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CARBONATE-SILICATE FILLERS MODIFIED WITH TWO TYPES OF PROADHESIVE COMPOUNDS

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Surface modification of precipitated carbonate-silicate fillers was performed. For this purpose silane coupling agents and stearic acid were used. The modification was performed employing two agents: silane, with affinity to silicate silanol groups, and stearic acid, adsorbing on the carbonate surface. The unmodified and the modified carbonate-silicate fillers were subjected to physicochemical analysis. Studies were also performed which aimed at determining dispersion and particle morphology using SEM and DLS techniques. Moreover, calorimetry permitted to establish the extent of hydrophobization of carbonate-silicate filler surface following the modification. The extent of hydrophobization of filler surface clearly correlated with the uniform character of particles formed in the course of surface modification.

Key words: carbonate-silicate fillers, silane coupling agents, stearic derivatives

INTRODUCTION

Activity of carbonate-silicate fillers depends to a significant extent upon chemical structure of their surface (Iler, 1979). Properties of carbonate-silicate fillers can be modified using various chemical reactions (Grodzka, 2001). Numerous studies have been published on reactions of silicate surface silanol groups with silane proadhesive compounds (Grodzka, 2000, Jesionowski, 2000; Jesionowski, 2001) as well as with acrylic and stearic derivatives (Domka, 1995). The principal aim of the efforts involved a decrease or removal of silicate hydrophilic properties as well as introduction to their surface of new organofunctional groups. Due to the gradual substitution of bound silanol groups by organic radicals, an interaction of carbonate-silicate fillers with silanes or acrylic and stearic derivatives results in organophilic properties of the filler surface.

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Modified and unmodified silicates and carbonates represent very good fillers of elastomers: butadiene-styrene rubbers and polyurethanes. The fillers provide vulcanizates with higher strength parameters and augment their chemical resistance (Krysztafkiewicz, 1997). Moreover, silicates can serve as carriers, adsorbing organic pigments on their surface (Binkowski, 2001).

The principal aim of the performed studies was definition of modifier effect on agglomeration and particle surface morphology in a carbonate-silicate filler. For this purpose we decided to modify in parallel the filler surface with one agent which showed affinity to silicates (e.g., silane coupling agent) and with another agent, showing affinity to carbonates (e.g., stearic acid).

EXPERIMENTAL

MATERIALS

For production of carbonate-silicate fillers, the following substrates were used:

- Sodium metasilicate (10 wt% solution of $M=3.3$ modulus),
- Calcium hydroxide (10 wt% solution),
- Carbon dioxide (gaseous),

For surface modification of carbonate –silicate fillers the following compounds were used:

- Stearic acid,
- Silane coupling agents:
 - N-2-(aminoethyl)- 3- aminopropyltrimethoxysilane (U-15D),
 - n-octyltrimethoxysilane (U-222).

METHODS

Carbonate-silicate fillers were precipitated using 10 wt% solution of calcium hydroxide, 10 wt% solution of sodium metasilicate, the modulus of $\text{SiO}_2/\text{Na}_2\text{O}=3.3$ and gaseous CO_2 with the flow rate equal $300 \text{ cm}^3/\text{min}$. On the other hand, modification of carbonate-silicate filler surface was performed by the „dry” technique (Grodzka, 2001). The carbonate-silicate filler, precipitated from solutions of sodium metasilicate and calcium hydroxide in the presence of gaseous CO_2 ($\text{Na}_2\text{SiO}_3:\text{Ca}(\text{OH})_2=2:1$ (v/v), the temperature of precipitation: 60°C), was placed in a mixer, adding appropriate amounts of the modifier. The mixing was conducted for 1h.

The carbonate-silicate filler with two types of proadhesion compounds was modified. In this aim selected modifiers were used – one which could react with the silicate surface silanol groups and the other one, with affinity to adsorption on the carbonate surface. The silanes were added at 1 to 5 weight parts per 100 weight parts of the filler and stearic acid at 1 to 5 weight parts per 100 weight parts of the filler. The carbonate-silicate filler at the first was modified with one proadhesion compound, and then, with the second agent. The changes of the physicochemical properties of modified fillers were observed.

Selected samples of modified fillers were subjected to microscopic analysis, mainly in order to characterize the surface morphology of respective particles and their tertiary butanol, application of the suspension on the microscope table and 10 min coating with gold atoms on an ionisation plate.

Particle size distribution was also examined using a Zeta Plus apparatus (Brookhaven Instruments Co, USA). The particle size was measured using, the dynamic light scattering (DLS) technique. The prepared sample was placed in a cuvette and size distribution of carbonate-silicate particles was then measured. Polydispersity represented a measure of heterogeneity of particle size distribution in the studied system.

Heats of immersion of the surface in water (H_i^W) and in benzene (H_i^B) for the unmodified and modified carbonate-silicate fillers were established using a calorimetric technique (Krysztalkiewicz, 1996). A KRM- type calorimeter permitted the detection of even slight thermal effect by a dynamic technique, under conditions approaching adiabatic. The extent of surface modification or hydrophobization was calculated using the following equation:

$$N = \frac{(H_i^B)_m - (H_i^B)_n}{(H_i^B)_m} \cdot 100\% \quad (1)$$

where $(H_i^B)_m$ is the heat of immersion of the modified filler surface in benzene and $(H_i^B)_n$ that of the unmodified filler surface in benzene, both in J/g.

RESULTS AND DISCUSSION

The samples of carbonate-silicate fillers precipitated from sodium metasilicate and calcium hydroxide solutions using gaseous CO_2 at various temperatures, are listed in Table 1.

Carbonate-silicate filler of best parameters was obtained at 60°C. The product showed the lowest bulk density, the highest paraffin oil and dibutyl phthalate absorbing capacities and a high value of flow-off point. Particle size distribution and electron micrograph of the unmodified carbonate-silicate filler are presented in Figs. 1a and 1b, respectively.

Table 1. Physicochemical properties of carbonate-silicate fillers precipitated with calcium hydroxide and sodium metasilicate solutions as well as gaseous carbon ($Na_2SiO_3:Ca(OH)_2=2:1$)

Temperature (°C)	Bulk density (g/dm ³)	Flow-off point (cm ³ /10g)	Dibutyl phthalate absorbing capacity (cm ³ /100g)	Paraffin oil absorbing capacity (cm ³ /100g)	Water absorbing capacity (cm ³ /100g)
40	243	26.5	300	400	250
60	235	26.5	300	450	200
80	282	23.0	250	300	200

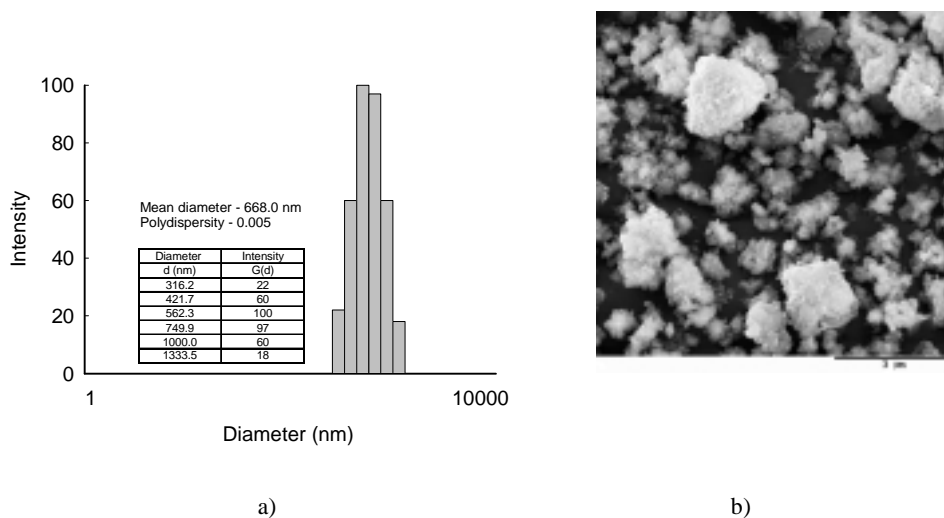


Fig.1. a) Multimodal particle size distribution and b) SEM of unmodified carbonate-silicate filler

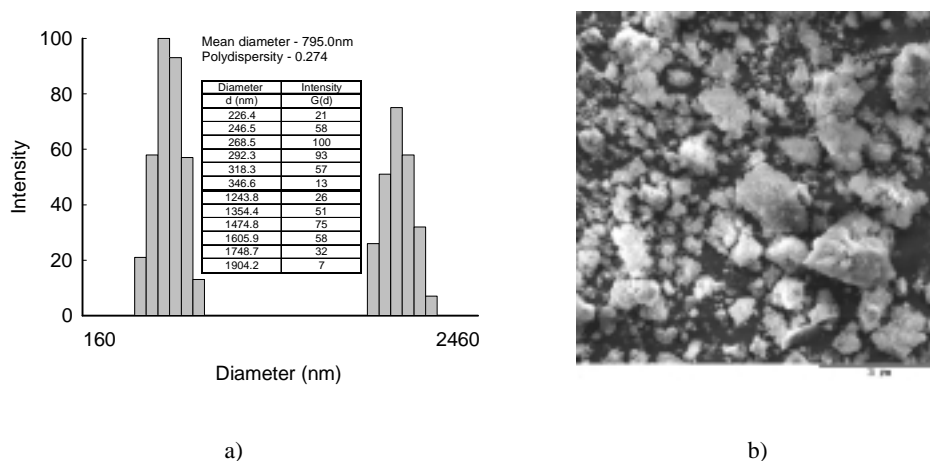


Fig. 2. a) Multimodal particle size distribution and b) SEM of modified carbonate-silicate filler with 5 w/w of U-222 silane

As evident from the particle size distribution, the precipitated filler manifested the presence of relatively large particles with strong tendency to form agglomerates. The broad band in Fig.1a fitted the range of 316.2-1.333.5 nm (maximum intensity of 100 corresponded to the particle diameter of 562.3 nm). Mean particle diameter of the unmodified filler was 688.0 nm. This was corroborated by respective electron micrograph (Fig.1b), which documented presence of large particles of the carbonate-silicate filler and their non-uniform character.

Following modification with 5 weight parts of octylsilane U-222, the carbonate-silicate filler demonstrated strong tendency to form agglomerates. The particle size distribution (Fig.2a) manifested two bands of a different intensity. The high intensity band corresponded to particles which formed primary agglomerates (aggregates) in the range of lower diameters. The band occupied the range of 226.4-346.6. nm (maximum intensity of 75 corresponded to the agglomerate diameter of 1,474.8 nm). Mean diameter of the agglomerates was 795.0 nm. The SEM electron micrograph (Fig. 2b) confirmed the pronounced non-uniform character of the sample: two types of agglomerates, primary and secondary ones, were present.

Following modification of carbonate-silicate filler with 2 weight parts of stearic acid also certain non-uniformity of the sample could be noted (Fig. 3).

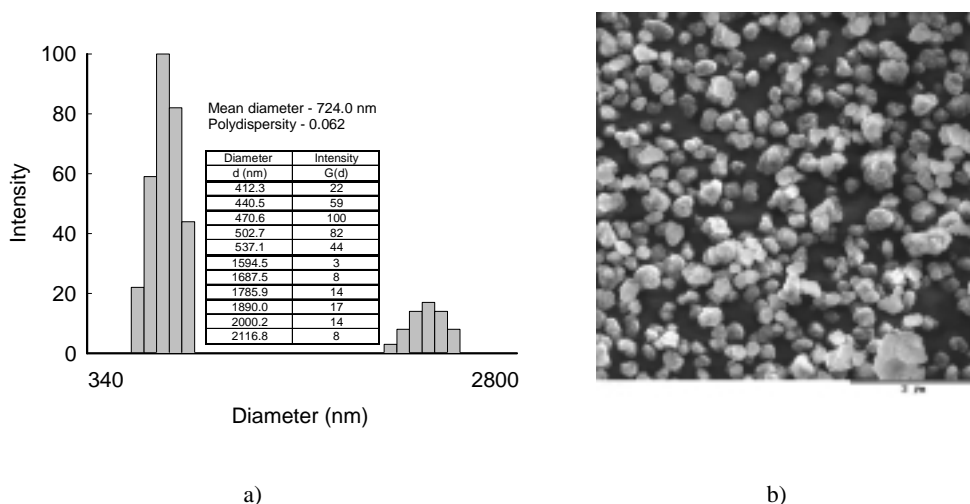


Fig. 3. a) Multimodal particle size distribution and b) SEM of modified carbonate-silicate filler with 2 w/w of stearic acid.

In the particle size distribution (Fig. 3a), two bands of different intensity could be noted. The more intense band corresponded to particles of 412.3-537.1 nm in diameter (maximum intensity of 100 corresponded to particles of 470.6 in diameter). The low intensity band documented the presence of secondary agglomerates within the range of 1,594.5-2,116.8 nm in diameter (maximum intensity of 17 corresponded to agglomerates of 1,890.0 in diameter). Mean size of agglomerate particles was 724.0 nm. The electron micrograph fully confirmed the presence of small amounts of secondary agglomerates, which comprised a very low fraction of all particles.

A significantly improved uniformity of carbonate-silicate filler particles was expected following the modification with two different coupling agents. The compounds were selected so that the carbonate and the silicate portion of the studied filler could be modified in parallel. The performed studies proved that application of

two modifying agents significantly improved the uniform character of carbonate-silicate filler particles.

The carbonate-silicate filler modified at first with 2 weight parts of stearic acid and, then, with 2 weight parts of octylsilane U-222 exhibited a very highly uniform character, as documented in Fig.4.

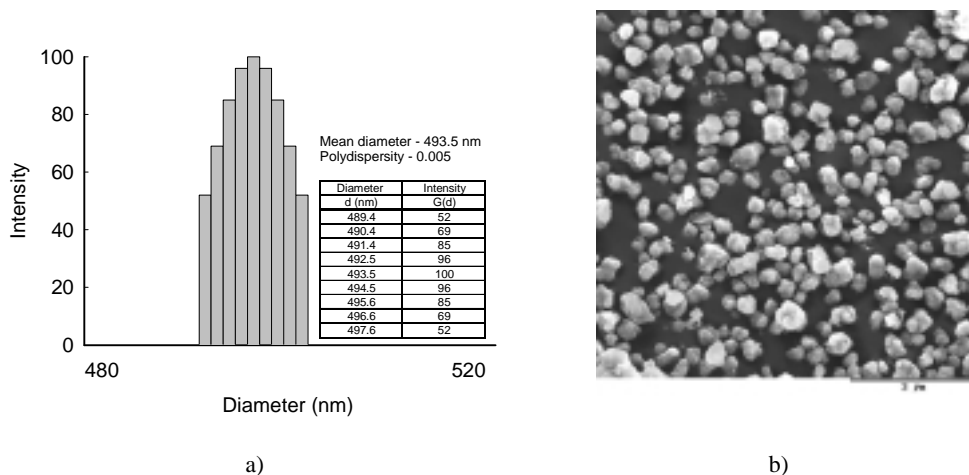


Fig. 4. a) Multimodal particle size distribution and b) SEM of modified carbonate-silicate filler with 2 w/w of stearic acid and subsequently with 2 w/w octylsilane

As shown in Fig. 4a, the particle size distribution manifested a very narrow range of particles of the so modified filler, 489.4-497.6 nm (maximum intensity of 100 corresponded to particles of 493.5 nm in diameter). The mean particle size was 493.5 nm. The particle size distribution was corroborated by SEM micrograph (Fig. 4b), which documented the presence of highly uniform shape and diameter of the particles. Following modification of the carbonate-silicate filler with higher amounts of the same modifiers (5 weight parts of stearic acid and 5 weight parts of octylsilane) the particles remained uniform but their minimum diameter increased. The mean particle diameter increased to 606.4 nm.

The altered sequence of applying the two coupling agents during modification of carbonate-silicate filler (octylsilane first, followed by stearic acid) also resulted in highly uniform samples. Particle size distribution for the carbonate-silicate filler modified first with 2 weight parts of octylsilane and, then, with 2 weight parts of stearic acid is presented in Fig. 5a. Only one band was noted, within the range of 370.2-376.4 nm (maximum intensity of 100 corresponded to particles of 373.3 nm in diameter). The mean particle size was also 373.3. nm.

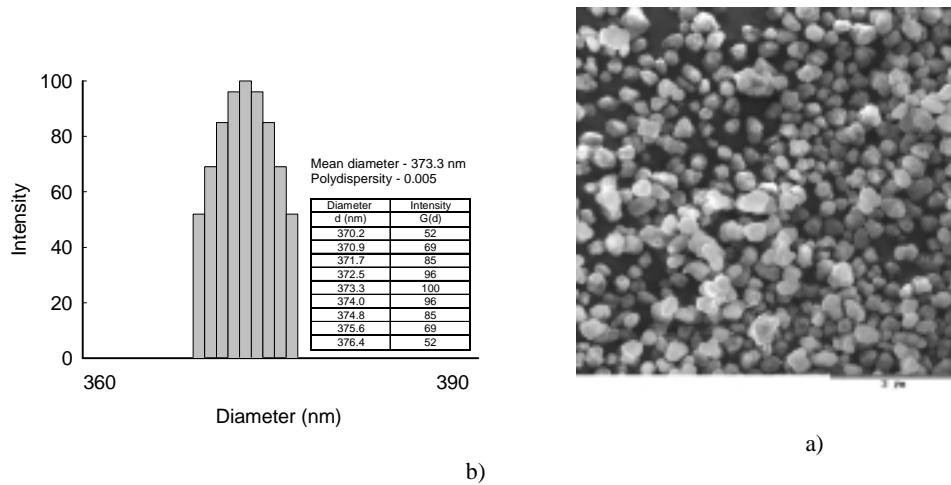


Fig. 5a) Multimodal particle size distribution and b.) SEM of modified carbonate-silicate filler with 2 w/w of octylsilane and subsequently with 2 w/w of stearic acid.

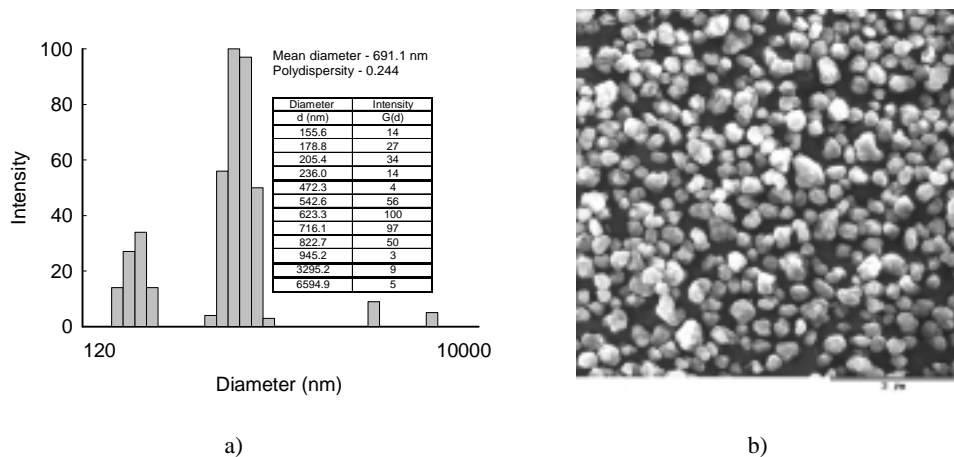


Fig. 6. a) Multimodal particle size distribution and b.) SEM of modified carbonate-silicate filler with 2 w/w of stearic acid and subsequently with 2 w/w of aminosilane.

The particle size distribution manifested two bands of different intensity. The band of lower intensity corresponded to particles of very low diameters: 155.6–236.0 nm (maximum intensity of 34 corresponded to particles of 205.4 nm in diameter). The more intense band represented particles of particles with slightly higher diameters, 472.3–945.2 nm (maximum intensity of 100 corresponded to particles of 623.3 nm in diameter). The mean particle diameter was 691.0 nm. The electron micrograph (Fig. 6b) corroborated the data obtained using the DLS technique.

Increase in amounts of the applied modifiers (to 5 weight parts of stearic acid and 5 weight parts of aminosilane) was accompanied by certain deterioration of particle uniformity and by increase in particle diameters (Figs. 7a and b).

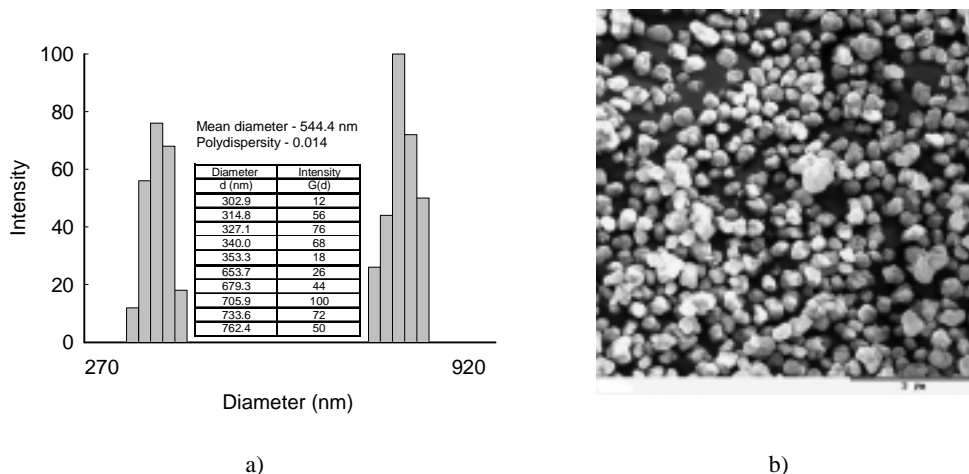


Fig. 7. a) Multimodal particle size distribution and b) SEM of modified carbonate-silicate filler with 5 w/w of stearic acid and subsequently with 5 w/w of aminosilane.

In the particle size distribution (Fig. 7a) two particle bands of different intensity were observed. The less intense band represented the smaller particles and occupied the range of 302.9-353.3 nm (maximum intensity of 76 corresponded to particles of 327.1 nm in diameter). The more intense band fitted the range of 653.7-762.4 nm (maximum intensity of 100 corresponded to particles of 705.9 nm in diameter). Mean diameter of the filler particles was 544.4 nm.

Modification using the reciprocal sequence of proadhesive compounds (aminosilane first, followed by stearic acid) again improved the uniformity of the carbonate-silicate filler.

The particle size distribution and SEM micrograph of carbonate-silicate filler modified with 2 weight parts of aminosilane and, then, with 2 weight parts of stearic acid is presented in Fig. 8. Clearly uniformity of the sample improved, as shown in Fig. 8.

In the particle size distribution (Fig. 8a) a single band was noted, within the range of 719.8-737.5 nm (maximum intensity of 100 corresponded to the particle diameter of 728.6 nm). The electron micrograph (Fig. 8b) fully confirmed the uniform character of the so modified filler.

Results of studies on heats of immersion of carbonate-silicate fillers in water or benzene, before and after modification, are shown in Table 2. In the Table, the calculated extent of surface hydrophobization is also given.

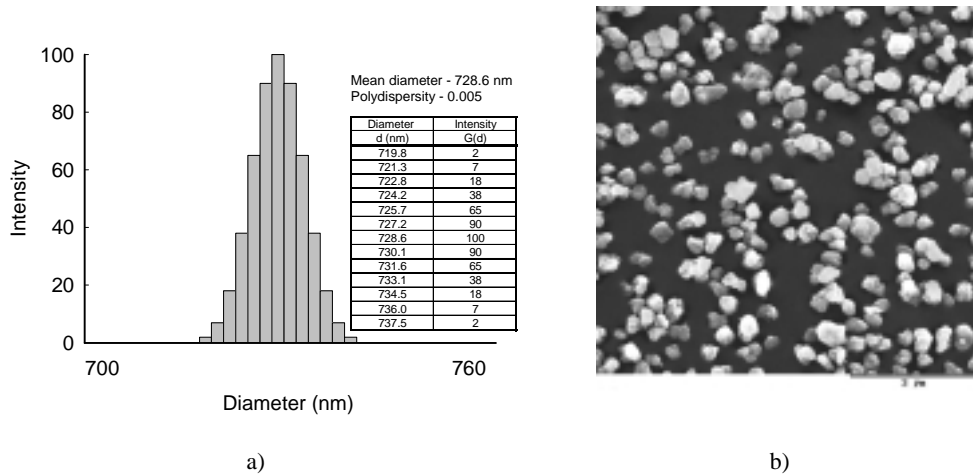


Fig. 8. a) Multimodal particle size distribution and b.) SEM of modified carbonate-silicate filler with 2 w/w of aminosilane and subsequently with 2 w/w of stearic acid.

As evident from data of Table 2, the modification of carbonate-silicate filler surface with proadhesive compounds was followed by an evident decrease in the heat of surface immersion in water while the heat of immersion in benzene showed increased values. The modification exerted particularly marked augmenting effect on the extent of surface hydrophobization and increased amounts of the applied modifying compounds clearly increased the effect. The extent of hydrophobization of carbonate-silicate fillers increased particularly following the modification with stearic acid and with octylsilane and the effect was most pronounced when the modification employed first 5 weight parts of stearic acid and, then, 5 weight parts of octylsilane U-222. A much lower extent of hydrophobization was observed when the modification involved the application of stearic acid and aminosilane U-15D. The changes in the hydrophobization extent might explain the increase in uniform character of the fillers following modification with the two types of proadhesive compounds.

Table 2. Heats of immersion of carbonate-silicate filler surface and extent of surface hydrophobization before and after modification with selected proadhesive compounds

Amount of modifying compound (w/w)	Heat of immersion in water H_i^w (J/g)	Heat of immersion in benzene H_i^B (J/g)	Extent of hydrophobization N (%)
Unmodified carbonate-silicate filler			
-	22.5	23.1	-
Carbonate silicate filler modified with U-222 silane			
2	20.2	25.0	7.6
3	18.7	26.3	12.2
5	17.2	28.9	20.1
Carbonate silicate filler modified with stearic acid			
2	20.7	24.2	4.6
5	18.5	27.6	16.3
Carbonate silicate filler modified with stearic acid and then with U-222 silane			
2/2	18.9	26.1	11.5
3/3	16.8	27.7	16.6
5/5	15.4	29.5	21.7
Carbonate silicate filler modified with U-222 silane and then with stearic acid			
2/2	19.1	25.7	10.1
3/3	17.2	27.1	14.8
5/5	15.7	28.9	20.1
Carbonate silicate filler modified with stearic acid and then with U-15D silane			
2/2	20.2	24.8	6.1
3/3	18.8	26.0	11.2
5/5	17.3	27.1	14.8
Carbonate silicate filler modified with U-15D silane and then with stearic acid			
2/2	19.3	25.5	9.4
3/3	17.7	27.0	14.4
5/5	16.9	28.4	18.7

CONCLUSIONS

- Carbonate-silicate filler modified at first with 2 weight parts of stearic acid and, then, with 2 weight parts of octylsilane exhibited the most uniform character and showed no tendency to form agglomerate structures.
- The extent of hydrophobization of carbonate-silicate filler surface increased in particular following the modification with two agents: stearic acid and octylsilane.
- The changes in hydrophobization extent of carbonate-silicate filler surface might explain the more pronounced uniform character of fillers following modification with the two types of proadhesive compounds.

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Grodzka J., Krysztafkiewicz A., Jesionowski T., *Napełniacze węglanowo-krzemianowe modyfikowane dwoma rodzajami związków proadhezyjnych*, Fizykochemiczne Problemy Mineralurgii, 36, (2002) 89-99 (w jęz. ang.)

Przeprowadzono modyfikację powierzchni strączonych napełniaczy węglanowo-krzemianowych. W tym celu wykorzystano silanowe związki wiążące oraz kwas stearynowy. Modyfikację przeprowadzono przy użyciu dwóch związków - silanu o powinowactwie do grup silanolowych krzemianu i kwasu stearynowego adsorbującego się na powierzchni węglanowej.

Nimodyfikowane i modyfikowane napełniacze węglanowo-krzemianowe poddano analizie fizykochemicznej. Przeprowadzono również badania mające na celu określenie dyspersji i morfologii cząstek za pomocą techniki SEM i DLS. Ponadto metodą kalorymetryczną określono stopień hydrofobizacji powierzchni napełniaczy węglanowo-krzemianowych po modyfikacji. Zauważono wyraźną korelację pomiędzy wzrostem stopnia hydrofobizacji powierzchni napełniaczy, a jednorodnością cząstek kształtowanych w trakcie powierzchniowej modyfikacji.