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FORMATION AND PHYSICOCHEMICAL PROPERTIES OF SILICA FILLERS PRECIPITATED IN EMULSION MEDIUM

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The studies were performed on production of silica particles in emulsion medium. Precipitation of silicon dioxide was performed from aqueous solutions of sodium metasilicate and hydrochloric acid. A non-ionic surfactant (Rokanol K7) was applied as the emulsifier. Heptane formed the organic phase. Optimum compositions of emulsion and appropriate parameters of silica precipitation were determined. Particle size and morphology of the formed dispersions were examined using scanning electron microscopy (SEM). Dispersion character of the examined colloids was also defined using the non-invasive back scattering method (NIBS). Moreover, studies were conducted on sedimentation and wettability of the products with water and, at the final stage, adsorptive analysis was conducted.

Key words: silica fillers, emulsion systems, polydispersity, adsorption, sedimentation and wettability
Słowa kluczowa:

INTRODUCTION

In recent years increasingly high quality requirements have to be met by polymer composites. Selection of appropriate filler represents an important variable which shapes composite properties. The most important criteria in classification of inorganic fillers include their physicochemical properties dispersion and morphological properties in particular (Yatsuyanagi 2001, Chen 2005, Mathew 2004).

Modern silica fillers have to exhibit highly uniform particles, a relatively well developed specific surface area (particularly the outer surface area) and a specific-chemical character of their surface (Wu 1997, Gun'ko 2002). Among several types of

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silica, synthetic colloidal silicas deserve huge attention. They are obtained mainly by combustion of silicon halides (flame technique) (Barthel 1995), by acidic agent-induced precipitation from aqueous solutions of sodium metasilicate (Jesionowski 2002a, Zhang 1997, Jesionowski 2002b), and also using the technique of Stöber (alkoxysilane hydrolysis and condensation) (Stöber 1968, Esquena 2001).

In this study we suggest an alternate way of formation of nanometric monodisperse silicas in emulsion medium using heptane as an organic phase. The precipitated silicas manifest a strictly defined morphological and dispersion character. Moreover, the numerous active chemical centres present at silica surface may participate in formation of bonds in the polymer-filler system. The principal aim of the study involved selection of optimum precipitation parameters (in emulsion medium) and a comprehensive physicochemical characterization of the produced silica fillers.

EXPERIMENTAL

MATERIALS

Silicas were obtained by precipitation from aqueous solutions of sodium metasilicate (Vitrosilicon S.A.) and hydrochloric acid (POCh S.A.). The organic phase was formed by heptane (POCh S.A.) while oxyethylenated fatty alcohol, Rokanol K7 (PCC Rokita S.A.) was used as an non-ionic emulsifier.

METHODS OF STUDIES

The silica precipitation process was preceded by preparation of two emulsions, of which one, the alkaline one (E1), contained appropriate volume of sodium silicate solution and heptane. The other, acidic emulsion (E2), contained hydrochloric acid and an organic solvent. The third component of both emulsion involved the same emulsifier, added to the emulsions in various amounts. Emulsion E2 was placed in a reactor and emulsion E1 was dosed to while the entire reactor content was mixed using a homogenizer. The precipitated silica was destabilized and, then, the organic solvent was distilled off.

Silica powders dispersion studies were performed, including determination of silica particle size distribution, with appropriate attention given to band intensity and particle volume, using the non-invasive back scattering method (NIBS) and employing Zetasizer Nano ZS (Malvern Instruments Ltd.). Silica particle shape and surface morphology were examined using scanning electron microscopy (Size VO40). Moreover, the course of sedimentation and wettability with water of the precipitated silicas were documented using K100 tensiometer (Krüss). At the last stage, specific surface area (BET) was estimated for selected silicas using ASAP 2010 (Micromeritics Instruments Co.).

RESULTS AND DISCUSSION

The results of the physicochemical tests of the obtained silicas fillers are presented in Table 1.

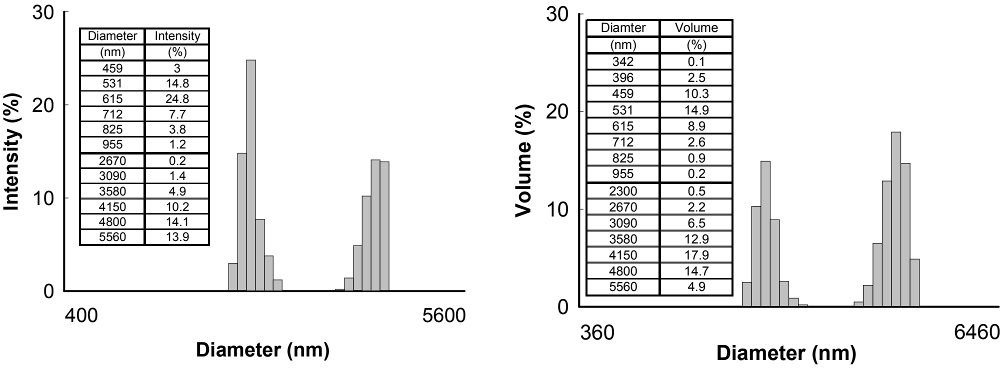
Table 1. Mean particle diameter and polydispersity of silica related to content of emulsifiers

Sample No.	Emulsifier content (g)		Range of particle diameters (nm)		Polydispersity
	E1	E2	by intensity	by volume	
1	3.0	1.0	459-955; 2670-5560	396-1110; 2670-6440	0.261
2	2.5	0.8	220-295; 615-1110; 4150-5560	190-342; 531-1280; 3580-6440	0.520
3	2.0	0.7	106-122; 164-190; 342-396; 3090-5560	106-220; 295-459; 2670-6440	1.000
4	3.0	0.8	1110-2670	955-3090	0.751

The evaluated results documented negative effects of insufficient amounts of the applied emulsifier in preparation of the two emulsions on the number of bands which appeared in the particle size distributions. Taking into account either band intensity of particle volumes, the multimodal particle size distribution was confirmed by the value of polydispersity, which amounted to 1.000 (Table 1). Much better physicochemical parameters were manifested by silicas precipitated in the presence of augmented amounts of surfactants (samples 1 and 4).

The silica of most advantageous parameters and physicochemical properties was obtained in sample 1. The respective particle size distributions are shown in Fig.1, taking into account the relationship between particle diameter and either band intensity (Fig.1a) or volume share (Fig.1b).

In Fig. 1a the intense band of primary agglomerates (aggregates) of silica particles could be noted in the diameter range of 459-955 nm, with maximum intensity of 24.8 for the particles of 615 nm in size. The other band, of a much lower intensity, reflected the presence of secondary agglomerates and showed maximum intensity of 14.1 which corresponded to agglomerate diameter of 4100 nm. In turn, in the particle size distribution which took into account volume share of the particles, domination of secondary agglomerates was observed (Fig.1b). In the precipitated silica the highest share was formed by particles of 2670-6440 nm in diameter. Approximate volume shares of the two bands may indicate that such conditions silica precipitation in emulsions resulted in a product of a highly uniform character, which was confirmed by the polydispersity value of 0.261.



Diameter (nm)	Intensity (%)
459	3
531	14.8
615	24.8
712	7.7
825	3.8
955	1.2
2670	0.2
3090	1.4
3580	4.9
4150	10.2
4800	14.1
5560	13.9

Diamter (nm)	Volume (%)
342	0.1
396	2.5
459	10.3
531	14.9
615	8.9
712	2.6
825	0.9
955	0.2
2300	0.5
2670	2.2
3090	6.5
3580	12.9
4150	17.9
4800	14.7
5560	4.9

(a) (b)

Fig.1. Particle size distribution of silica precipitated in sample 1 (a) by intensity and (b) by volume

Electron micrograph of silica precipitated in sample 4 is shown in Fig. 2.

The silica precipitated under conditions listed in Table 1 manifested only one intense band, representing particles of 1110-2670 nm in diameter. The SEM photograph confirmed the near uniform character of the sample and low tendency to form larger accumulations of the particles while polydispersity of the sample amounted to 0.751.

Silica particle sedimentation profile in water is shown in Fig. 3 as a function weight gain with time for the samples precipitated using heptane as the organic solvent of the emulsion system.

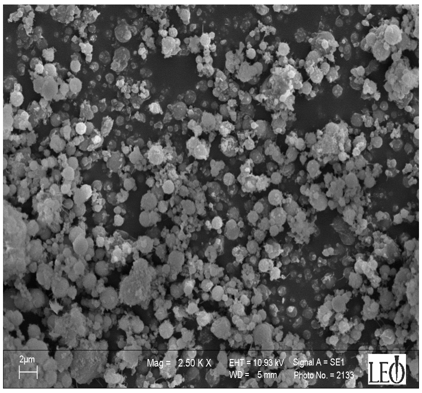


Fig. 2. Electron micrograph (SEM) of silica precipitated in sample 4

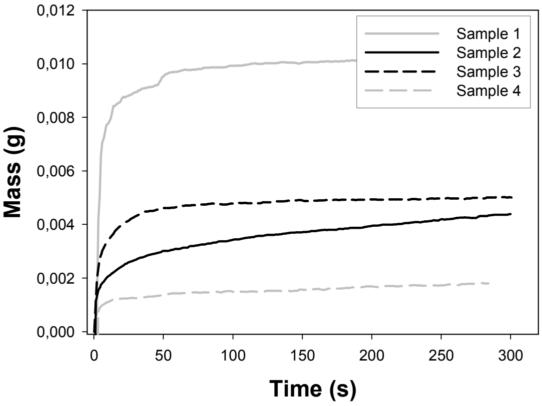


Fig. 3. Sedimentation profile for obtained silicas

Course of the curves permitted to note that the lowest weight increased vs. time was shown by silica precipitated in sample 4. Slightly more particles sedimented in silicas precipitated in samples 2 and 3. The weight increased in time was reciprocally related to the amount of applied emulsifier: it was increasing in line with decreasing weight share of the surfactant applied in preparation of the two emulsions.

Curves of wettability with water for selected silicas are shown in Fig.4.

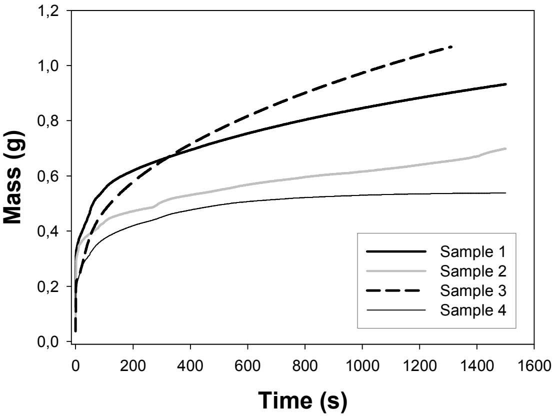


Fig. 4. Wettability with water for selected silicas

Studies conducted on wettability of the analyzed products with water demonstrated that the most hydrophilic silica was obtained when the added emulsifiers comprised the lowest weight share (sample 3). The silica manifested complete wetting before the time set at 1500 s. Silicas precipitated in samples 1, 2, 4 manifested a relatively slower wetting. The curve of wetting for silica precipitated in the latter sample, diverged most from a hydrophilic type (mass of the wetted silica amounted to just 0.5 g in the course of entire measurement).

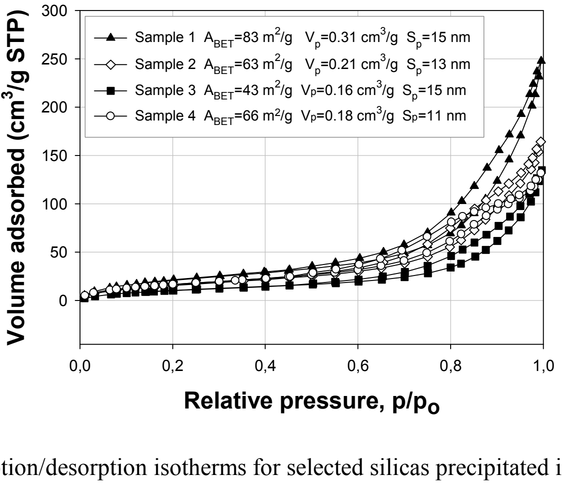


Fig. 5. Nitrogen adsorption/desorption isotherms for selected silicas precipitated in emulsion medium

Results of adsorption studies and isotherms of nitrogen adsorption/desorption for selected silicas are shown in Fig.5.

As indicated by the data of Fig.5, silicas precipitated in an emulsion medium demonstrated similar specific surface areas and depended upon the amount of added surfactant in the course of emulsion preparation. In the range of relative pressures p/p_0 = 0.0-0.7 the amount of adsorbed nitrogen increased only slightly. When the pressure was exceeded, however, the amount of adsorbed nitrogen abruptly increased to reach the highest value of 250 cm^3/g at $p/p_0=1$ in silica precipitated in sample 1. The graph indicated also that the range of hysteresis loop was the highest for the product, which was confirmed by the high value of BET specific surface area equal 83 m^2/g.

CONCLUSIONS

Silica of best dispersive and morphological properties was obtained, with optimized amounts of emulsifier (Rokanol K7), amounting to 3 g for emulsion E1 and 1.0 g for emulsion E2. Just a slight increase in weight of the added surfactant in emulsion E2 resulted in markedly higher polydispersity, in appearance of larger particle clumps and particle shape diverged slightly from the ideal, spherical one. Sedimentation curves demonstrated that weight of the sedimenting silica particles increased in line with decreasing amounts of added of emulsifiers added in the course of silica precipitation. Silicas precipitated under the suggested conditions were, in general, well wettable with water. Adsorption studies showed that the obtained silicas manifested a moderately developed specific surface area (BET: 40-85 m^2/g) and showed mesoporous character.

ACKNOWLEDGEMENTS

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W przedstawionej pracy podjęto próbę uzyskania napełniaczy krzemionkowych metodą strąceniową w układzie emulsyjnym z roztworu metakrzemianu sodu i kwasu solnego, z zastosowaniem heptanu jako fazy organicznej oraz z dodatkiem Rokanolu K7. Otrzymane krzemionki poddano badaniom sedymentacji i zwilżaniu, określono wielkość powierzchni właściwej BET, a następnie wyznaczono rozkłady wielkości cząstek oraz dokonano obserwacji morfologii i mikrostruktury. Kolejnym etapem było omówienie i porównanie wyników świadczących o odpowiednim doborze parametrów, podczas syntezowania krzemionek. Badania dowiodły, że osiągnięto podstawowy cel, uzyskano wysoko zdyspergowane sferyczne krzemionki z układów emulsyjnych dla zastosowanej fazy organicznej. Użycie heptanu jako medium organicznego pozwoliło otrzymać krzemionkę o odpowiednich właściwościach fizykochemicznych, a uzyskane produkty mogą mieć szerokie zastosowanie w różnych gałęziach przemysłu, między innymi jako napełniacze wzmacniające w produktach elastomerowych, nośniki czynników zabezpieczających plony (nośniki konserwantów) oraz w środkach ochrony roślin, czynniki wybielające i czyszczące w pastach do zębów, pigmenty do produkcji papieru, czy też jako wypełniacze w farbach i lakierach itp.

słowa kluczowa:wypełniacze krzemionkowe, systemy emulsyjne,polidyspersja, adsorpcja, sedymentacja, zwilżalność