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Comparison of waste silica fillers modified with various proadhesive compounds

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Results are presented on the improvement of the degree of surface hydrophobization of post-fluorine waste silicas. Two types of waste silica were used, representing by-products of aluminium fluoride and hydrofluoric acid production, respectively. The silicas were subjected to surface modification to obtain appropriately active fillers for the production of rubber vulcanizates and urethane elastomers. To this end, proadhesive compounds were used including surfactants, silane and titanate coupling agents, and organic compounds with oxyethylene chains. The effects of the type of proadhesive compound used and its amount on the mechanical properties of Ker 1500 butadiene–styrene rubber vulcanizates and of urethane elastomers were examined.

1. Introduction

Silica and silicate fillers find increasingly frequent application, including addition to plastomers and elastomers to improve their physicomechanical parameters, preparation of catalysts, preparation of carriers for drugs and insecticides, fillers of dispersion paints, paper-coating materials, agents controlling the flow rate of powders, tabletting-promoting agents, silicone rubber curing agents, thickeners and thixotropic agents in lacquers and paints and in liquid paste-like plastics, tarnishing agents for varnish manufacture, supplements for toothpastes, fire-extinguishing media, production of thermic and electric insulation elements and many others [1–3].

Silicas exhibit defined affinities for various polymers into which they are introduced to improve their physicomechanical properties. They are hydrophilic and therefore their chemical reactivity with polymers is restricted [4]. Thus, the problem of silica surface modification is of immense importance and has to be solved in various aspects and for various modifying agents. The selection of appropriate modifying agents seems significant as well as the chosen procedure of powdered substance surface modification [5, 6]. For this purpose, surfactants [7–10], silane [11–14] or titanate [15, 16] coupling agents can be applied as well as a number of long-chain organic compounds which exhibit an evident hydrophobic character.

2. Experimental procedure

2.1. Materials

In these studies two types of waste silica were used, both representing by-products of fluorine compound production in the Dr R. May Poznań Chemical Works in Luboń. The silicas were purified of admixtures of aluminium and fluorine compounds. Due to the low solubility of AlF_3 in water, waste silicas originating from the production of aluminium fluoride were leached in hydrochloric acid solutions, while silicas from hydrofluoric acid production were washed in hot water and then in water plus ammonia.

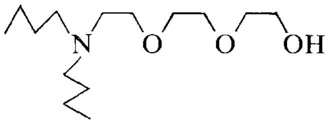
The following chemical compounds were used to modify the surface of the purified silicas:

(i) Surfactants: polyethylene glycol (Polyglycol 4000), sodium dodecylsulphate and tetrabutyl chloride.

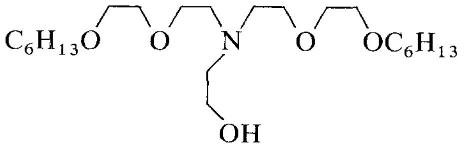
(ii) Silane coupling agents: γ-mercaptopropyltrimethoxysilane (A-189), β-mercaptoethyltriethoxysilane (A-1893), γ-aminopropyltriethoxysilane (A-1100), vinyl-tri-(β-methoxyethoxy)silane (A-172), di-(3-triethoxysilylpropyl)tetrasulphide (Si-69).

(iii) Titanate coupling agents: isopropyltriisostearoyl titanate.

(iv) Organic compounds with oxyethylene groups containing nitrogen atoms: (1) 9-butyl-3,6-dioxa-9-azatridecanol



and (2) 13-(2′-hydroxyethyl)-7,10,16,19-tetraoxa-13-azapentacosane



2.2. Methods

The specific surface (S) of waste silicas was determined by a comparative chromatographic technique [17].

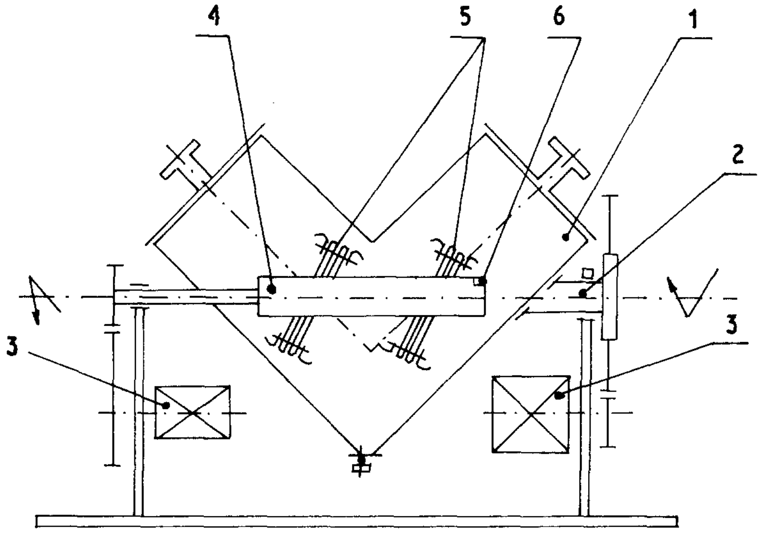


Figure 1 Drum mixer used to modify silica: (1) V-shaped drum, (2) axis of drum and feeder rotations, (3) motors, (4) feeder of modifying agent, (5) two pairs of ring-like discs, positioned at angle to feeder axis, (6) outlet of modifying agent.

Their particle size and surface morphology were examined by transmission electron microscopy, using a one-step indirect replica technique [18]. The remaining physicochemical parameters were established using research techniques generally accepted for fillers reinforcing polymer systems [19].

Surface modification of waste silicas was conducted in a mixer consisting of a closed, rotating V-shaped drum containing a feeder dosing the modifying solution. The appliance was equipped with a rake capable of collecting silica attached to the walls of the mixer drum. The scheme of the mixer is shown in Fig. 1.

Depending upon the modifying substance and upon its solvents, solutions of the substances were prepared in various solvents. Silane coupling agents (except tetrasulphide Si-69) were dissolved in methanol–water (4:1) mixture. Solutions of the tetrasulphide and titanate were prepared in carbon tetrachloride. Surfactants were dissolved in water while the two organic compounds with oxyethylene groups were dissolved in methanol.

Surface modification of waste silicas was conducted in solutions containing 0.5 to 3.0 parts by weight of modifying substance per 100 parts of the filler.

The degree of hydrophobization of the waste silica surface following modification was evaluated by estimating the heat of immersion for the surface. The estimations were conducted in a differential calorimeter of type KRM [20] which permitted the performance of estimations in a dynamic manner, in conditions approaching adiabatic ones. The heat of silica surface immersion was estimated for a polar (water) and a non-polar (benzene) liquid. The method permitted estimation of the increase or decrease in surface hydrophilicity. The degree of hydrophobization, N, was calculated as follows:

$$N = 100 \frac{{}^{\mathrm{m}}H_{\mathrm{i}}^{\mathrm{B}} - {}^{\mathrm{n}}H_{\mathrm{i}}^{\mathrm{B}}}{{}^{\mathrm{m}}H_{\mathrm{i}}^{\mathrm{B}}} \%$$

where ${}^{\mathrm{m}}H_{\mathrm{i}}^{\mathrm{B}}$ is the heat of immersion of modified silica surface in benzene and ${}^{\mathrm{n}}H_{\mathrm{i}}^{\mathrm{B}}$ the heat of immersion of unmodified silica in benzene.

In order to examine the quality of the modified waste silicas they were tested in rubber mixtures and urethane elastomers. Rubber mixtures were prepared consisting of the following components (in parts by weight): butadiene–styrene rubber Ker 1500, 100; zinc oxide, 3; stearic acid, 2; modified or unmodified waste

TABLE I Physicochemical properties of waste post-fluorine silicas following purification

Physicochemical parameter	Silica from AlF_3 production purified with 25% HCl	Silica from HF production purified with water and ammonia solution
pH of water dispersion	6.5	6.0
Specific weight (g cm^{-3})	2.08	2.05
Bulk density (g dm^{-3})	165	150
Packing density (g dm^{-3})	250	230
Water absorption (g/100 g)	350	380
Dibutyl phthalate adsorption (g/100 g)	350	400
Degree of whiteness (%)	75	80
Specific area (m^2 g^{-1})	25.5	30
Particle size (nm)	110	100
Dominating particle shape	Aggregates of irregular shape	Aggregates of irregular shape
Tendency to form agglomerates	High	High
Content (%)		
fluorine	0.10	0.08
Al_2O_3	0.20	0.05
Fe^{2+} and Fe^{3+}	0.01	0.01

silica, 50; dibenzothiazole, 2.2; N,N'-diphenyloguanidine, 1.4; sulphur, 2. Vulcanization was conducted in a hydraulic press with steam heating, at 143°C under a press cylinder pressure of 150 atm. The vulcanization optimum was determined by using a Monsanto oscillation rheometer [21].

For polyurethane synthesis, toluilene diisocyanate (Izocyn T-80, produced by Zachem, Bydgoszcz, Poland, isocyanate group content: 42%), polyoxypropylene glycol (Rokopol 2002, produced by Odra Works of Organic Industry "Rokita" in Brzeg Dolny, Poland, average molecular weight 2000) and polyoxypropylene triol (Rokopol 303, produced by Odra Works of Organic Industry "Rokita" in Brzeg Dolny,

TABLE II Heats of immersion in water (H_i^W) and in benzene (H_i^B), specific area and degree of hydrophobization of silica fillers, unmodified or modified with proadhesive compounds

		Waste silica from AlF_3 production				Waste silica from HF production			
Proadhesive compound[a]	Content (% w/w)	S ($m^2 g^{-1}$)	H_i^W ($J g^{-1}$)	H_i^B ($J g^{-1}$)	N (%)	S ($m^2 g^{-1}$)	H_i^W ($J g^{-1}$)	H_i^B ($J g^{-1}$)	N (%)
Unmodified		25.5	10.2	10.2	–	30.0	11.0	10.9	–
Polyglycol 4000	1	25.0	11.0	12.0	15.0	29.2	11.7	12.7	14.2
	2	25.0	11.7	14.3	28.7	29.5	12.4	15.0	27.3
Tetrabutyl ammonium chloride	1	25.0	9.0	14.1	27.6	29.4	10.3	15.9	31.4
	2	25.2	8.0	16.9	40.0	29.5	9.9	17.7	38.4
Sodium dodecyl sulphate	1	24.5	10.0	10.6	3.7	29.0	10.7	11.5	5.2
	2	24.5	9.8	11.7	12.8	29.3	10.4	12.3	11.4
A-189	1	25.1	6.1	14.3	27.2	29.0	7.0	15.0	27.3
	2	25.1	4.4	15.6	34.6	29.0	5.6	16.8	35.1
A-1893	1	25.0	6.6	13.9	26.7	29.2	7.4	14.5	24.8
	2	25.1	5.0	15.0	32.0	29.0	6.7	16.2	32.7
A-1100	1	25.2	12.1	13.6	25.0	29.0	12.9	14.1	22.7
	2	25.0	12.9	14.8	31.1	29.3	13.6	16.0	31.9
A-172	1	25.2	6.5	13.8	26.1	29.1	7.5	14.6	25.3
	2	25.3	5.7	15.2	32.8	29.2	6.4	16.2	32.7
Si-69	1	24.2	5.8	14.9	31.5	29.3	6.6	15.8	31.0
	2	24.5	4.0	17.3	41.0	29.2	5.0	18.1	39.8
KRTTS	1	25.0	6.0	17.7	42.4	29.5	6.7	18.4	40.9
	2	25.0	4.1	19.2	47.0	29.6	4.9	20.0	45.5
zw (1)[a]	1	24.0	6.3	16.8	39.3	29.0	7.7	17.7	38.4
	2	23.8	4.6	19.0	46.0	29.2	6.0	19.6	44.4
zw (2)[a]	1	23.8	6.2	16.5	38.2	29.0	7.6	17.2	36.6
	2	24.0	5.0	18.7	45.4	29.3	6.4	19.1	42.9

[a] zw (1) = compound (1) with oxyethylene group, zw (2) = compound (2) with oxyethylene group (see section 2.1).

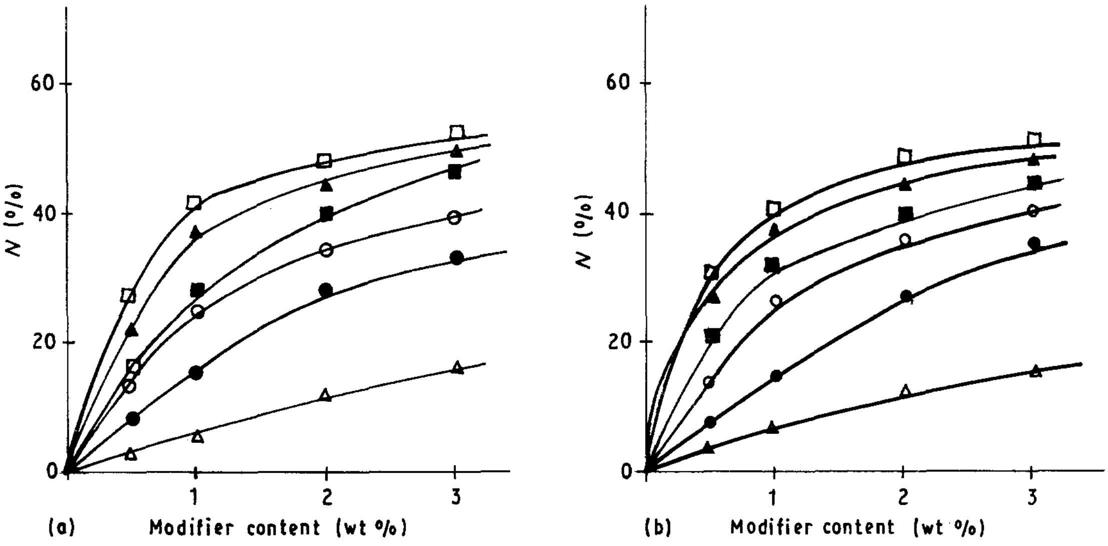


Figure 2. Effect of the amount of chosen proadhesive compounds on silica surface degree of hydrophobization: (a) waste silica from AlF_3 production following purification with 25% HCl solution, (b) waste silica from HF production after purification with water and ammonia solution. (●) Polyglycol 4000, (■) tetrabutylammonium chloride, (○) silane A-189, (□) KRTTS, (▲) compound with oxyethylene group (1), (△) sodium dodecylsulphate.

Poland, average molecular weight 3600) were used. Phenylmercuric oleinate (Bayer, FRG) served as a synthesis catalyst [22].

3. Results and discussion

The structure of waste silicas released in the production of aluminium fluoride and hydrofluoric acid depends upon multiple variables, like duration of the reactions, temperature, the way in which reagents are introduced, the purity of fluorosilicic acid, the structure of aluminium hydroxide and others.

The principal physicochemical parameters established for purified post-fluorine silicas are listed in Table I. The Table presents also the contents of fluorine, aluminium oxide and ferric oxides. The silicas demonstrate a purity appropriate for employing them as elastomer or rubber fillers. As demonstrated in Table I, the waste silica formed in the process of hydrofluoric acid production is somewhat more active (greater specific surface, higher surface absorbing capacity for dibutyl phthalate, lower particle size).

Since unmodified waste silicas either from hydrofluoric acid or aluminium fluoride production were inefficient in increasing the tensile strength and modulus of vulcanizates, a surface modification method was worked out. The unmodified silicas showing low activity could at best be used in rubber products which are not required to exhibit high reinforcing parameters.

Filler evaluation following modification was performed by measuring the heat of immersion of the silica surface in water and benzene. In particular, the heat of immersion of the surface in benzene (non-polar solvent) may point to increased hydrophobization of silica surface. Knowing the heats of immersion of modified and unmodified silica surfaces in benzene,

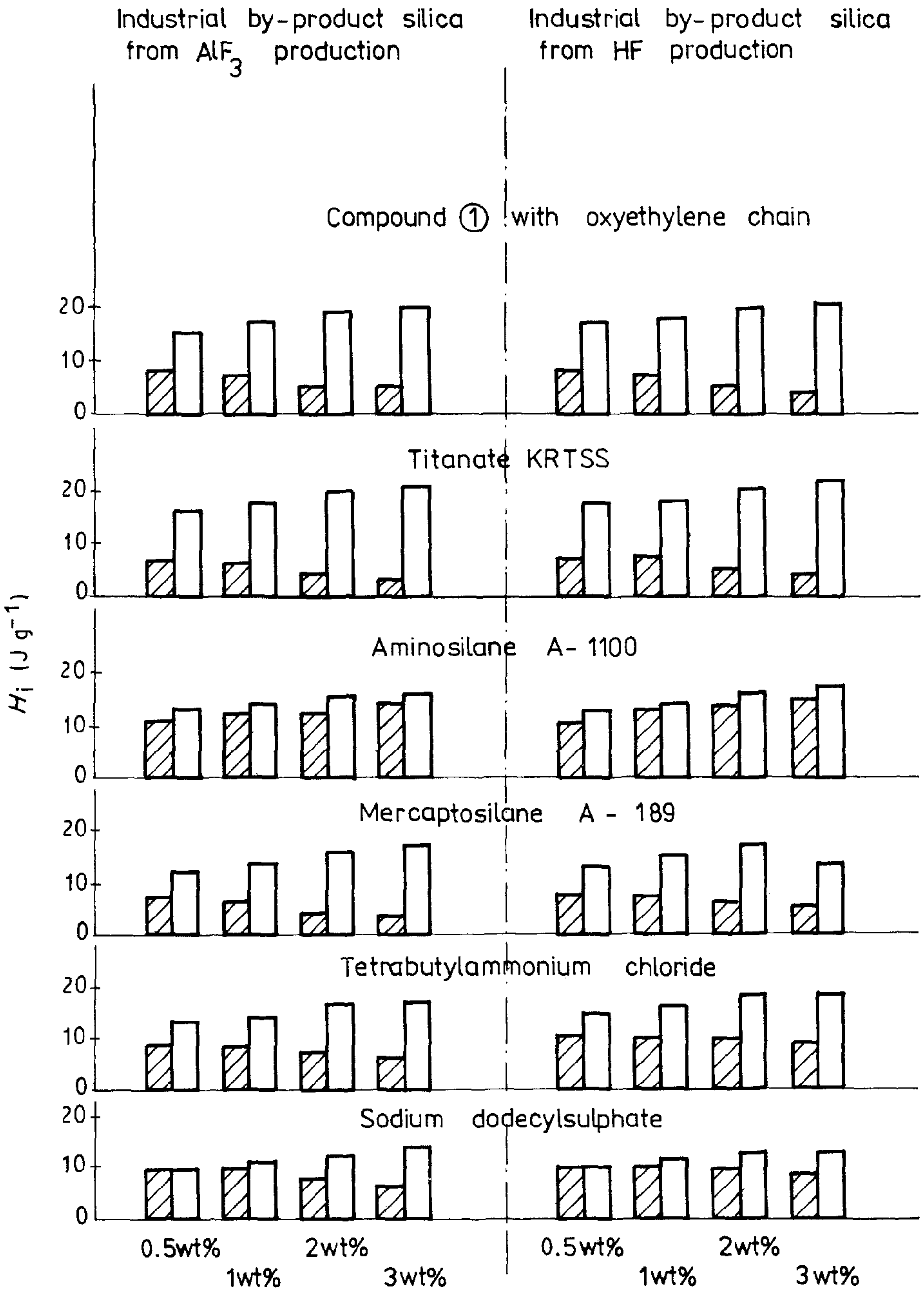


Figure 3 Comparison of heats of immersion in water and benzene for waste silica surface with chosen proadhesive compounds: ▨ heat of immersion in water, H_i^W; □ heat of immersion in benzene, H_i^B.

the so-called degree of silica surface hydrophobization was calculated. The heats of immersion in water or benzene and their changes on silica modification with various proadhesive compounds and the calculated degrees of hydrophobization for the silica are presented in Table II.

The effect of the applied amount of chosen proadhesive compound on the degree of hydrophobization of waste silica surface is presented in the graphs of Fig. 2. The heats of immersion of the surface of the waste silica in water and benzene following modification with proadhesive compounds are compared in the diagram of Fig. 3.

Modification of waste silica surface with proadhesive compounds, performed according to our own technique, has resulted in more or less extensive hydrophobization of silica surface. As exemplified in Table II and Fig. 2, the highest degree of surface hydrophobization for each of the silicas was reached by using for their modification isopropyltriisostearoyl titanate, 9-butyl, 3, 6-dioxa-9-azatridecanol and tetrabutylammonium chloride. Somewhat lower degrees of silica surface hydrophobization were reached by using for modification γ-mercaptopropyltrimethoxysilane A-189 and polyethylene glycol (Polyglycol 4000). Application of sodium dodecylsulphate for silica surface modification resulted in only a negligible effect on silica surface hydrophobization.

The greatest increase in heat of immersion silica surface in benzene was observed (as indicated in Figs 3 and 4), and the greatest increase in surface hydrophobization noted, by using for modification solutions containing up to two parts by weight of proadhesive compounds. Further increase in proadhesive compound content (e.g. to 3 parts by weight) induced a much lower increase in the heat of immersion of silica surface in benzene and, thus, a much smaller increase in degree of hydrophobization. This reflects a saturation of silica surface centres by proadhesive compounds and, in particular, reaction of silica surface silanol groups with the respective groups of proadhesive compounds. Optimum surface hydrophobization and, thus, sufficiently effective modification of the silica surface was found to take place when 1 to 2 parts by weight of proadhesive compounds were used to modify the surface of either silica. Proadhesive compound-modified silicas seem to offer fillers of medium activity, intensely searched for in the technology of many polymer-based products.

The modified silicas were tested in rubber mixtures containing butadiene–styrene rubber and in urethane elastomers. The mechanical properties of rubber vulcanizates filled with post-fluorine waste silicas, unmodified or modified with 2 parts by weight of proadhesive compounds, are listed in Table III. Among the modified silicas, those modified with proadhesive compounds exhibited the most advantageous effect on the physicomechanical properties of vulcanizates as well as the greatest surface hydrophobization. In particular, one should mention mercaptosilane-modified

TABLE III Mechanical properties of vulcanizates filled with waste postfluorine silicas, unmodified or modified with 2 parts by weight of proadhesive compound (vulcanization time: 30 min)

Proadhesive compound	Elasticity (%)	M-200 (MPa)	R_r (MPa)	E_r (%)	E_t (%)	R_{rd} (kN m^{-1})
Waste silica from AlF_3 production following purification in 25% HCl						
Unmodified	50	2.84	3.34	270	8	16.1
Polyglycol 4000	50	3.33	4.08	240	4	21.8
Tetrabutylammonium chloride	48	4.20	5.11	260	4	22.5
Sodium dodecylsulphate	48	3.00	3.95	270	6	18.8
A-189	50	6.13	7.16	260	4	24.2
A-1893	50	5.90	6.75	260	4	23.4
A-1100	48	3.52	4.43	240	4	22.6
A-172	50	4.81	5.54	260	4	24.0
Si-69	50	6.20	7.35	250	4	24.5
KRTTS	50	6.15	6.89	260	5	24.3
zw (1)[a]	52	5.25	6.02	260	5	24.2
zw (2)[a]	52	5.02	5.93	260	5	24.0
Waste silica from HF production following purification in hot water and ammonia solution						
Unmodified	52	3.02	3.57	250	8	18.9
Polyglycol 4000	50	3.61	4.34	240	4	23.3
Tetrabutylammonium chloride	48	4.75	5.63	240	4	24.5
Sodium dodecylsulphate	52	3.45	4.00	240	4	19.9
A-189	50	6.45	7.52	240	4	27.2
A-1983	50	6.20	7.15	240	4	26.6
A-1100	48	3.88	4.31	230	4	23.2
A-172	48	5.12	5.62	240	4	27.0
Si-69	48	6.64	7.82	240	4	27.9
KRTTS	48	6.55	7.75	250	5	27.8
zw (1)[a]	48	5.48	7.15	260	4	27.5
zw (2)[a]	48	5.40	7.01	250	4	27.5

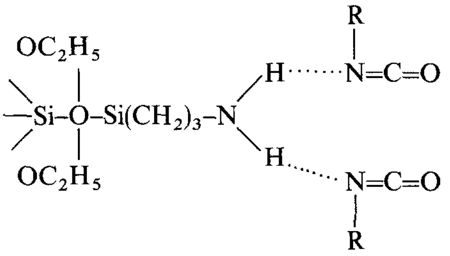
[a] zw (1) = compound (1) with oxyethylene group, zw (2) = compound (2) with oxyethylene group.

silicas which give vulcanizates of increased tensile strength and modulus. Both gamma and beta mercaptosilanes improved very effectively the reinforcing of vulcanizate filled with the modified silica. Mercapto groups of the silanes are responsible for interaction with macroparticles of sulphur-vulcanized butadiene–styrene rubber, thus improving vulcanizate reinforcing.

The relation between the three principal physicomechanical parameters of rubber vulcanizates (200% modulus, tensile strength and tearing strength) and the amount of chosen proadhesive compounds used to modify the surface of waste silica filling the vulcanizate is shown in Fig. 4.

The introduction of purified post-fluorine silicas to urethane elastomer led to a regular increase in reinforcing parameters such as M-100 modulus, tensile strength, relative elongation and hardness. The physicomechanical parameters of polyurethanes filled with various amounts of unmodified or modified silicas are presented in Table IV. Optimum values of reinforcing parameters were obtained when the elastomer mass contained 20 to 30% silica.

The greatest reinforcing effects were observed in elastomers filled with waste silicas modified with aminosilane A-1100. Significant effects were associated with the amount of silane used; it proved economical to use two parts by weight of silane A-1100 per 100 parts of waste silica. Silicas modified with mercaptosilane A-189 proved less effective in the system with urethane elastomer. The effects of the remaining proadhesive compounds used for modification of waste silica surface were negligible and they proved useless as reinforcing agents of urethane elastomers. The decisive improvement of urethane elastomer strengthening parameters under the effect of aminosilane-modified silicas is associated with the chemical interaction of silane A-1100 amino groups with isocyanate groups of urethane elastomer, as presented below



The tensile strength of urethane elastomers containing 30 parts by weight of waste silica modified with some of the chosen proadhesive compounds is illustrated in Fig. 5. For silica modification, one to three parts by weight of proadhesive compound were applied per 100 parts of silica.

4. Conclusions

1. Waste post-fluorine silicas when used unmodified are inefficient in improving the physicomechanical

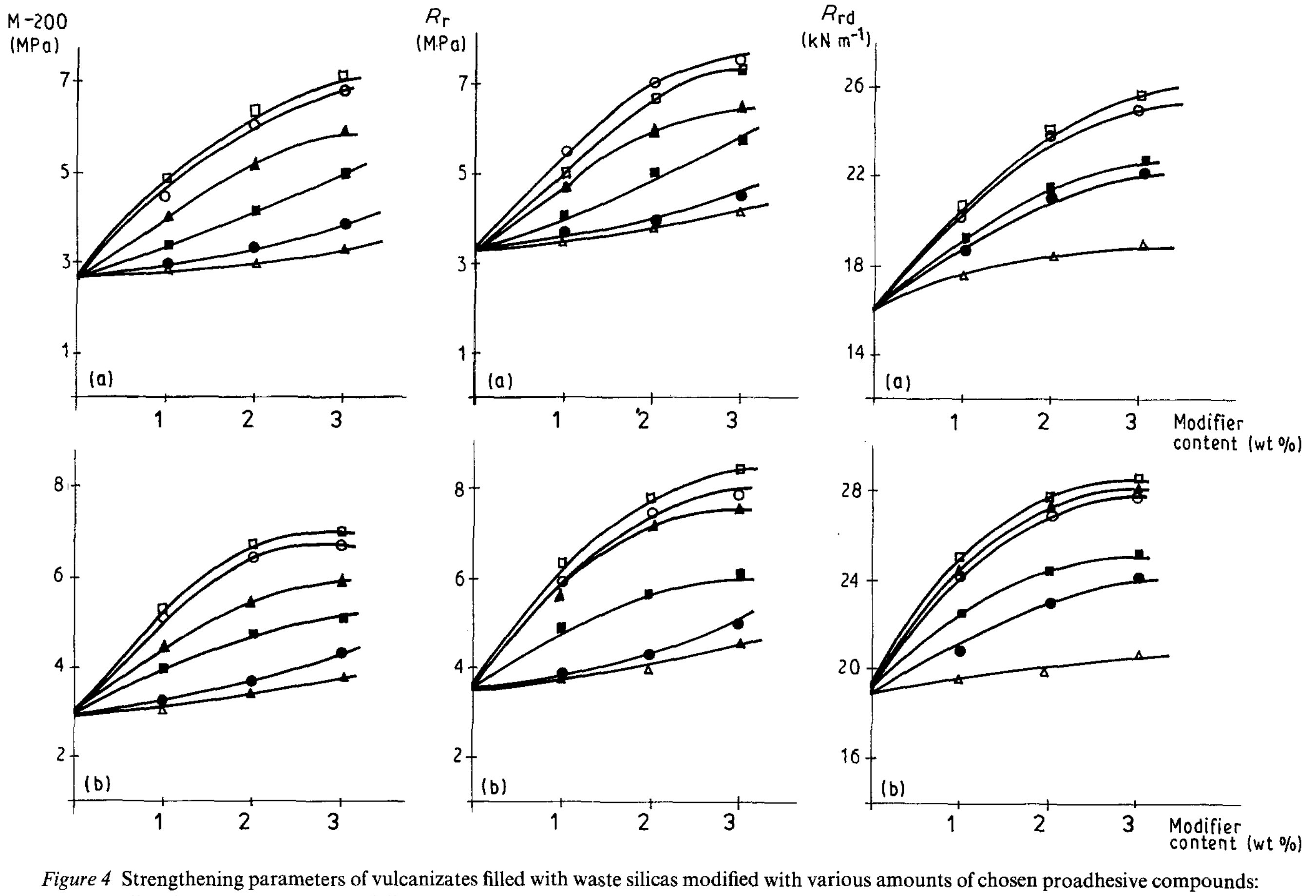


Figure 4 Strengthening parameters of vulcanizates filled with waste silicas modified with various amounts of chosen proadhesive compounds: (a) waste silica from AlF_3 production following purification using 25% HCl, (b) waste silica from HF production following purification with water and ammonia solution. (●) Polyglycol 4000, (■) tetrabutylammonium chloride, (○) silane A-189, (□) KRTTS, (▲) compound with oxyethylene group (1), (△) sodium dodecylsulphate.

TABLE IV Physicochemical parameters of polyurethanes filled with unmodified and modified waste silicas

Silica content g/100 g polyurethane (% w/w)	M-100 (MPa)	R_r (MPa)	E_r (%)	H (°Sh)
Waste silica from AlF_3 production, purified in 25% HCl, unmodified				
5	0.70	0.80	155	40
10	0.79	1.30	145	43
20	1.10	1.50	145	53
30	1.60	1.90	250	63
40	–	0.51	30	67
50	–	0.37	25	71
Waste silica from AlF_3 production, modified with silane A-189 (2 parts by weight)				
10	0.88	1.35	140	42
20	1.15	1.68	140	53
30	1.60	2.10	185	63
40	–	0.60	40	67
Waste silica from AlF_3 production, modified with silane A-1100 (2 parts by weight)				
10	1.50	1.75	150	43
20	1.85	2.08	150	53
30	2.70	2.70	210	68
40	–	0.89	50	67
Waste silica from HF production purified in water and ammonia solution				
10	0.90	1.44	160	43
20	1.25	1.72	160	52
30	1.82	2.04	240	62
40	–	0.80	40	67
Waste silica from HF production, modified with silane A-189				
30	2.15	2.32	240	63
Waste silica from HF production, modified with silane A-1100				
30	2.75	3.12	250	63

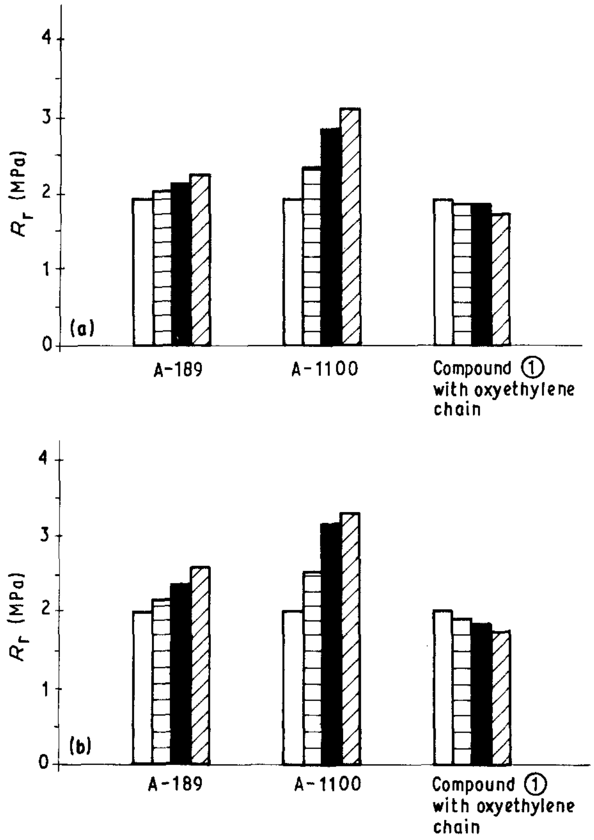


Figure 5 Tensile strength of urethane elastomers containing 30 parts by weight of waste silica modified with some of the proadhesive compounds studied: (a) waste silica from AlF_3 production following purification using 25% HCl solution, (b) waste silica from HF production following purification with water and ammonia solution. □ Unmodified, ⊟ modified with one part by weight of proadhesive compound, ■ modified with 2 parts by weight of proadhesive compound, ▨ modified with 3 parts by weight of proadhesive compound.

parameters of rubber vulcanizates consisting of butadiene–styrene rubber and urethane elastomers.

2. Surface modification of purified waste silica assures an increase in the activity of the filler and, in particular, leads to increased hydrophobization of its surface. This results in augmented chemical affinity of the silica to the polymer.

3. Out of the spectrum of proadhesive compounds used to modify the silica surface, the greatest increase in degree of hydrophobization has been obtained with isopropyltriisostearoyl titanate, 9-butyl,3,6-dioxa-9-azatridecanol, tetrabutyl chloride and somewhat lower with γ-mercaptopropyltrimethoxysilane, and β-mercaptoethyltriethoxysilane.

4. In the case of filling butadiene–styrene rubber with waste silica, the best effects have been obtained by using for modification of the silica the mercaptosilane coupling agents, isopropyltriisostearoyl titanate, organic compounds with oxyethylene chains and tetrasulphide in the ratio of 2 to 3 parts by weight per 100 parts of rubber.

5. The relation between the physicomechanical parameters of urethane elastomers and the content of purified waste silica has an optimum. Optimum properties are reached in compositions containing 20 to 30% silica. A higher content of silica is associated with deterioration of all reinforcing parameters of the filled polyurethanes.

6. Modification of waste silica surface with aminosilane (at 2 to 3 parts by weight) improves the strengthening parameters of urethane elastomers as compared to elastomers filled with unmodified silica or filled with silicas modified with the other proadhesive compounds examined.

References

1. K. H. SCHMIDT, *Chem. Ind.* **106** (1983) 17.
2. J. E. STEWART, *Gummi, Asbest, Kunstst.* **30** (1977) 44.
3. M. P. WAGNER, *Rubber World* **164** (1971) 46.
4. A. KRYSZTAFKIEWICZ, M. MAIK and L. DOMKA, *Chemik* **33** (1980) 202.
5. A. KRYSZTAFKIEWICZ, *Chemia Stosowana* **33** (1989) 561.
6. L. DOMKA, B. MARCINIEC and A. KRYSZTAFKIEWICZ, Patent PRL 115671 (1983).
7. A. W. KISIELEW, *J. Colloid Interf. Sci.* **28** (1968) 430.
8. P. A. REBINDER, *Kolloidn. Z.* **20** (1958) 527.
9. H. FERCH, *Chem. Ing. Techn.* **48** (1976) 922.
10. A. KRYSZTAFKIEWICZ and L. DOMKA, *Tenside* **24** (1987) 227.
11. M. KRANZ, L. DOMKA, A. KRYSZTAFKIEWICZ and M. MAIK, *Polimery* **24** (1979) 86.
12. E. P. PLUDDEMANN, "Silane Coupling Agents" (Plenum, New York, 1982) pp. 10–31.

13. M. W. RANNEY, G. M. CAMERON and B. W. LIPINSKI *Gummi, Asbest, Kunstst.* **27** (1974) 600.
14. L. P. ZIEMIANSKI, C. A. PAGANO and M. W. RANNEY, *Rubber World* **82** (1970) 53.
15. S. J. MONTE and M. W. SUGERMAN, "Titanate coupling agents in filler reinforces thermosets", in 33rd Annual Technical Conference, 1978, Kenrich Petrochemicals Inc., Bayonne, NJ (Reinforced Plastics/Composites Institute).
16. S. J. MONTE, US Patent 2 751 314 (1976).
17. T. PARYJCZAK, "Chromatografia gazowa w bandaniach adsorpcji i katalizy" (PWN, Warszawa, 1975) *str.* p. 96.
18. D. E. BRADLEY, *Br. J. Appl. Phys.* **5** (1954) 65.
19. A. KRYSZTAFKIEWICZ, *Chemia Stosowana* **31** (1987) 443.
20. A. KRYSZTAFKIEWICZ, L. DOMKA and W. WIECZOREK, *J. Colloid. Polym. Sci.* **263** (1985) 804.
21. A. KRYSZTAFKIEWICZ *Tenside* **26** (1989) 420.
22. A. KRYSZTAFKIEWICZ, M. MAIK, *Colloid. Polym. Sci.* **265** (1987) 704.

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