JOURNAL OF MATERIALS SCIENCE **32** (1997) 1333–1339

The effect of surface modification on physicochemical properties of precipitated silica

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The main goal of this study was to obtain hydrophobic silica whose properties would allow their application as plasto- and elastomer fillers. Thus, hydrated silica was modified by silane and titanate coupling agents. The modification procedure and appropriate modification apparatus were developed. The degree of silica surface modification was evaluated by different methods. As grounds for this evaluation, changes in the physicochemical properties, brought about by the condensation reaction of surface silanol groups with alkoxyl or hydroxyl groups of the molecules of coupling agents, were used. The degree of hydrophobicity of the silica surface was determined on the basis of the heat of immersion of this surface, and silanol groups were identified by the infrared spectroscopy. Moreover, changes in the tendency to form agglomerates and aggregates of molecules were studied by microscopy. It was found that modification with silane and titanate coupling agents leads to an increase in silica activity. Application of these agents results in the change of the hydrophilic character to the hydrophobic one.

1. Introduction

Precipitated silicas are good fillers of plasto- and elastomers. Their introduction to a system with polymers contributes to a marked improvement of the tensile strength parameters of the polymer–silica system. Moreover, precipitated silicas are used as carriers of drugs and pesticides, paint and lacquer fillers, agents regulating the flow-rate of solids, condensing and thixotropic agents, and as admixtures in toothpastes.

Silanol groups present on the silica surface promote their interaction with polymers. However, their presence leads to an increase in the hydrophilic character of the surface, as a result of immersion, and then due to water sorption [1, 2]. Moreover, because of the presence of silanol groups, the silica surface assumes an acidic character, due to the possibility of proton abstraction ($-\mathrm{Si{-}O^-} + \mathrm{H^+}$) [3].

Quantitative estimation of silanol groups has been performed by both chemical [4] and physical techniques [5]. Spectroscopic techniques, such as solid-state NMR, reflection spectroscopy [6], photoacoustic technique [7] and infrared transmission [8] are of particular significance. However, determination of the amount of these groups and, in particular, of their decrease following modification with proadhesive agents, presents difficulties. In the case of silica modification with the compounds, a decrease in the amount (number) of surface silanol groups takes place due to their chemical reaction with alkoxyl and chloro-groups of silanes. Determination of the group loss also allows the calculation of the extent of modification in silica fillers. So far, a number of techniques have been developed for quantitative appraisal of surface silanol groups, but all of them yield markedly biased results, linked either to measurements of the released gas volumes (in chemical techniques) or to interference of silanol group bands with bands of adsorbed water in infrared spectroscopy [9]. In high-frequency bands, between 4000 and 8000 $\mathrm{cm^{-1}}$, there is a possibility of distinguishing clearly between silanol groups and water adsorbed on the silica surface [10–12]. Zettlemoyer and Hsing [13, 14] have pioneered the application of near infrared spectroscopy (NIR) techniques to water adsorption studies on silica.

Because the reaction on the silica surface may take many different courses, it is possible to change the properties of the surface by substituting new groups of atoms. Therefore, the process of surface modification involved treatment of silica with different coupling agents. By selecting proper multi-functional groups, containing not only groups able to react with the silica surface, but also groups showing chemical affinity to the polymer, it is possible to modify the strengthening of polymers by adding fillers. Many ways of silica surface modifications were described [15]. The modification method is closely dependent on the type of chemical compound used for modification.

The structure of an external silica surface precipitated from a solution of sodium metasilicate by carbon dioxide is shown (I).

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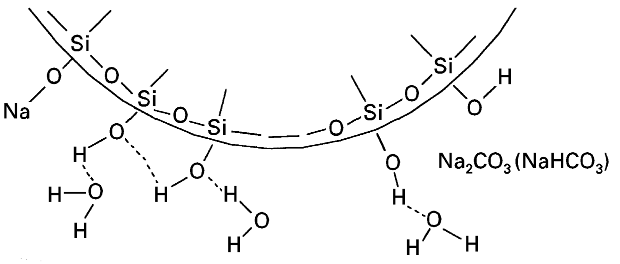


I

The surface modification of silica is a complex process, affected by many parameters. Among them are: the type of solvent and modifying substance, its amount in solution, pH of the medium, modification time, and additives catalysing the course of the modification process. The optimum coupling promoter for the silica filler–polymer systems should bind not only the filler, but also polymers (bound by functional groups of elastomer) [16, 17]. The group of coupling agents comprises silane, titanate, borate, zirconate, and hafnate coupling agents containing alkoxyl groups [18–23].

The main objective of our studies was to obtain hydrophobic silicas that would exhibit properties permitting their application as fillers of plasto- and elastomers. To this end, they were submitted to surface modification by using silane and titanate coupling agents.

The hydrophobic character of the silica surface may be determined by different methods, e.g. by measuring the stationary contact angle of the silica surface with water [24], the conventional water repellancy, or the calorimetric method (measuring the heat of immersion of surface with water and benzene) [25]. For the evaluation of the degree of hydrophobicity, the calorimetric method was chosen.

2. Experimental procedure

2.1. Materials

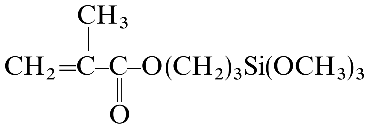
The precipitated silica, obtained according to the method developed in our laboratory, was used for the studies [26]. In the first stage of the precipitation process, into a reactor containing sodium metasilicate, an appropriate amount of coagulant dissolved in water was added with intensive stirring. In the second stage, gaseous carbon dioxide was added to a reactor filled with a solution heated to 85 °C. The silica precipitate after saturation was neutralized in a solution diluted with sulphuric acid to obtain the value of pH 4–6. After washing, the silica was filtered off and dried.

For modification of the silica surface, the following coupling agents were used:

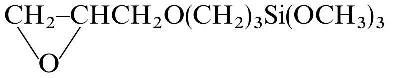
(a) from the group of silane coupling agents (the Union Carbide Company)

A-189 γ-mercaptopropyltrimethoxysilane
$(CH_3O)_3Si{-}(CH_2)_3{-}SH$
A-1893 β-mercaptoethyltriethoxysilane
$(C_2H_5O)_3Si{-}(CH_2)_2{-}SH$
A-1100 γ-aminopropyltriethoxysilane
$(C_2H_5O)_3Si{-}(CH_2)_3{-}NH_2$
A-1120 *N*-β(aminoethyl)-γ-aminopropyltrimethoxysilane
$(CH_3O)_3Si{-}(CH_2)_3{-}NH{-}(CH_2)_2{-}NH_2$

A-174 γ-methacryloxypropyltrimethoxysilane


$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O(CH_2)_3Si(OCH_3)_3$$

A-187 γ-glycidoxypropyltrimethoxysilane



(b) from the group of titanate coupling agents (from the Kenrich Petrochemicals Company)
trimethyl isostearoyl titanate (I)
$(CH_3O)_3{-}Ti(C_{17}H_{35}COO)$
triethyl isostearoyl titanate (II)
$(C_2H_5O)_3{-}Ti(C_{17}H_{35}COO)$
triisopropyl isostearoyl titanate (III)
$(i\text{-}C_3H_7O)_3{-}Ti(C_{17}H_{35}COO)$
KR TTS isopropyl triisostearoyl titanate
$(i\text{-}C_3H_7O){-}Ti(C_{17}H_{35}COO)_3$
KR 33CS isopropyl trimethacryl titanate
$(i\text{-}C_3H_7O){-}Ti[OCOC(CH_3){=}CH_2]_3$

2.2. Methods of study

The specific surface area was determined chromatographically [27]. Because of higher symmetry, the adsorbed amount of nitrogen was calculated from the desorption peak. The bulk and packing densities were determined with a WE-5 electromagnetic volumeter.

To obtain a more complete characterization of the fillers under study, absorption of water, dibutyl phthalate, and paraffin oil was also determined. The end point of water absorption was determined to occur when an excess of one drop of water caused a clear liquefacation of the forming mass, while in the case of absorption of the phthalate and oil, it was when the excess of one drop suddenly changed the consistency of the paste which adhered to a glass plate.

Modification of the precipitated silica surface was carried out in a mixer [28] and according to the method given elsewhere [29]. For the titanate modification, solutions of titanate coupling agents in carbon tetrachloride were prepared, whereas the solutions of silane coupling agents were in a water–methanol (4:1) solution. The prepared solutions contained 0.5–3.0 wt/wt of these compounds in appropriate solvents per 100 wt/wt modified silica. Modification consisted in wetting the silica surface in a mixer with a minimum amount of an appropriately prepared modifying solution. To this effect, 150 cm^3 solution was used for ~500 g silica. After a mixing cycle, the solvent was removed by evaporation, and the modified silica was dried at 110 °C in a drier.

The degree of modification of the silica surface was estimated using different methods. For this purpose, changes in physicochemical properties of silica caused by the reaction of the condensation of surface silanol groups with alkoxy groups or after hydrolysis with hydroxyl groups of coupling compounds were determined. Of all the applied methods, the most reliable methods and those that yielded comparable results, involved:

(a) determination of the degree of hydrophobization on the basis of the value of the heat of immersion of the silica surface in water and benzene,

(b) determination of the degree of condensation of the silica surface silanol groups by the infrared spectroscopy method, and

(c) observation of agglomerates and aggregates of silica molecules in an electron microscope.

The heat of immersion of the silica (unmodified and modified) surface in water ($\mathscr{H}_i^W$) and benzene ($\mathscr{H}_i^B$) was determined by a calorimetric method. According to this method, ampoules were filled with appropriate silica, then outgassed under vacuum for 6 h at 110 °C and only then were the heats of immersion measured [30]. By using the KRM calorimeter, it is possible to determine the heat effects by a dynamic method under conditions close to the adiabatic ones. Moreover, relative heats of immersion of surface h_i^W and h_i^B were also calculated and referred to the value of the specific surface area of silica ($\sim 140\ \mathrm{m^2\,g^{-1}}$).

The degree of hydrophobicity was calculated from the formula

$$N = \frac{(\mathscr{H}_i^B)_m - (\mathscr{H}_i^B)_n}{(\mathscr{H}_i^B)_m} 100\% \qquad (1)$$

where $(\mathscr{H}_i^B)_m$ is the heat of immersion in benzene of the surface of modified silica, and $(\mathscr{H}_i^B)_n$ is the heat of immersion in benzene of the surface of unmodified silica.

Surface silanol groups were determined in the near infrared, in the 7326 band $\mathrm{cm^{-1}}$. To this effect, silica suspended in carbon tetrachloride was used in which highly dispersed silicas form transparent gels. Maximum amounts of suspended silica particles in CCl_4 were defined, in which the slowest settling of these particles occurs [31]. NIR spectra were recorded for silicas prior to and after modification, by a UV-Visible-NIR Beckman Acta spectrophotometer. The condensation degree was calculated from

$$K = \frac{H - h}{H} 100\% \qquad (2)$$

where H is the height (or surface) of the peak of the unmodified silica (in cm or $\mathrm{cm^2}$), and h is the height (or surface) of the peak of silica after modification (in cm or $\mathrm{cm^2}$).

The NIR spectrum for unmodified precipitated silica is shown in Fig. 1.

Examples of band 7326 $\mathrm{cm^{-1}}$ peaks for silica, unmodified or modified with A-189 mercaptosilane are shown in Fig. 2.

The degree of condensation of surface silanol groups of silica in reaction with coupling agents was calculated as a relative value always referred to the height (or surface) of peaks determined for unmodified (standard) silica. The results of electron microscopy can be helpful in the interpretation of the effect of modification of silica on its surface properties. Silicas were observed using a one-step replica method [32] in a JEM 7A electron microscope (made in Japan).

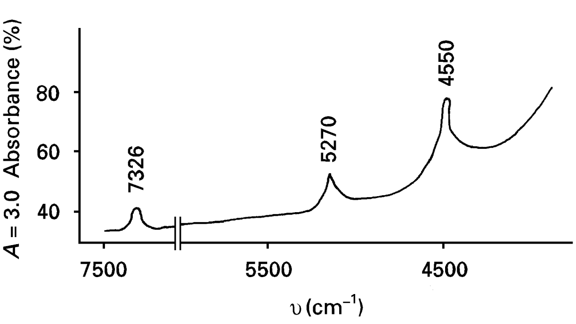


Figure 1 NIR spectrum for precipitated silica.

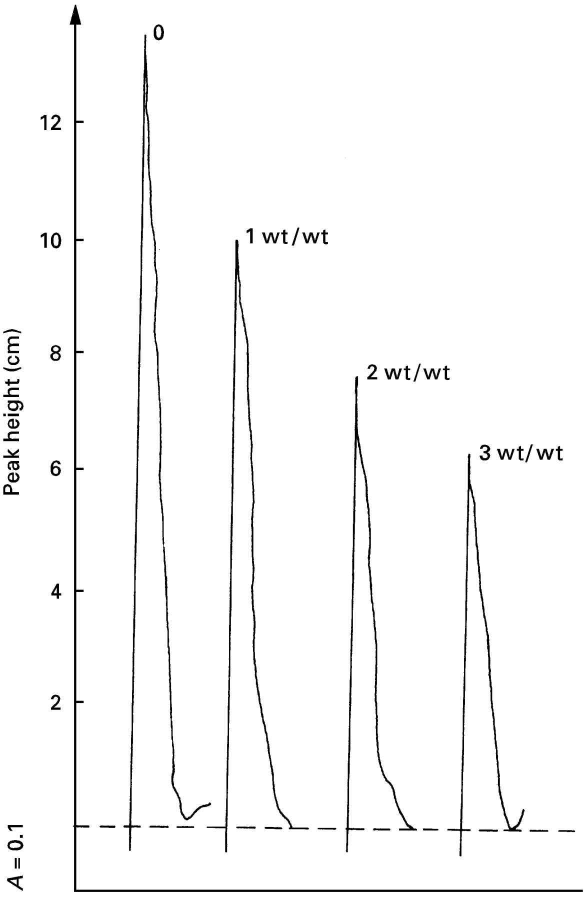


Figure 2 7326 $\mathrm{cm^{-1}}$ band of unmodified precipitated silica and modified by silane A-189.

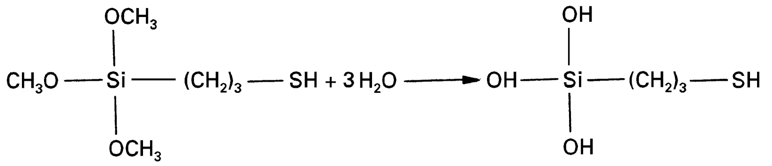
3. Results and discussion

Table I gives the physicochemical properties of precipitated silica applied for studying the modification. Because the boiling points of the applied coupling agents are high (in the range 200–280 °C), for surface modification of fillers, either organic or aqueous solutions of these compounds were used, and then the solvent was evaporated. Owing to the ageing processes of the modifying solutions, they were prepared directly prior to the modification process. The most effective solvents of silanes appeared to be methanol, water, and a mixture of methanol and water. Water is

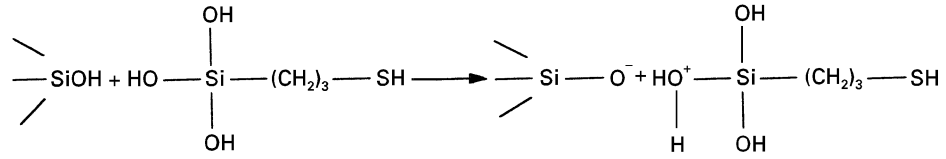
TABLE I Physicochemical properties of precipitated silica

Physicochemical properties	Precipitated silica
Appearance	White powder
Structure	Amorphous
pH of water dispersion	6.5
Specific weight (g cm^{-3})	2.11
Bulk density (g dm^{-3})	80
Packing density (g dm^{-3})	190
Water absorption (g/100 g)	550
Dibutyl phthalate absorption (g/100 g)	850
Paraffin oil absorption (g/100 g)	1200
Degree of whiteness (%)	98.5
Specific surface area (m^2/g^{-1})	140
Size of particles (nm)	15–20

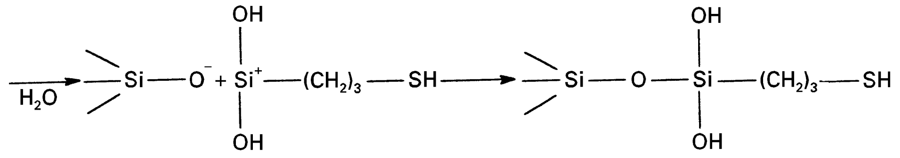
indispensable for the hydrolysis of alkoxy groups in the molecules of silane. Titanates, owing to their decomposition in water (they decompose, yielding TiO_2), prior to modification were dissolved in carbon tetrachloride. During modification, silane coupling agents are substituted by silanol groups present on the silica surface according to the mechanism of electrophilic proton substitution, SE [15]. In this mechanism, the contribution of centres of this surface has been taken into account.



$$CH_3O-\underset{OCH_3}{\overset{OCH_3}{Si}}-(CH_2)_3-SH + 3H_2O \longrightarrow OH-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH \qquad (3)$$



$$\equiv SiOH + HO-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH \longrightarrow \equiv Si-O^- + \underset{H}{HO^+}-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH \qquad (4)$$



$$\xrightarrow[H_2O]{} \equiv Si-O^- + \underset{OH}{\overset{OH}{Si^+}}-(CH_2)_3-SH \longrightarrow \equiv Si-O-\underset{OH}{\overset{OH}{Si}}-(CH_2)_3-SH \qquad (5)$$

By using this method of measuring the heat of immersion of the silica surface in water or benzene in a differential calorimeter, it is possible to estimate the modification of the filler surfaces, either a decrease or increase in hydrophilicity or hydrophobicity, respectively.

Table II presents results of studies on the heat of immersion in water and in benzene of unmodified and modified surfaces of precipitated silica. The heat of immersion in water $\mathscr{H}_i^W$, of fillers treated with mercaptosilane, metacryloxysilane, glycidoxysilane and all types of titanates decreases proportionally with the increase in the amount of the coupling agents added. During modification of the silica surface with aminosilanes, the values of $\mathscr{H}_i^W$ are observed to increase slowly, depending on the amount of silane. The heat of immersion in benzene, on the other hand, of surfaces of the fillers modified with all types of coupling agents, increases, depending on the amount of the agent added. The observed increase in the heat of immersion in benzene of the surfaces of already modified silica testifies to hydrophobicity of their surfaces. The highest degree of hydrophobicity was observed for silicas modified with KR TTS and KR 33CS titanates, while it was a little lower after modification with 3 wt/wt aminosilane and metacryloxysilane. It appeared, therefore, that the method involving measurement of the heats of immersion of the silica surface in water and benzene proved to be most useful in estimating the hydrophobicity of silicas. The calculated degrees of hydrophobicity indicate a progress of modification. On the basis of the values of hydrophobicity, however, it is not possible to draw any conclusions concerning the type of absorption of the applied substances: whether it involves chemical reactions or the formation of adhesive groups based on physical interactions. As a result, it is not possible, from the calculated heats of immersion and degrees of hydrophobicity, to determine the mechanism of the reaction of the silica surface modification, and as a consequence, to account for the role played by the modified filler in a polymer mixture. This is why a new method for estimating the degree of silica surface modification was developed. This method involved measuring the amount of silanol groups bound on these surfaces.

Table III gives the degrees of condensation calculated for surface silanol groups of silicas after their modification with silane and titanate coupling agents. As follows from the presented data, the condensation degree of surface silanol groups increases rapidly as a result of their modification with silanes at the ratio 3 wt/wt modifier 100 wt/wt silica. In the case of silica modified with titanates, the condensation degree is lower. At small amounts of silanes and titanates, the condensation degree is significantly high, whereas with increasing percentage of silanes and

TABLE II Compilation of the heats of immersion in water, $\mathscr{H}_i^W$, and in benzene, $\mathscr{H}_i^B$, for silica unmodified and modified with silane and titanate coupling agents

Type of coupling agent	Amount (wt/wt)	$\mathscr{H}_i^W$ (J g^{-1})	$\mathscr{H}_i^B$ (J g^{-1})	h_i^W (J m^{-2})	h_i^B (J m^{-2})	Degree of hydrophobicity (%)
Unmodified silica	–	25.5	26.0	0.18	0.19	–
Mercaptosilane A-189	1	21.9	29.3	0.16	0.21	11.3
	2	19.2	31.7	0.14	0.23	18.0
	3	16.8	35.1	0.12	0.25	25.9
Mercaptosilane A-1893	2	20.0	31.1	0.14	0.22	16.4
Aminosilane A-1100	1	26.6	28.1	0.19	0.20	7.5
	2	28.8	30.4	0.21	0.22	14.5
	3	30.2	34.0	0.22	0.24	23.5
Aminosilane A-1120	2	27.9	34.7	0.20	0.25	25.0
Metacryloxysilane A-174	1	21.5	30.2	0.15	0.22	13.9
	2	19.0	32.0	0.14	0.23	18.8
	3	16.6	36.3	0.12	0.26	28.4
Glycidoxysilane A-187	2	18.9	32.4	0.13	0.23	19.8
Titanate KRTTS	1	20.7	30.6	0.15	0.22	15.0
	2	18.7	32.8	0.13	0.23	20.7
	3	16.1	37.4	0.12	0.27	30.5
Titanate I	2	19.3	31.1	0.14	0.22	16.4
Titanate II	2	19.5	31.3	0.14	0.22	16.9
Titanate III	2	19.2	31.3	0.14	0.22	16.9
Titanate KR 33CS	1	20.9	30.0	0.15	0.21	13.3
	2	19.1	32.2	0.14	0.23	19.3
	3	16.6	36.8	0.12	0.26	29.3

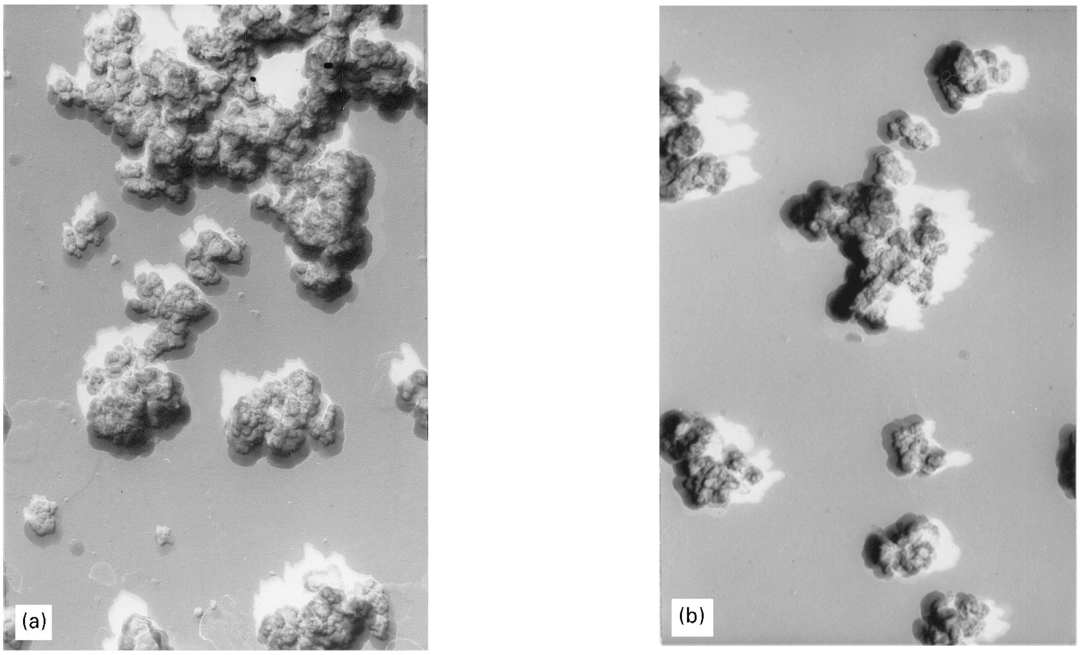
TABLE III Condensation degrees of silanol groups on the surface of unmodified and modified silica

Modifying compounds	Amount (wt/wt)	Geometric method		Planimetric method	
		Peak area (cm^2)	Condensation degree (%)	Peak area (cm^2)	Condensation degree (%)
Unmodified silica	–	8.40	–	7.70	–
A-189	1	7.12	15.23	6.45	15.88
	2	6.74	19.76	6.10	20.78
	3	6.09	27.50	5.66	26.49
A-174	1	6.95	17.26	6.30	18.18
	2	6.13	27.02	5.63	26.88
	3	5.66	32.62	5.11	33.64
KR TTS	1	7.52	10.48	6.96	9.61
	2	7.01	18.55	6.50	15.58
	3	6.38	24.05	5.92	23.11
KR 33 CS	1	7.40	11.90	6.80	11.69
	2	7.05	16.07	6.48	15.84
	3	6.50	22.62	6.03	21.68

titanates, the condensation degree increases much more slowly.

Development of a method for determining the condensation degree of surface silanol groups on the surface of silica after modification permitted recognition of the quantitative course of modification of these surfaces. By using this method, it was possible to select an appropriate coupling agent for a given type of silica, as well as to follow the kinetics of the modification process, and to ascertain the mechanism of the condensation reaction of silanol groups in the presence of a catalyst.

The results of electron microscopy may also be of help in interpreting the effect of surface modification of fillers on their surface properties. Modification of the silica surface by both silane and titanate coupling agents substantially changes the morphology and agglomeration of particles. On the microscope pictures, one can clearly see a decreasing size of aggregates and agglomerates of particles in the presence of, for example, mercaptosilane A-189. In the case when approximately 5 wt/wt mercaptosilane is used for modification, even single, i.e. primary, particles of silica appear. Such an effect is probably related to the



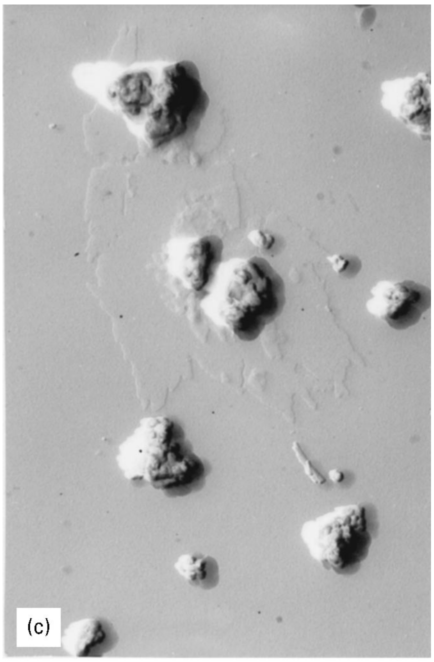


Figure 3 Electron micrographs of precipitated silica (× 20 000): (a) unmodified silica, (b) modified silica with 1 wt/wt A-189 silane, (c) modified silica with 3 wt/wt A-189 silane.

change of hydrophilic properties of silica into hydrophobic or partially hydrophobic ones, depending on the amount of silane coupling agent added. Increase in the degree of condensation of surface silanol groups causes a decrease in the number of these groups. The distances between them increase, and by the same token the hydrogen bonds between particular silanol groups become weakened. As a result, decomposition of the aggregates and agglomerates takes place, which leads to homogenization of silica particles and is of great importance when they are used as fillers of plasto- and elastomers.

Fig. 3 shows micrographs of precipitated silica either modified or unmodified with mercaptopropyltrimethoxysilane. The results of electron microscopy provide evidence for a positive effect of modification on the decomposition of agglomerates and aggregates of silica particles. Modification of silica leads to substantial changes in the chemical character of their surface, yet only slightly affects the fundamental physicochemical properties(specific surface area, bulk density, etc.). The coupling agents adsorbed on the surface of silica induce hydrophobicity of the surface. As a result, the silica surface assumes an organophilic character, i.e. its chemical affinity to a group of organic polymers increases.

4. Conclusions

1. Modification of the surface of precipitated silica results in an increase in its activity. Application of both silane and titanate coupling agents leads to an increase in the chemical affinity of silica to polymer and, in the first place, to a change of its character from hydrophilic to hydrophobic.
2. Modification of the silica surface is performed in a device ensuring a minimum usage of the solution of modifying agent, i.e. both the solvent and the coupling agent; modification involves surface wetting of silica.
3. Modification by silane and titanate coupling agents is a reaction involving substitution of these compounds on silanol groups present on the silica surface, according to a mechanism of electrophilic proton substitution (SE).
4. The efficiency of the modification can be estimated with high accuracy by using the following methods:

(a) NIR studies of changes in the intensity of bands of silanol groups bound to the silica surface;

(b) measurement of the heat of immersion of the surfaces of modified silicas, which indicates the degree of hydrophobicity of these surfaces;

(c) electron microscopy studies that permit interpretation of the effect of modification of silica on agglomeration of its particles.

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*Received 8 August 1995
and accepted 2 July 1996*