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Janina GRODZKA*, Andrzej KRYSZTAFKIEWICZ*, Teofil JESIONOWSKI*,
Dominik PAUKSZTA*

CARBONATE-SILICATE FILLERS PRECIPITATED FROM SOLUTIONS OF ALKALINE SILICATES AND CALCIUM HYDROXIDE USING CARBON DIOXIDE

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A procedure was worked out to precipitate highly dispersed carbonate-silicate fillers using solutions of sodium metasilicate, calcium hydroxide and gaseous carbon dioxide. In course of fillers precipitation effects of changes of Na_2SiO_3:$Ca(OH)_2$ solutions v/v ratios and temperature were examined. The precipitated fillers were subjected to a comprehensive physicochemical analysis (bulk density, capacities to absorb water, dibutyl phthalate and paraffin oil, flow-off point were estimated). Also particle size and particle size distribution, homogeneity of particles, their tendency to form agglomerates and particle surface morphology were examined using SEM and DLS techniques. Carbonate-silicate fillers were evaluated also in respect to their structure by means of WAXS method. Carbonate-silicate filler precipitated at the Na_2SiO_3:$Ca(OH)_2$ v/v ratio=4:1 characterized high particles homogeneity, high values of paraffin oil absorbing capacity and flow off point, as well as low bulk density.

Key words: carbonate-silicate fillers, precipitation, SEM, DLS, calcite structure

INTRODUCTION

The non-toxic character of both the chalk and of the silicate fillers argues for their increasingly comprehensive application, particularly in polymer processing (Niedermeier, 2002; Hasse, 2002). Common carbon black fillers, which are produced in laborious processes, loose their popularity (for example, in rubber industry) (Donnet, 1993). In this regard, carbonate-silicate filler, composed of two non-toxic components, may provide a very attractive alternative. In addition, it is of significance that such a filler is obtained in the process of precipitation and, therefore, it forms a uniform composition, representing a nanofiller of calcium carbonate and calcium

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* Poznan University of Technology, Institute of Chemical Technology and Engineering,
Pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland, e-mail: Teofil.Jesionowski@put.poznan.pl

silicate (Krysztafkiewicz, 1990). Moreover, the precipitation process can be controlled in such a way that the co-precipitated calcium carbonate may exist in two crystalline forms, calcite and aragonite (Domka, 1996).

Presence of the co-precipitated calcium carbonate favours augmented activity of the carbonate-silicate filler. In this case, of particular importance is the presence of silanol groups, directly linked to the silicate portion of the filler (Daniels, 1998). Silanol groups at the surface of the carbonate-silicate filler may form active centres, so significant in processes of modification of the surface (Chu, 1998; Trens, 1996). For example, silane coupling agents could react with hydroxyl surface groups of fillers (Plueddemann, 1982; Mittal, 1992). Precipitated calcium carbonates are not suitable to chemical modification due to the absence at their surface of hydroxyl groups (Pizzi, 1994). Therefore, the hybrid calcium carbonate/calcium silicate system can be subjected to physical interaction with modifiers which are popular for chalks, e.g., with fatty acids and their salts and with silane coupling agents which chemically react with silicate silanol groups.

Carbonate-silicate fillers can be applied not only in the rubber industry and in processing of plastics but also in shoe industry, production of paints and varnishes, in pharmaceutical industry, cosmetics, food and paper industry.

EXPERIMENTAL

MATERIALS

Substrates for production of a carbonate-silicate filler included: solution of calcium hydroxide, solution of sodium metasilicate of silicate modulus - 3.3, gaseous carbon dioxide. The process was conducted as specified by the following scheme (Fig.1).

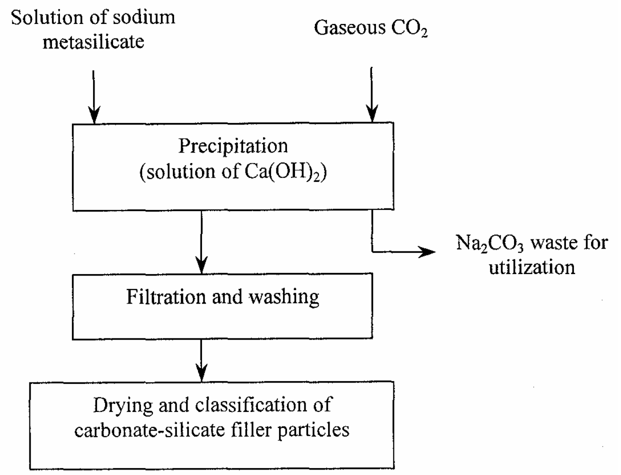


Fig. 1. Block diagram of precipitation of carbonate-silicate fillers

METHODS

Following precipitation, the carbonate-silicate fillers were subjected to physicochemical tests, their bulk density as well as, water, dibutyl phthalate and paraffin oil absorbing capacities were estimated (Krysztafkiewicz, 1987). Their flow-off point was also estimated, the typical parameter of chalk (carbonate) fillers (Katz, 1978). In order to obtain data on dispersion, particle size, surface morphology, structure of individual particles and agglomeration of carbonate-silicate fillers, their samples were studied by scanning electron microscopy (SEM) to obtain reliable images of the filler surface (using Philips SEM 515 equipment).

The identification analysis involved studies using WAXS technique. The results were analysed employing XRAYAN software (Marciniak, 1998). The diffraction patterns were executed employing the horizontal diffractometer TUR-M62. Nickel-filtered CuKα radiation (λ=1.5418 Å) was used in the measurements. The following measuring conditions were employed: anode voltage - 30 kV, anode current - 25 mA the measurement range of 2θ: 3-60^o, measuring step - 0.04^o.

Particle size and their size distribution, also representing principal property of carbonate-silicate fillers, were measured taking advantage of the dynamic light scattering (DLS) technique (Żurawska, 2002), using optoelectronic systems of ZetaPlus apparatus. Aqueous suspension of the filler was stabilised, placed in a cuvette and particle size distribution of the sample was measured using equipment of Brookhaven Instruments, USA.

RESULTS AND DISCUSSION

Principal physicochemical properties of precipitated carbonate-silicate fillers for various v/v ratios of calcium hydroxide and sodium metasilicate solutions are listed in Table 1.

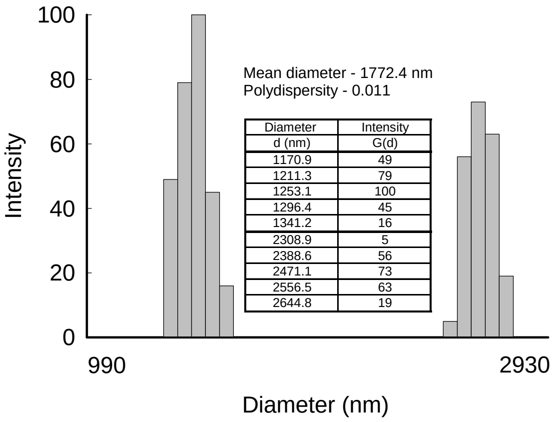
As demonstrated by data in Table 1, samples of fillers precipitated at v/v ratio of Na_2SiO_3:$Ca(OH)_2$=1:2, independently of temperature, exhibited relatively high bulk densities (above 260 g/dm^3) and low values of flow-off point (as low as 13-18 cm^3/10g). Capacities to absorb dibutyl phthalate and paraffin oil were also low. Fillers precipitated at Na_2SiO_3:$Ca(OH)_2$ ratio equal to 1:1 exhibited slightly lower bulk densities (of the order of 210-225 g/dm^3) and higher values of flow-off point (17-18.5 cm^3/10g). The capacities to absorb dibutyl phthalate and paraffin oil were comparable.

Very interesting results were obtained following precipitation of carbonate-silicate fillers at the v/v ratio of Na_2SiO_3:$Ca(OH)_2$=2:1 (particularly at 60^{o}C). The sample manifested low bulk density (170 g/dm^3), a high flow-off point (26.5 cm^3/10g) and high capacities to absorb dibutyl phthalate (300 cm^3/100g) and paraffin oil (450 cm^3/100g). Even higher physicochemical parameters were demonstrated by sample 10, precipitated at Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 4:1 at 60^{o}C. The sample manifested low bulk density, 165g/dm^3 and a high flow-off point, 27.0 cm^3/10g. Capacities to absorb dibutyl phthalate and paraffin oil amounted to 310 cm^3/100g and 470 cm^3/100g, respectively.

Table 1. Physicochemical properties of obtained carbonate-silicate fillers

Sample No.	Temp. (^{o}C)	Bulk density (g/dm^3)	Flow-off point (cm^3/10g)	Water absorbing capacity (cm^3/100g)	Dibutyl phthalate absorbing capacity (cm^3/100g)	Paraffin oil absorbing capacity (cm^3/100g)
Na_2SiO_3 : $Ca(OH)_2$ = 1:2						
1	40	275	13.0	200	250	300
2	60	260	13.0	250	250	350
3	80	270	18.0	200	220	300
Na_2SiO_3 : $Ca(OH)_2$ = 1:1						
4	40	220	18.0	200	250	250
5	60	210	18.5	250	250	350
6	80	225	17.0	250	220	250
Na_2SiO_3 : $Ca(OH)_2$ = 2:1						
7	40	170	25.5	250	300	400
8	60	170	26.5	305	300	450
9	80	180	23.0	200	250	300
Na_2SiO_3 : $Ca(OH)_2$ = 4 :1						
10	60	166	27.0	310	300	470

Particle size distribution of the carbonate-silicate filler precipitated at the Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 1:1 at 60^{o}C is presented in Fig. 2.



Mean diameter - 1772.4 nm
Polydispersity - 0.011

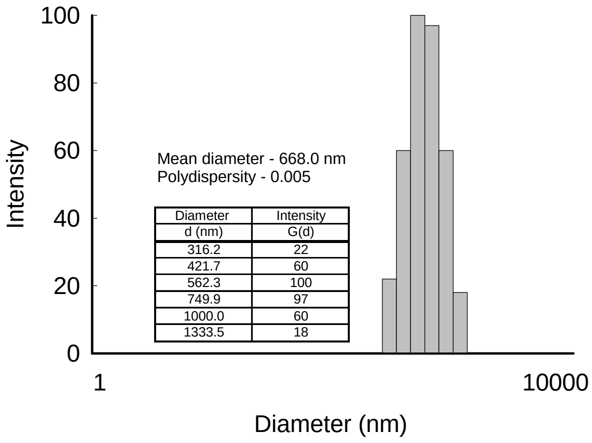
Diameter d (nm)	Intensity G(d)
1170.9	49
1211.3	79
1253.1	100
1296.4	45
1341.2	16
2308.9	5
2388.6	56
2471.1	73
2556.5	63
2644.8	19

Fig. 2. Multimodal particle size distribution of carbonate-silicate filler (sample 5)

As demonstrated by the particle size distribution for the carbonate-silicate filler (sample 5), the specimen demonstrated relatively low homogeneity. In the particle size distribution presence of two bands of distinct intensity could be noted, which represented particles of smaller and larger diameters, respectively, frequently linked into agglomerate structures. The band of higher intensity could be ascribed to primary particles and primary agglomerates (aggregates) and it fitted the range of 1170.9 – 1341.2 nm (maximum intensity of 100 corresponded to aggregates of 1253.1 nm in diameter). The less intense band corresponded to larger secondary agglomerate structures and was positioned in the diameter range of 2,308.9-2,644.8 nm (maximum intensity of 73 corresponded to agglomerates of 2,471.1 nm in diameter). Mean diameter of particles was 1,772.4 nm, and polydispersity was 0.011.

Particle size distribution of the carbonate-silicate filler precipitated at the Na_2SiO_3 :$Ca(OH)_2$ v/v ratio = 4:1, at 60°C (sample 10) is presented in Fig.3.

As demonstrated by the size distribution, only one particle band was present, pointing to highly increased homogeneity of the filler particles. Moreover, as compared to sample 5, particles of sample 10 formed band with particles of much lower diameters, present within the range of 316.2 – 1,333.5 nm (maximum intensity of 100 corresponded to particles and primary agglomerates of 562.3 nm in diameter). The mean particle diameter was 668.0 nm, and polydispersity was 0.005.



Mean diameter - 668.0 nm
Polydispersity - 0.005

Diameter d (nm)	Intensity G(d)
316.2	22
421.7	60
562.3	100
749.9	97
1000.0	60
1333.5	18

Fig. 3. Multimodal particle size distribution of carbonate-silicate filler (sample 10)

SEM microphotograph of the carbonate-silicate filler (sample 10) is presented in Fig. 4. The photograph confirmed extensive homogeneity of the sample precipitated in such conditions.

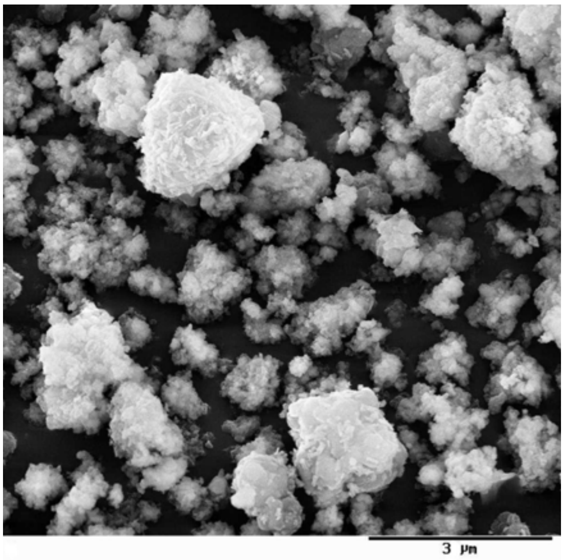


Fig. 4. SEM micrograph of carbonate-silicate filler (sample 10)

X-ray patterns of carbonate-silicate filler samples precipitated at 60°C at various Na_2SiO_3:$Ca(OH)_2$ v/v ratios (samples 8 and 10) are shown in Figs. 5 and 6 (the diffraction maxima, originating from calcite, were analyzed).

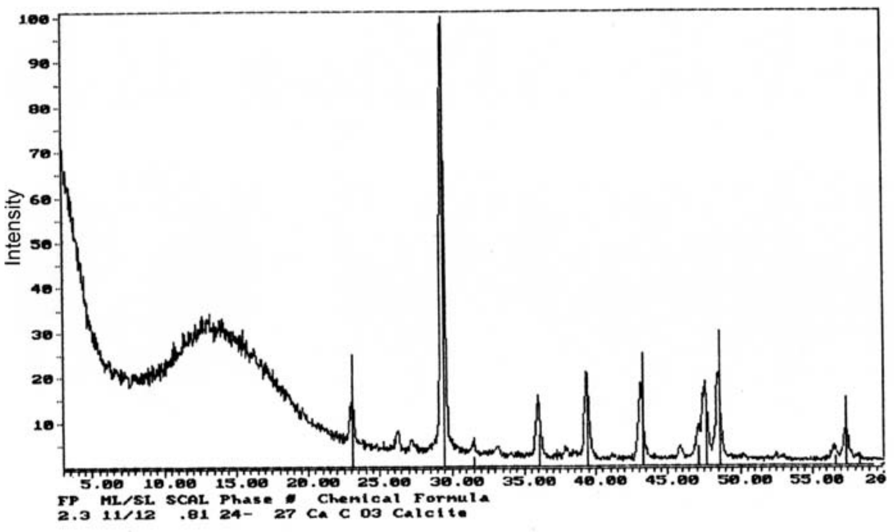


Fig. 5. WAXS pattern of carbonate-silicate filler (sample 8)

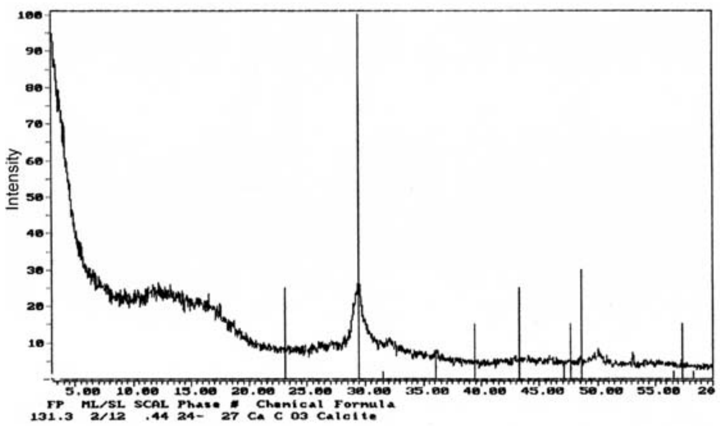


Fig. 6. WAXS pattern of carbonate-silicate filler (sample 10)

Diffraction pattern of sample 8 (Fig. 5) unequivocally demonstrated that the carbonate-silicate filler obtained from solutions of calcium hydroxide and sodium metasilicate (Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 2:1) contained exclusively calcite. No traces of other polymorphic forms, as well as, aragonite and waterite, were detected. Carbonate-silicate filler precipitated at larger volumes of sodium metasilicate (Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 4:1) exhibited a significantly amorphic character, as proven by the respective diffraction pattern (Fig. 6). However, presence of the crystalline form of calcite could be noted although maxima typical for the structure were much less intense than those noted for the sample 8. Also in this case not even minimum amounts of aragonite and waterite forms could be noted.

The amorphic phase was accompanied by higher amounts of co-precipitated calcium silicate. Such a filler manifested more advantageous physicochemical parameters as well as the presence of fine particles with a decreased tendency to form agglomerates. The data were confirmed by SEM and DLS studies.

CONCLUSIONS

- Carbonate-silicate filler precipitated at the Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 2:1, at 60^{o}C exhibits relatively good physicochemical parameters, an average homogeneity and a tendency to form large complexes of agglomerates.
- Sample of carbonate-silicate filler precipitated in the presence of increased amounts of sodium metasilicate (Na_2SiO_3:$Ca(OH)_2$ solution v/v ratio = 4:1) manifests higher homogeneity and markedly improved physicochemical parameters (high values of flow-off point).
- Carbonate-silicate filler precipitated in the presence of augmented amounts of sodium metasilicate shows an amorphic character while the filler precipitated at Na_2SiO_3:$Ca(OH)_2$ v/v ratio = 2:1 is crystalline (in the polymorphic form as a calcite).

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Grodzka J., Krysztafkiewicz A., Jesionowski T., Paukszta D., *Napełniacze węglanowo-krzemianowe strącanie z roztworów krzemianów alkalicznych i wodorotlenku wapnia za pomocą dwutlenku węgla,* Physicochemical Problems of Mineral Processing, 37 (2003) 123-130 (w jęz. ang.).

Opracowano metodykę strącania wysoko zdyspergowanych napełniaczy węglanowo-krzemianowych, stosując roztwory metakrzemianu sodu i wodorotlenku wapnia oraz gazowy dwutlenek węgla. W trakcie strącania tych napełniaczy zmieniano między innymi stosunek objętościowy Na_2SiO_3:$Ca(OH)_2$ oraz temperaturę. Strącone napełniacze poddawano wszechstronnej analizie fizykochemicznej (oznaczono gęstość nasypową, chłonności wody, ftalanu dibutyu i oleju parafinowego oraz punkt spływania). Analizowano również wielkość cząstek oraz rozkład wielkości cząstek, jednorodność, tendencję do tworzenia aglomeratów, jak również morfologię powierzchni cząstek przy pomocy technik SEM i DLS. Napełniacze węglanowo-krzemianowe oceniano również pod względem krystaliczności metodą dyfraktometrii rentgenowskiej. Napełniacz węglanowo-krzemianowy strącony przy stosunku objętościowym Na_2SiO_3:$Ca(OH)_2$=4:1 odznacza się dużą jednorodnością cząstek, dużymi wartościami chłonności oleju parafinowego i punktu spływania oraz małą gęstością nasypową.