Surface-modified microporous talcs as fillers of polymers and pigments

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We present four modification methods for previously micronized Korean talcs using surfactants, polyoxyethylene glycols, silane and titanate coupling agents. The modifications provide an increase of activity of the talc towards polymers. After the modifications, the wettability of the talcs in water and benzene were measured by a calorimetric technique. A correlation between the heat of immersion and the coverage of the talc surface has been determined. Attempts were made to apply the modified Korean talcs in rubber mixtures (with butadiene–styrene rubber), in PVC and in highly dispersed pigments.

The ability of mineral fillers to reinforce polymers may be controlled by substitution of the hydrophilic surface by a partially or fully hydrophobic one. For this purpose modifying substances are used termed proadhesive compounds. A few techniques are available to change the filler particle surface, which leads to improved interaction between the polymer and the filler (organophilic transformation). Techniques used include change in the type of superficial layer of the filler due to adsorption of modifiers,[1] physical adsorption of a modifying compound to the filler surface (*e.g.* polymer surface),[2] or modification by processing of the filler in solutions of the proadhesive compounds.[3]

The most convenient method is the latter technique.[4] Mineral fillers after surface modification are more difficult to wet with water and demonstrate affinity towards non-polar organic fluids.[5] This results in several advantages. Physico-mechanical properties of the polymers are improved (they show greater tensile strength, tearing strength, and they show higher modulus values). In this way superior rubber products can be obtained with potential exploitation. Moreover, improved processing of the rubber mixture is observed (shorter preparation time, higher plasticity, improved drawing and injection properties).

For surface modification of mineral fillers, various proadhesive coupling agents and adhesion promoters can be applied. The optimum adhesion promoter for systems including mineral filler and a polymer should couple not only the filler but also the polymers. The proadhesive compounds (coupling agents) include silane, titanate, borate, zirconate, hafnate species containing alkoxy groups.[6–10]

Among mineral fillers, particular attention has been devoted to talc. Since it is a passive filler it has to be subjected to activation before application to a polymer mixture. Talc has a chain structure[11] consisting of the layers of $(Si_2O_5)_n{}^{2n-}$ and $[Mg_3(OH)_2]_n{}^{n-}$.

Apart from the hydrophobic centres associated with the presence of siloxane groups the siloxane layer also contains hydrophilic silanol groups. Moreover, the brucite layer contains a clear-cut hydrophilic centre (Mg—OH). As a result of this structure, talc is a naturally hydrophobic filler with a wetting angle of 85°.[12]

The present study is aimed at obtaining talcs with an increased chemical affinity toward polymers. This may be achieved by introduction of functional groups to the talc surface capable of interacting with the polymer functional groups (*e.g.* amino, sulfanyl,† vinyl, *etc.*). It is for this purpose that the talc surface is subjected to modification.[12]

Experimental

Materials

Talc originating from deposits in South Korea was used in these studies. The Korean talc was also used following additional grinding using pressurised air. Physicochemical characteristics of the studied talcs are given in Table 1.

Various proadhesive compounds were used to modify the surface of the talc. Among surface-active agents, tetrabuthylammonium chloride and poly(oxyethylene glycol) (PG 4000) were used, while the silane coupling agents γ-sulfanylpropyltrimethoxysilane, γ-aminopropyltrimethoxysilane, vinyltris(β-methoxyethoxy)silane and γ-methacryloxypropyltrimethoxysilane were used or the titanate coupling agent isopropyltriisostearoyl titanate was applied.

Methods of study

The used talcs had an average particle size ranging between 10 and 20 µm. Such fillers show no strengthening properties toward polymers and, therefore, they were subjected to grinding. For this purpose a stream-circulatory horizontal mill of a Jet Mizer type model 0202 (USA) was used. The grinding medium involved pressurised air at a pressure of 6 atm. Particle sizes were determined using an electron microscope (model JEM 1200 EX II, Japan).

The degree of dispersion and the range of particle size distribution were determined using a Sedi Graph 5100 analysis of particle size. Studies related to talc of particle size ranging between 0.5 and 60.0 µm.[13]

Surface modification of talc was carried out by a variety of procedures listed below.

Table 1 Physicochemical parameters of Korean talc before and after micronization

parameter	Korean talc	micronized Korean talc
humidity (%)	0.60	0.40
pH of aqueous dispersion[a]	9.50	9.50
decrease in mass (%) following calcination at 900 °C	5.25	5.35
specific mass/g cm^{-3}	2.75	2.75
bulk density/g dm^{-3}	770	640
packing density/g dm^{-3}	1020	880
specific surface area/m^2 g^{-1}	10.40	13.60
mean particle diameter/µm	15	0.85

[a] 4–5 g of talc dispersed in 100 cm^3 of water

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† The prefix 'sulfanyl' is preferred to 'mercapto' (see *A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations 1993*, Blackwell, Oxford, 1993).

Modification by evaporation of solvent (method 1). Since the boiling points of the applied coupling agents are quite high (ranging between 200 and 280 °C), the talc surface modification process was conducted in a solution of the proadhesive compound in CCl_4 (bp = 76.5 °C). With continuous mixing at 80 °C CCl_4 was evaporated from the reaction system. The studies were performed in solutions with a concentration of 0.5, 1.0, 2.0, 3.0 and 5.0% of the appropriate modifying compound in CCl_4.

Heating of a talc-modifying solution system under a reflux condenser (method 2). Proadhesive compounds of various concentration were used in solutions of carbon tetrachloride, methanol, water or water–methanol (1:4). The choice of the solvent depended upon the applied proadhesive compound. The system was warmed under a reflux condenser for 2 h under continuous stirring. Following heating under a reflux condenser, all samples were subjected to solvent evaporation, and then dried at 110 °C.

Surface modification on a laboratory scale (method 3). The modification was performed in an evaporating apparatus. The vacuum evaporator was charged with talc and proadhesive compound solution in an appropriate solvent. A minimum amount of solution was added so that the talc surface was just wetted by the solution and the reaction was carried out for 1 h at room temperature. Subsequently the talc was dried at 105 °C with an electric drier with circulation of the warm air.

Talc surface modification at a semitechnical scale (method 4). At a semitechnical scale, a mixer of our own construction with a capacity of 3.5 dm^3 was used,[14] and is schematically shown in Fig. 1.

The mixer consists of a V-shaped container which slowly turns around the axis, parallel to the plane of the V. A dosing appliance is fixed on the axis, which rapidly revolves in the opposite direction, which, as a result of the metal wings placed on its surface, distributes the wetted filler formed during the process, while the modifying solution is introduced under centripetal force to the container from the dosing appliance *via* special openings during rapid spinning.

Owing to the rapid spinning of the dosing appliance and slow mixing of talc inside the container, full mixing of talc particles with the solution of the appropriate modifying compounds was achieved. The complete mixing cycle lasted 1 h and 500 g talc and 150 cm^3 of modifying solution were used. After the mixing cycle the solvent was removed and the talc was dried.

Heats of immersion of the surface in water (H_i^W) and in benzene (H_i^B) for the modified and unmodified talcs were established using a calorimetric technique. A KRM-type calorimeter[15] enabled the detection of even slight thermal effects by a dynamic technique under conditions approaching adiabatic. The extent of surface modification or hydrophobization was calculated using eqn. (1),

$$N = \frac{(H_i^B)_m - (H_i^B)_n}{(H_i^B)_m} \times 100\%$$

where $(H_i^B)_m$ is the immersion heat of the modified talc surface in benzene in J g^{-1} and $(H_i^B)_n$ is the immersion heat of the unmodified talc surface in benzene in J g^{-1}.

The unmodified and modified talcs were tested in rubber mixtures. The mixtures consisted of: 100 SBR rubber (Ker 1500) : 5 zinc oxide : 2 stearic acid : 100 unmodified or modified talc : 2.2 DM accelerator (sulfanylbenzothiazolyl disulfide) : 1.4 accelerator (2-sulfanylbenzothiazole) : 2 sulfur, by mass. Vulcanization was conducted in a hydraulic press under steam heating at 143 °C, under a pressure in the press cylinder of 150 atm for 20–40 min.

Unmodified and modified talcs were also applied as fillers for PVC.[16]

The mixture compositions were as follows: PVC (type 568; 280 g), DOP (dioctyl phthalate) (120 g), Ergotherm SBK II (stabilizer) (1.4 or 2.8 g) and filler (120 g).

The thermal stability of the PVC foil was determined using typical thermal tests, while gelling time and plasticity were examined in a Plasti–Corder–Brabender type of apparatus.

PVC mixtures were prepared in a laboratory drum at the following conditions: drum temperature = 165 °C, slit approximately 0.5 mm, friction = 1 : 1.4, speed of the free drum = 25 rev min^{-1}, duration of rolling *ca.* 10 min.

In addition, pigment studies were conducted, such as estimation of solubility, in water, acids and alkali, and determination of the sedimentation volume. In order to estimate the sedimentation volume in an aqueous medium, a graduated cylinder (10 cm^3) was used, with a ground stopper and graduation marks spaced by 0.10 cm^3. In the cylinder, 1 g of the sample was shaken in 10 cm^3 distilled water. The volume of the sediment (V_s) was measured after 6 h of sedimentation.

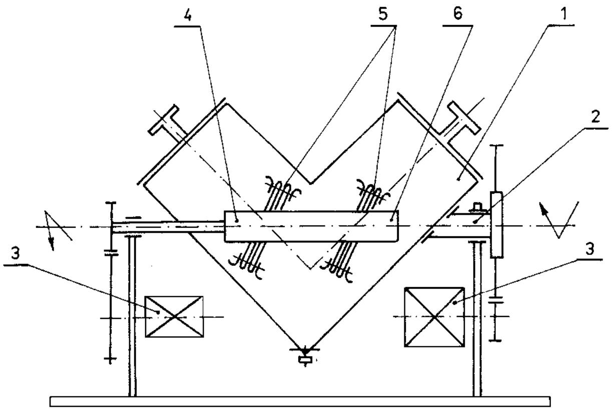


Fig. 1 Blender for surface modification of mineral fillers. 1, V-shaped container; 2, axis of rotation; 3, motors; 4, revolving dosing appliance for the modifying solution; 5, metal wings; 6, dosing appliance opening for introduction of the solution.

Discussion

Additional disintegration of talcs, performed in an air jet mill, decreased significantly the size of particles and also improved significantly the extent of dispersion. The particle size and the extent of grinding in individual ranges of grain size distribution before and after micronization of the studied filler samples are compared in Table 2.

As evident from the results of Table 2, a significant decrease in the talc particle diameter (on average a 10- to 15-fold decrease) was achieved. For example, particles of Korean talc,

Table 2 Degree of dispersion of studied talcs determined by analysis of particle size (Sedi Graph 5100)

particle diameter/μm	mean mass%	av. particle diameter/μm
	Korean talc	
<0.5	1.1	
0.5–3.0	4.8	
3.0–5.0	6.3	
5.0–15.0	72.3	15.0
>15.0	15.6	
	micronized Korean talc	
<0.5	8.3	
0.5–3.0	68.8	0.95
3.0–5.0	14.6	
5.0–15.0	6.8	
>15.0	1.5	

ranging in size originally between *ca.* 12 and 15 µm, following micronization ranged from *ca.* 0.8 to 1.0 µm.

The modification studies have established that it is most advantageous to introduce surfactants to the talc surface from aqueous solution, silane coupling agents, after dissolving them in water–methanol (1 : 4), while titanate coupling agents should ideally be introduced from CCl_4 solution.

During evaporation of the solvent (modification according to method 1) products were obtained with an uneven surface coating of proadhesive compounds. This has been demonstrated by irreproducible results of measuring talc surface wetting enthalpies following modification by this technique. This method may find application only in the case of small samples (*ca.* 10 g) of modified talcs.

Talc modification using methanol solution of silanes is easier to perform than when dissolving the silane in CCl_4. It has also been noted, that heating for 2 h has no effect on the properties of the modified talc and thus the time may be shortened to 1 h.

Values of surface wetting enthalpies for micronized talcs in water and in benzene and the calculated degree of surface hydrophobization following modification with various methods are compared in Table 3.

During talc modification, an increased amount of proadhesive compounds used is associated with their increased adsorption on the surface (as indicated by increasing values of the extent of hydrophobization for the modified talc surface). This is most probably associated with the fact that, with lower amounts of proadhesive compounds available, the most active centres of the talc surface become saturated first, while with higher amounts of available proadhesive compounds centres of lower activity become gradually saturated. Moreover, under the effect of the applied proadhesive compounds, splitting of talc particle agglomerates may take place with a resulting increase in talc outer surface area and appearance of new active centres, capable of chemisorption of consecutive modifying agent molecules. As is evident from the presented data (Table 3), increasing amounts of proadhesive compounds introduced to the surface of the studied talcs (except for polyoxyethylene glycol and aminosilane) are associated with a decrease in values of the immersion enthalpy of the talc surface in water, while immersion heats of the talc surface in benzene increase. For modified talcs, particularly when they are modified with titanate, tetrabutylammonium chloride, sulfanylsilane, vinylsilane or methacryloxysilane, hydrophobization is pronounced. Talc surface modification with aminosilane and polyoxyethylene glycol leads to production of talc particles with clearly increased immersion enthalpies of the surface with water. Increased hydrophilicity of the talc surface in this case results from the ability of amine groups (silane) and hydroxy groups (glycol) to form hydrogen bonds with silanol groups on its surface.

The measurements of wetting enthalpies for the modified talc surfaces have enabled evaluation of the applied modification techniques, performed according to methods 3 and 4. In each of the techniques the modification is conducted using surface wetting of the filler surface with a solution of proadhesive compound. Application of modifying compounds at the talc surface from solution (method 2) is less advantageous and lower degrees of talc surface hydrophobization are served. Moreover, a significant amount of the solvent has to be evaporated, which significantly affects economic factors.

Results of strengthening studies of vulcanizates filled with some modified and unmodified micronized talcs are shown in Table 4; modification was conducted at a semitechnical scale (method 4).

The dependence between basic strengthening parameters of vulcanizates and the amount of proadhesive compounds used for the talc modification is shown in Fig. 2.

As is evident from the presented data (Table 4 and Fig. 2) the best strengthening parameters have been obtained for vulcanizates containing talcs modified with sulfanylsilane, methacryloxysilane or isostearoyl titanate. The sulfanyl, methacrylic and isostearoyl groups exhibit high chemical affinity toward functional groups of sulfur vulcanized butadiene–styrene rubber. During the vulcanization of SBR with sulfur, already filled with talc modified with sulfanylsilane, the filler couples with the rubber matrix according to the proposed Scheme 1.

In the case of talcs modified with surfactants, less significant strengthening of vulcanizates is observed. This arises from the absence on the surface of these talcs of groups capable of interacting with the rubber by a specific chemical reaction. On

Table 3 Comparison of degrees of immersion surface hydrophobization for micronized talcs after modification by various methods

proadhesive compound	mass%	method 2			method 3			method 4		
		H_i^w/J g^{-1}	H_i^B/J g^{-1}	N(%)	H_i^w/J g^{-1}	H_i^B/J g^{-1}	N(%)	H_i^w/J g^{-1}	H_i^B/J g^{-1}	N(%)
unmodified talc	—	12.5	14.0	—	12.5	14.0	—	12.5	14.0	—
tetrabutylammonium chloride	1	9.0	16.0	12.5	8.5	16.7	16.2	8.8	16.9	17.2
	2	8.2	17.2	18.6	7.7	17.9	21.8	8.0	18.1	22.7
	3	6.6	19.1	26.7	6.0	20.0	30.0	6.5	20.0	30.0
polyoxyethylene glycol (PG 4000)	1	12.9	15.2	7.9	12.9	15.8	11.4	12.6	16.0	12.5
	2	13.4	16.9	17.2	13.8	17.4	19.5	13.5	17.5	20.0
	3	14.7	18.1	22.7	15.1	18.7	25.1	14.7	19.0	26.3
γ-sulfanyl-propyltrimethoxy silane	1	10.5	16.0	12.5	9.8	16.8	16.7	9.7	17.0	17.6
	2	8.6	17.5	20.0	8.3	18.2	23.1	8.5	8.4	23.9
	3	7.0	19.2	27.1	6.5	20.3	31.0	6.3	20.2	30.7
γ-amino-propyltrimethoxy silane	1	13.0	15.4	9.1	13.6	16.1	13.0	13.5	16.4	14.6
	2	14.1	17.0	17.6	14.8	17.5	20.0	15.0	17.8	21.3
	3	15.7	18.3	23.5	16.2	18.9	25.9	16.4	19.3	27.5
vinyltri(β-methoxy-ethoxy) silane	1	9.8	14.9	6.0	9.4	15.3	8.5	9.3	15.5	9.7
	2	8.2	16.6	15.7	7.5	17.0	17.6	7.2	17.3	19.1
	3	6.0	19.1	26.7	5.2	19.5	28.2	5.0	19.8	29.3
γ-methacryloxy propyltrimethoxy silane	1	9.7	15.4	9.1	9.6	16.0	12.5	9.6	16.2	13.6
	2	8.0	17.0	17.6	7.8	17.6	20.5	7.7	17.8	21.3
	3	6.2	20.3	31.0	5.9	20.8	32.7	5.9	21.1	33.6
isopropyltriisostearoyl titanate	1	9.6	17.0	17.6	9.3	17.3	19.1	9.1	17.7	20.9
	2	8.0	18.8	25.5	7.5	19.4	27.8	7.0	20.1	30.3
	3	6.3	21.7	35.5	5.9	22.5	37.8	5.0	23.0	39.1

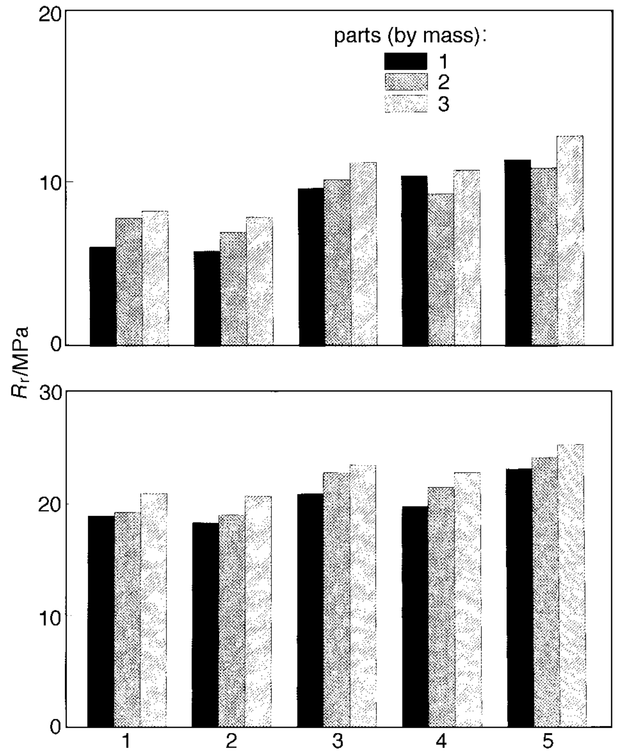


Fig. 2 Dependence of strengthening parameters (tensile strength, R_r and tearing strength R_{rd}) of vulcanizates containing SBR rubber and modified talc as related to the amount of proadhesive compounds used to modify talc surface [the relations are given for 1, and parts (by mass) of the following five proadhesive compounds]. 1, Tetrabutylammonium chloride; 2, polyoxyethylene glycol; 3, sulfanylsilane; 4, vinylsilane; 5, isostearoyl titanate.

the other hand, the presence of hydrocarbon residues on the surface causes an increase in the hydrophobicity of the surface. This is reflected by the fact that strengthening parameters of vulcanizates filled with surfactant modified talcs depend not only on the talc surface wettability but also on the presence of groups capable of interacting with the rubber functional groups on those surfaces. Results of studies on PVC foils, filled with selected talcs, are given in Table 5.

Talcs with largest particle diameter (with no additional micronization) were easiest to modify. The rotational modulus is a significant variable as it determines the extent of mixture plasticity at a given temperature. The higher the moment, the lower is the degree of plasticity. As is evident from Table 5, addition of modified talcs essentially does not affect the PVC gelling time, which is 1.5 min. On the other hand, addition clearly affects the stability and the rotational modulus of PVC foil. Talc modified with γ-methacryloxypropyltrimethoxysilane or with isostearoyl titanate deserves particular attention. The observed decrease in both rotational moments in these cases points to increased plasticity of the foil, which indicates that their strengthening parameters are improved. Talcs modified with γ-sulfanylpropyltrimethoxysilane and γ-aminopropyltriethoxysilane scarcely affect the stability or plasticity of PVC foil.

Properties of the modified talcs, typical for pigments, are listed in Table 6. The sediment volume characterizes the ability of powder material to sediment in a liquid (*e.g.* in linseed oil or solvent used for pigment dispersion). The quality of the paints obtained depends to a significant degree on the stability of the dispersed pigment suspension.

The sedimentation volume of talc pigments was clearly influenced with sulfanyl- and vinyl-silane and isostearoyl titanate, in particular, exhibited a high sedimentation volume which results in improved coating by the pigment. The effect of the amount of proadhesive compounds used is also evident.

Studies on the solubility of talcs in water, hydrochloric acid and sodium hydroxide solutions demonstrated the negligible solubility of talcs in water. On the other hand, the talcs clearly dissolved in hydrochloric acid (coprecipitated magnesium oxides are transformed into chlorides, *i.e.* $MgCl_2$). In sodium hydroxide solution the talc shows a threefold lower solubility than in the acid and dissolution is associated with the formation of $Mg(OH)_2$.

Summary

(1) The optimum technique of talc surface modification was elaborated using various types of proadhesive compounds. According to the recommended technique, the modification is conducted by wetting the filler surface with a proadhesive compound solution. A mixer for modification at the semitechnical scale seems best for this purpose.

(2) Silane coupling agents should be introduced to the talc surface from a methanol–water (4 : 1) solution while titanate coupling agents should be introduced from CCl_4 solution and surfactants should be applied from aqueous solutions.

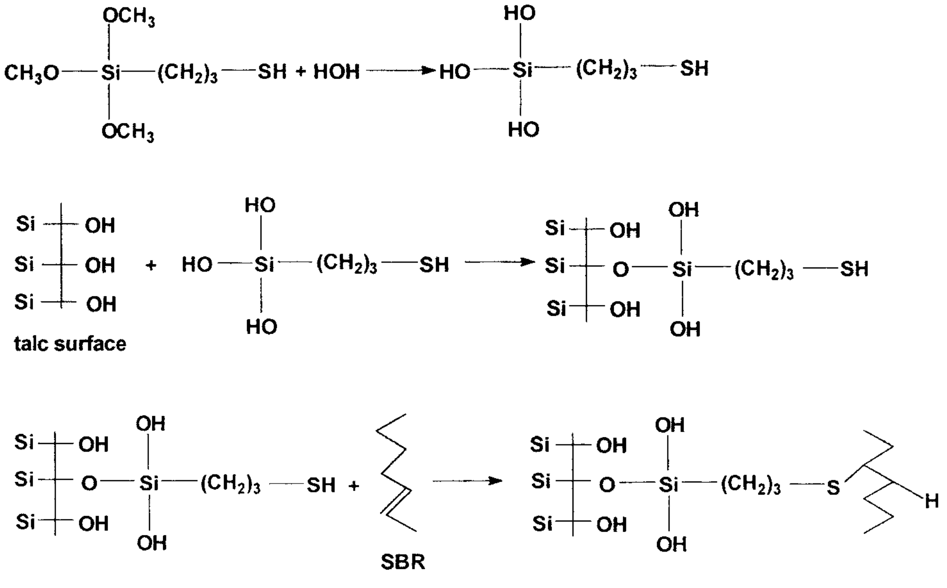
(3) All the applied proadhesive compounds promote hydrophobization of the talc surface. Talc modification with increasing amounts of proadhesive compounds is accompanied by a gradual increase in their adsorption on the surface (as indicated by increasing values of modified talc surface hydrophobization).

(4) The highest strengthening of SBR vulcanizates has been obtained after filling them with talcs modified with sulfanylsilane or isostearoyl titanate. Both of the applied proadhesive compounds not only induce an increase in surface hydrophobicity but, most importantly, promote coating of the surface with functional sulfanyl and isostearoyl groups. Interaction of

Table 4 Effect of proadhesive compounds on strengthening parameters of vulcanizates consisting of SBR rubber and micronized talc (for modification of talc 2 mass% proadhesive compounds were used)

proadhesive compound	tensile strength (R_r)/MPa	300% modulus (M-300)[a]/MPa	tearing strength (R_{rd})/kN m^{-1}	hardness of compound (H)/°Sh
unfilled vulcanizate	0.5	0.6	10.1	30
vulcanizates filled with:				
unmodified talc	5.2	1.5	17.4	64
talc modified with:				
tetrabutylammonium chloride	7.8	2.0	19.2	65
polyoxyethylene glycol	6.9	2.0	19.0	65
sulfanylsilane	10.0	3.0	22.8	65
aminosilane	9.0	2.6	20.6	65
vinylsilane	9.1	2.6	21.5	65
methacryloxysilane	10.1	3.0	23.0	65
isostearoyl titanate	10.6	3.2	24.1	65

[a] Modulus at 300% elongation.



Scheme 1

Table 5 Quality evaluation of PVC foil filled with modified or unmodified talcs

modifying agent	amount of modifying agent (mass%)	temperature of PVC mixture[a]/°C	start of gelling/min	time of gelling/min	stability/min	max. rotational moment/pm	min. rotational moment/pm
unmodified talc	—	180 (134)	1.5	5.0	21.0	2400	1200
methacryloxysilane	1	176 (130)	1.5	8.5	24.0	2000	1050
	2	174 (129)	1.5	9.0	25.0	2000	1040
isostearoyl titanate	1	175 (135)	1.5	7.5	22.5	2150	1050
	2	172 (132)	1.5	8.0	23.0	2250	1060

[a] Temperature during preparation of PVC mixture. Numbers in parentheses are the temperature of the PVC mixture in the crusher during mixture packing.

Table 6 Properties of modified talcs used as pigments in paints

hydrophobicity inducing substance	amount (mass %)	V_s/cm^3	solubility[a]/g water	HCl	NaOH
unmodified talc (after micronization)	—	1.2	0.0180	0.2590	0.1130
sulfanylsilane	1	1.8	0.0185	0.2590	0.1130
	2	1.9	0.0170	0.2512	0.1125
	3	2.0	0.0196	0.2515	0.1123
vinylsilane	1	1.9	0.0188	0.2538	0.1125
	2	2.0	0.0190	0.2498	0.1136
	3	2.1	0.0169	0.2505	0.1129
isostearoyl titanate	1	2.0	0.0175	0.2515	0.1135
	2	2.1	0.0182	0.2513	0.1138
	3	2.1	0.0182	0.2504	0.1127

[a] Talc (1 g) was dissolved in 100 cm^3 of solvent. The no. of grams which did not dissolve is given.

the functional groups with the polymer results in improved mechanical parameters of the rubber.

(5) For PVC, optimum strengthening effects have been obtained using talcs modified with methacryloxysilane or with isostearoyl titanate.

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