1.7	5.6	900	36	58	45
aminosilane A-1100	1.8	5.2	900	36	58	45
isostearoil titanate KRTTS	4.1	10.5	800	22	60	40
organic compound I	3.6	9.4	840	24	60	50
organic compound II	3.5	9.2	840	26	60	50
Precipitated calcium carbonate						
unmodified	2.1	6.0	700	18	52	30
modified with stearic acid	2.5	7.4	750	20	52	30
magnesium stearate	2.7	7.7	750	20	52	30
calcium stearate	2.6	7.7	750	20	52	30
oleinic acid	2.8	8.0	680	20	51	30
sorbic acid	2.4	6.4	700	20	53	25
tall oil	3.0	7.8	640	18	53	25
tetrabutylammonium chloride	2.9	7.9	600	16	53	25
sodium dodecylsulphate	2.6	7.0	740	18	52	25
sodium glutamate	2.7	7.4	660	16	52	25
polyoxyethylene glycol (PG 10 000)	2.7	7.4	760	18	52	25
mercaptopilane A-189	2.0	6.2	710	20	51	30
aminosilane A-1100	2.1	6.1	710	18	52	30
isostearoil titanate KRTTS	3.7	10.2	540	16	53	20
organic compound I	3.0	9.4	660	18	52	20
organic compound II	2.9	9.1	640	18	52	20
KOG-kaolin						
unmodified	4.5	5.5	500	8	52	25
modified with stearic acid	4.6	5.7	500	16	51	25
tetrabutylammonium chloride	5.2	8.1	420	10	52	25
sodium dodecylsulphate	4.5	5.6	500	14	51	25
polyoxyethylene glycol (PG 10 000)	4.8	7.2	450	12	52	25
mercaptopilane A-189	5.6	8.9	420	10	52	20
mercaptopilane A-1893	5.4	8.6	420	10	52	20
vinylsilane A-172	5.2	8.0	460	10	52	20
aminosilane A-1100	5.2	8.0	440	12	52	20
aminosilane A-1120	5.3	8.2	440	12	52	20
methacryloxysilane A-174	5.5	8.5	420	10	52	20
glycydoxy silane A-187	5.0	7.9	420	14	52	20
isostearoil titanate KRTTS	6.1	10.1	400	10	52	25
organic compound I	5.5	8.7	420	10	52	20
organic compound II	5.4	8.6	420	10	52	20

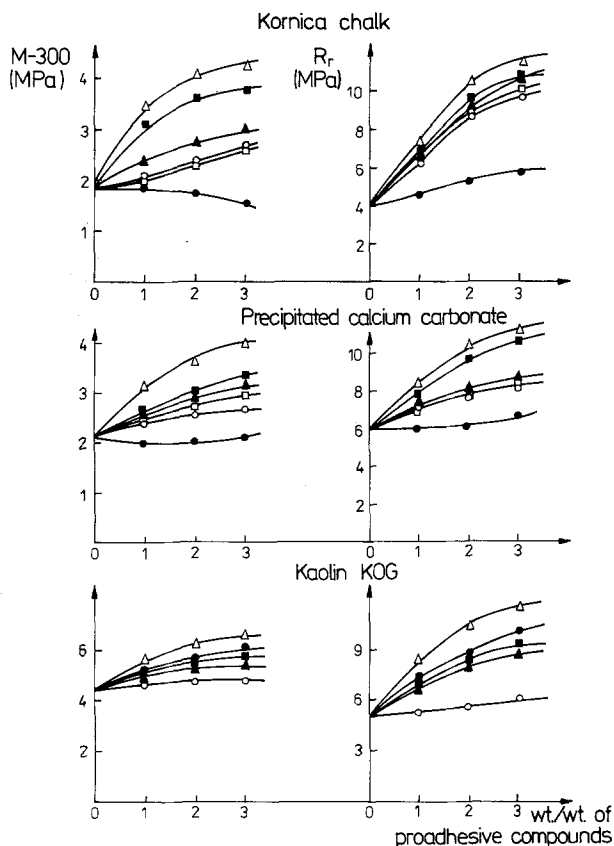


Fig. 4. Effect of the amount of proadhesive compounds used for modification of the fillers studied on the basic strength parameters from butadiene-styrene rubber (vulcanization time—30 min.)

obtained for vulcanizates containing chalk fillers modified with an optimum amount of titanate is incomparably greater than that observed for parameters obtained for vulcanizates filled with these chalks modified with fatty acids or their parameters. In the case of chalk fillers in the system with rubber, good effects can also be reached when these fillers are modified with organic oxyethylene compounds of an evidently hydrophobic nature.

As far as the application of kaolin as filler of rubber mixtures is concerned, the best results are observed when its surfaces are modified with stearoil titanate or silane-coupling agent A-189. When, however, it is modified with stearic acid or stearate, the strength parameters of the vulcanizates are barely improved irrespective of the amount of these compounds used for modification. Application of cation surface-active com-

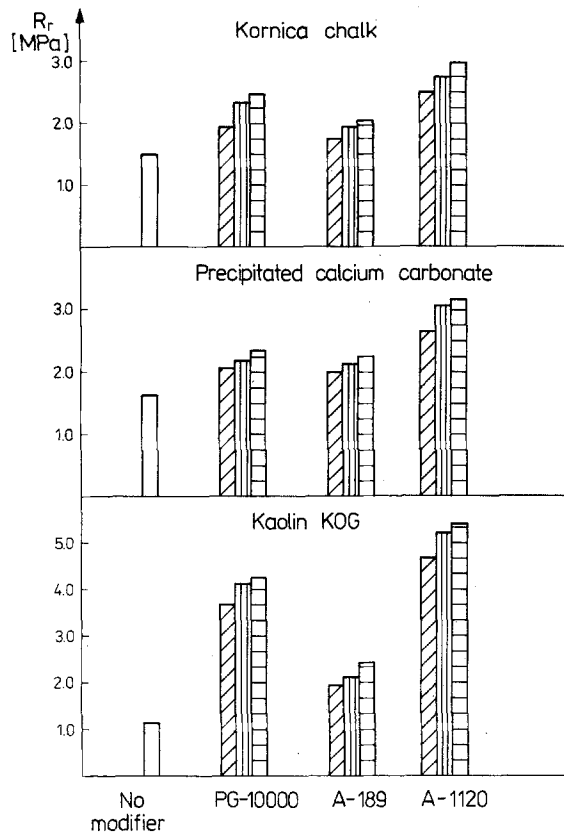


Fig. 5. Tensile strength of urethane composites containing various modified or unmodified fillers: no modified \square 1 percent [wt/wt] of proadhesive compound agent \square 2 percent [wt/wt] of proadhesive compound agent \blacksquare 3 percent [wt/wt] of proadhesive compound agent \square

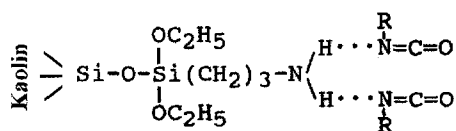
pounds for modification of all kinds of fillers causes some increase in the strength parameters of vulcanizates, yet this increase is rather mediocre.

Table 6 and Fig. 5 shows results of the studies of application of chalk fillers, precipitated CaCO_3 , and kaolin in polyurethanes. Unmodified fillers in the urethane system exert only a slight effect on the increase in strength parameters, unlike in the processing of polyurethanes, where the unmodified fillers contribute to a large increase in the strength parameters (in some case the tensile strength increases by 300 to 500%). This in particular applies to aminosilanes (A-1100 and A-1120). Such an improvement of the strength parameters of polyurethanes filled with unmodified fillers, eg. aminosilane A-110, is probably due to the fact that the aminosilane absorbed on the surface may form crosslinkings between polyurethane and filler. Especially,

Table 6. Physico-mechanical properties of polyurethanes filled with unmodified and modified fillers (for modification used 2 wt./wt. proadhesive compounds: for filled polyurethanes used 30 wt./wt. fillers)

Type of sample	M-100 [MPa]	Rr [MPa]	Er [%]	H [°Sh]	Hysteresis [%]
no filler	0.76	0.92	100	39	1.00
Kornica chalk					
unmodified	1.10	1.50	145	60	4.12
modified with: polyoxyethylene glycol (PG-10000)	1.60	2.32	165	62	5.60
sodium glutamate	1.65	2.55	160	61	6.95
mercaptosilane A-189	1.40	1.90	155	61	4.82
aminosilane A-1100	1.70	2.60	155	62	7.49
aminosilane A-1120	1.75	2.72	155	62	7.70
glycidoxysilane A-187	1.42	2.00	160	61	4.90
Precipitated calcium carbonate					
unmodified	1.10	1.65	205	55	6.30
modified with: polyoxyethylene glycol (PG-10000)	1.58	2.20	170	58	7.30
sodium glutamate	1.70	2.75	180	58	7.10
mercaptosilane A-189	1.50	2.18	180	57	7.20
aminosilane A-1100	1.90	2.88	165	58	9.15
aminosilane A-1120	1.95	3.02	165	57	9.20
glycidoxysilane A-187	1.58	2.15	180	57	7.20
isostearoil titanate KRTTS	1.08	1.60	200	56	5.36
KOG Kaolin					
unmodified	0.80	1.20	200	60	—
modified with: polyoxyethylene glycol (PG-10000)	2.65	4.15	200	60	—
sodium glutamate	2.35	3.12	200	60	—
mercaptosilane A-189	1.82	2.08	200	60	—
aminosilane A-1100	5.22	5.25	200	61	—
aminosilane A-1120	4.70	5.30	200	60	—
glycidoxysilane A-187	1.92	2.02	200	60	—
isostearoil titanate KRTTS	—	—	300	60	—

kaolins modified with silane A-1100 may also interact with isocyanate groups in the following way:



The dependence between the strength properties of polyurethanes and the amount of filler is extreme in character, whereas the optimum modules and tensile strength parameters are obtained for systems containing 20–30% of either modified or unmodified filler.

Conclusion

1. All proadhesive compounds used for modification of the fillers under study bring about increase in surface hydrophobization of these fillers.

a. for the Kornica chalk and precipitated calcium carbonate, the hydrophobization degree is the highest, against titanate, organic oxyethylene compounds, fatty acids and their derivatives, as well as against sodium glutamate.

b. for kaolins the highest hydrophobization degree is obtained when they are modified with titanate and silane proadhesive compounds, organic oxyethylene compounds, and cationic surface-active compounds.

c. hydrophobization degree is closely dependent on the amount of proadhesive compound used for modification (the optimum amount is 2–3 weight parts per 100 weight parts of filler).

2. The studies performed allow us to claim that titanate proadhesive compounds may interact with fillers either containing on their surface or not bonded hydroxyl groups.

3. Studies on the application in butadiene-styrene rubber proved that surface modification of all fillers by proadhesive or hydrophobizing compounds result in improvement of strength parameters of the vulcanizates.

4. A strengthening effect has been noticed in the filler-polyurethane system when unmodified fillers are applied. In particular, a very favorable influence is induced by silane coupling agents from the amine group.

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