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PHYSICOCHEMICAL ANALYSIS OF SILICAS COATED WITH NATURAL LATEX MILK

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Studies were presented on the ways surface character of colloidal silica (SYLOID[®]244) can be altered from a hydrophilic to hydrophobic using natural latex milk. Effects of concentration and volume of the applied latex emulsion, LATEKS KAGETEX[®]FA, were examined on structure of hydrophobic silicas and their physicochemical properties, including bulk density, capacities to absorb water, dibutyl phthalate and paraffin oil. Sedimentation rate and wettability with water were also examined for the modified and unmodified silicas.

Key words: modification of silica surface, latex milk, sedimentation, particle wettability

INTRODUCTION

Due to the presence on the surface of precipitated silicas, of reactive silanol groups, the silicas find several technological applications, including their use as valuable fillers of elastomers and plastomers. The silica-filled elastomers and plastomers manifest higher tearing and abrasive strength, higher thermic and chemical resistance and improved mechanical parameters.

The inorganic-organic composites represent increasingly interesting materials in technology, due to their unusual properties reflecting parallel manifestation of characters typical for each type of the compounds.

The polymer-inorganic hybrids co-express the characters of inorganic particles, such as mechanical and thermal resistance, stability with processing potential and thermoplasticity of organic compounds. Introduction of inorganic substances to a polymer matrix may induce radical alterations in mechanic, thermal, electrical or magnetic properties as compared to those of pure organic compounds.

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Polymer-coated inorganic particles such as silica are applied in several branches of industry, including biomedical, optical or microelectronic industries. Their use in cosmetic products, inks and paints improves the dispersion of the products. Fillers coated with macromolecular compounds increase affinity of the filler to a polymer.

Impregnation of silica surface using polymers may proceed in a physicochemical, physical (physical adsorption) or a chemical way (chemical adsorption). In the physicochemical procedure macromolecules are placed on a mineral surface due to evaporation of a solvent or become adsorbed due to chemical, biochemical or electrostatic interactions.

In a chemical process polymerization (i.a., emulsive, radical or suspension polymerization) is conducted directly in the presence of inorganic particles. In either case, the polymer must exhibit specific interactions with the inorganic surface. Various types of interactions may develop between the polymer and the inorganic material, including strong interactions (covalent, coordinate or ionic interactions) or weak ones (van der Waals interactions, hydrogen bonds, or hydrophilic-hydrophobic interactions) or the interactions may be absent (Kickelbick 2003, Luna-Xavier 2001, 2002, Bourgeat-Lami 1995, 1995).

The techniques of obtaining the polymer-inorganic hybrids may be classified into:

- „grafting onto the surface”: attaching the polymer to the mineral surface due to interaction with functional groups present on the surface (most frequently involving a chemical reaction),
- „grafting from the surface”: polymerization of monomers starting at active compounds (initiators, co-monomers) covalently grafted to the inorganic surface.

Polymer grafting onto the surface, involving condensation of polymer functional groups with reactive groups of the solid, does not allow for formation of “polymer brushes of various length”. The adsorbed polymer diminishes diffusion of subsequent chains to the inorganic surface and due to steric hindrance blocks the surface of active centers. The technique of grafting from the surface allows for a more dense packing of polymer on inorganic particles and, thus, for augmentation of their resistance to friction and corrosion (Laruelle 2004, Quingye Zhou 2002).

EXPERIMENTAL

MATERIALS

In the experiments of alteration of silica surface character by coating with the natural latex, poly(cis-isoprene) the commercial precipitated SYLOID[®]244 silica was used (produced by GRACE DAVISON). It was obtained by precipitation from sodium metasilicate solutions using sulphuric acid solution at room temperature in the form of a silica gel. The obtained gel in the form of a thin filtration cake was subsequently washed with water, dried and, then, dispersed and segregated. For the surface modification of silica latex milk was used, with the general formula of $(-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-)_n$, produced by SAMIC-ALCAN GmbH.

METHODS OF STUDIES

The LATEKS KAGETEX[®]FA latex emulsion was used to change the type of surface the SYLOID[®]244 silica. The process of silica surface modification was conducted in a reactor of 500 cm³ capacity, charged before the reaction with 5 g of SYLOID[®]244 silica to which latex milk was dosed of appropriate concentration and in adequate volume. In the prepared reactor the reaction was implemented in 3 h, at the temperature of 100°C under a reflux cooler. The resulting white sediment was washed with water and filtered under a reduced pressure and the filtration cake was subjected to a stationary drying at the temperature of 105°C for 48 h.

For all the samples principal physicochemical parameters were estimated which characterize highly dispersed fillers (including bulk density, capacities to absorb water and appropriate organic agents). Sedimentation rate and wettability were also determined using the TENSIOMETR K100 type apparatus (Krüss). Silica particle size and particle size distribution were documented in the NANO ZS type apparatus (Malvern) using the technique of dynamic light scattering (DLS). Selected samples were subjected to morphological and microstructural analysis using scanning electron microscopy (SEM) and the Philips SEM 515 electron microscope. Particle size distribution allowed to determine polydispersity of the particles (as a measure of uniform character of examined powders).

RESULTS AND DISCUSSION

The relationship between bulk density of the impregnated silicas on one hand and concentration and volume of the applied latex emulsion on the other is presented in Fig. 1. Bulk density of the original, unmodified SYLOID[®]244 silica amounted to 57 g/dm³.

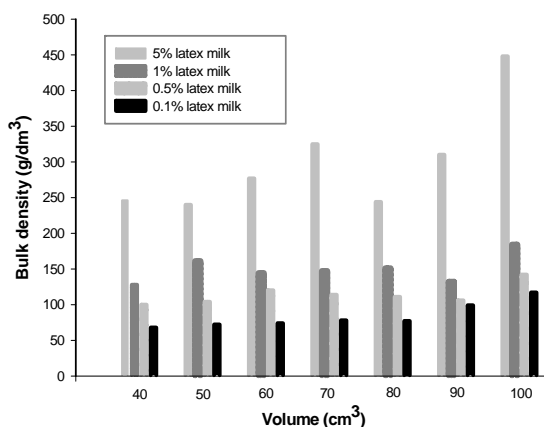


Fig. 1. Bulk density of silicas impregnated with a variable concentration and a defined volume of natural latex milk

The performed studies showed that increase in concentration and volume of latex milk used for modification of SiO₂ surface was accompanied by increasingly high bulk density of the silica.

Alterations in principal physicochemical properties of silicas impregnated with natural latex milk are illustrated in Fig. 2. The original SYLOID[®]244 silica manifested the following physicochemical parameters: capacity to absorb water: 775 cm³/100g, capacity to absorb dibutyl phthalate: 1275 cm³/100g capacity to absorb paraffin oil: 1900 cm³/100g.

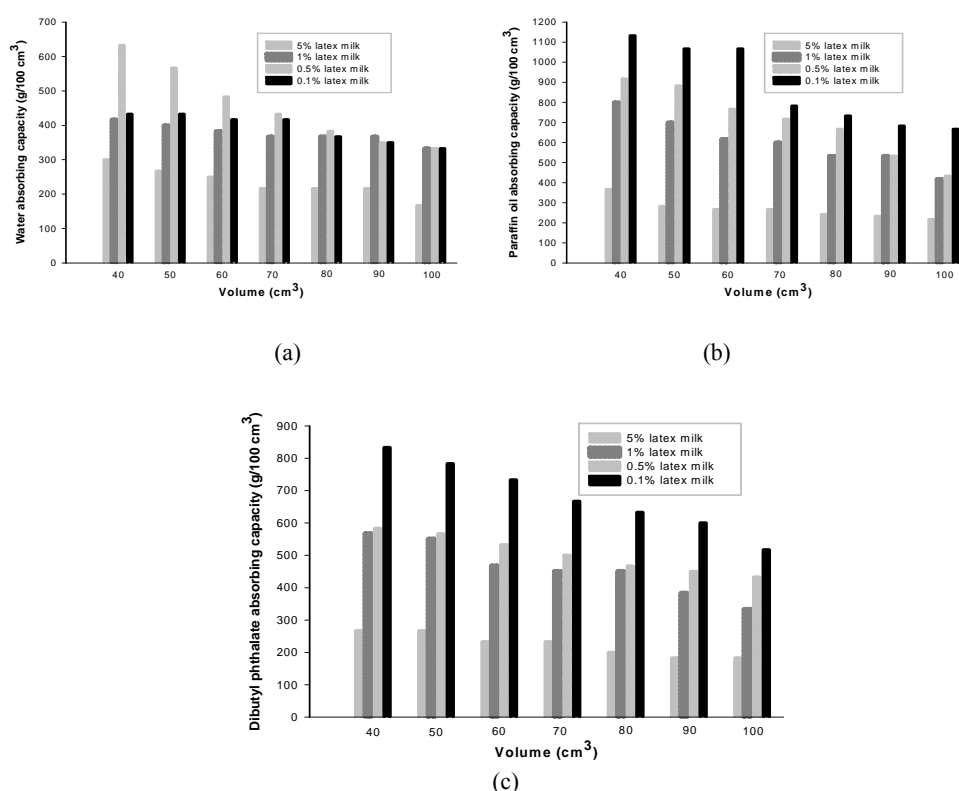


Fig. 2. Capacity to absorb water (a), paraffin oil (b), dibutyl phthalate (c) manifested by silica samples impregnated with natural latex milk of a known concentration and a variable volume

The above data allowed to note that augmented volume and concentration of the latex applied for surface modification resulted in decreasing capacities to absorb paraffin oil, dibutyl phthalate (hydrophobic substances) and even water. In every case impregnation of silica surface with natural latex took place as indicated not only by the low absorbing capacities but also by visual exponents of polymer adsorption. The silica surface showed alteration in its colour intensity: coating of silica with poly(cis-

isoprene) resulted in yellowish shade of the colour. With increasing concentration and volume of the applied latex milk the colour became darker, turning to a dark-yellow colour of the product. On the other hand the unmodified SYLOID[®]244 silica manifested white colour. Monitoring effects of latex milk applied for modification its increased concentrations could be noted to result in increased hydrophobicity of the silicas.

Particle size distribution and SEM microphotograph of silica modified with 100 cm³ 5% latex milk are presented, respectively, in Figs. 3 - 4.

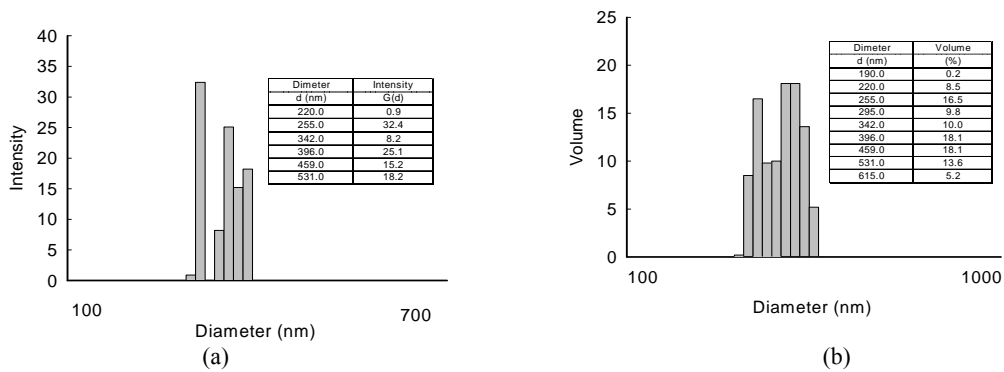


Fig. 3. Particle size distribution of silica modified with 100 cm³ 5% latex milk, as affected by the concentration of the intensity (a) and volume (b)

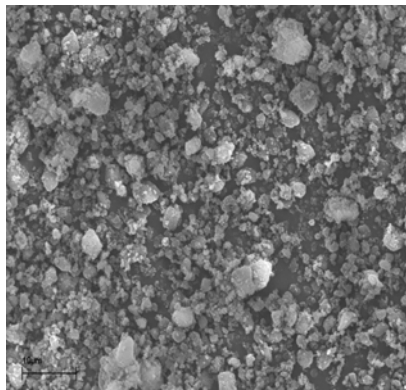


Fig. 4. SEM microphotograph of silica impregnated with 100 cm³ 5% latex milk

The particle size distribution, which reflected intensity of representation, manifested two bands. The first band corresponded to the modified silica particles of lower diameters and fitted the range of 220–255 nm (maximum intensity of 32.4 corresponded to the particle diameter of 255 nm). The other band of the particle size

distribution corresponded to particles of higher diameters and covered the range of 342–531 nm (maximum intensity of 25.1 corresponded to the particles of 396 nm in diameter). The polydispersity index amounted to 0.773. On the other hand, only one band could be observed when volume was taken into account in the particle size distribution. The band corresponded to particles of diameters ranging from 190 to 615 nm, with maximum volume of 18.1 for particles of 396 and 459 nm in diameter. The SEM microphotograph (Fig. 4) confirmed the presence of particles of low diameters, which clumped with each other forming larger aggregates and agglomerates of particles.

Particle size distribution and SEM microphotograph of silica modified with 90 cm³ 1% latex milk are shown in, respectively, Fig. 5 and Fig. 6.

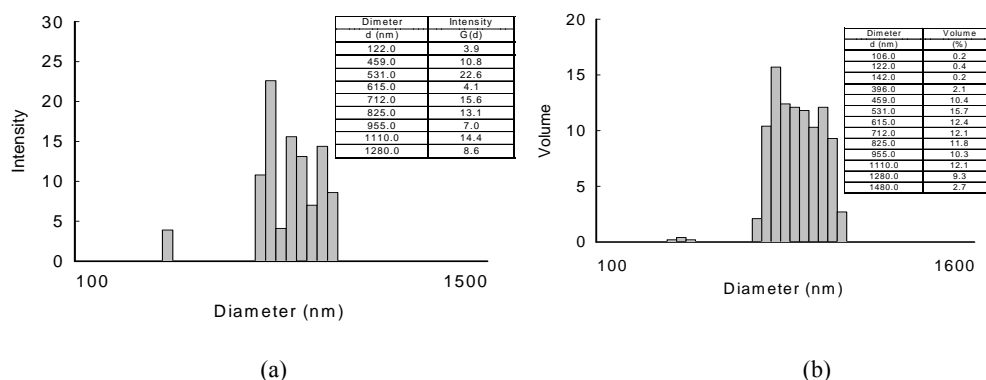


Fig. 5. Particle size distribution of silica modified with 90 cm³ 1% latex milk, as affected by the concentration, of the intensity (a) and volume (b)

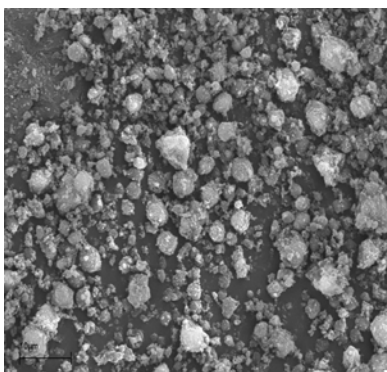


Fig. 6. SEM microphotograph of silica impregnated with 90 cm³ 1% latex milk

As demonstrated by the particle size distribution the sample was not fully uniform. The particle size distribution demonstrated the presence of two bands of distinct intensities. The first band, of a definitely lower intensity, could be ascribed to particles

of 122 nm in diameter, manifesting intensity of 3.9 and polydispersity of 0.357. The other band in the particle size distribution could be ascribed to the presence of secondary agglomerates. The band spanned the range of 459–1280 nm (maximum intensity of 22.6 corresponded to the agglomerates of 531 nm in diameter). Taking into account particle volume distribution also two bands could be distinguished. The first band of a very low intensity could be ascribed to particles of 106–142 nm in diameter, which corresponded to maximum volume of 0.4. On the other hand, the other, more intense band corresponded to particles of higher diameters, ranging from 396 to 1480 nm, with maximum volume of 15.7 for particles of 531 nm in diameter. SEM microphotograph (Fig. 6) confirmed the presence of particles with higher diameters, resulting from clumping of smaller particles into aggregates and agglomerates.

Particle size distribution and SEM microphotograph of silica modified with 60 cm³ 0.5% latex milk are presented in, respectively, Fig. 7 and Fig. 8.

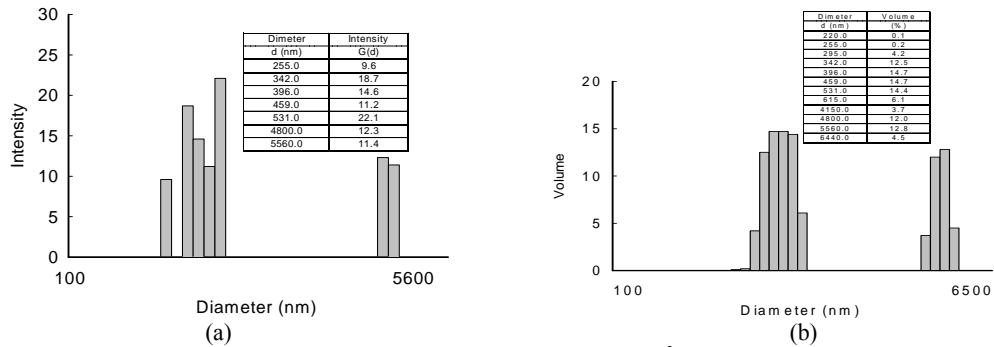


Fig. 7. Particle size distribution of silica modified with 60 cm³ 0.5% latex milk, as affected by concentration, (a) intensity (b) volume

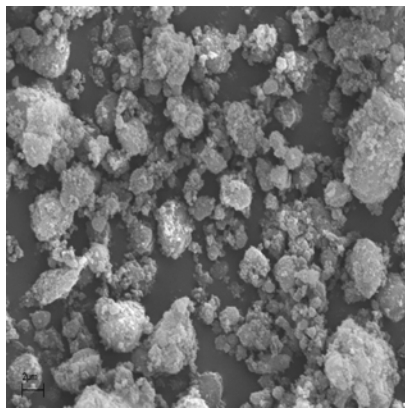


Fig. 8. SEM microphotograph of silica impregnated with 60 cm³ 0.5% latex milk

In this case particle size distribution manifested the presence of three bands of a variable intensity. The first two of them fitted the range of, respectively, 255 nm and 342–531 nm (in the second of them, maximum intensity of 22.1 corresponded to the modified silica particle size diameter of 531 nm). The third band in the particle size distribution could be ascribed to agglomerates of higher diameters. The band spanned the range of 4800–5560 nm (maximum intensity of 12.3 corresponded to particles of 4800 nm in diameter). The polydispersity index amounted to 0.750. On the other hand, taking into account particle volumes two bands could be noted. The first, more intense band was ascribed to particles of lower diameters, ranging from 220 to 615 nm, which corresponded to aggregates (maximum volume of 14.7 corresponded to aggregates of 396 and 459 nm in diameter). The other, less intense band reflected the presence of particles of higher diameters, ranging from 4150 to 6440 nm (with maximum volume of 12.8 for particles of 5560 nm in diameter). The presence of particles of the higher diameters was confirmed by SEM microphotograph (Fig. 8).

Upon modification of silica surface using 50 cm^3 0.1% latex milk the particle size distribution (Fig. 9) demonstrated, as in the previous case, the presence of three bands.

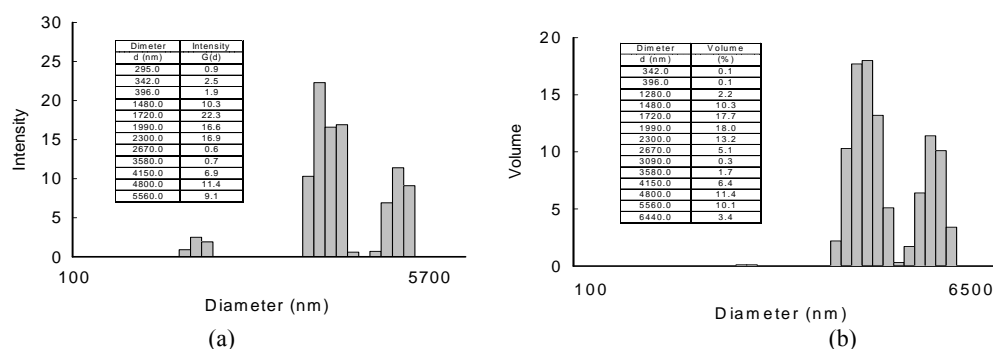


Fig. 9. Particle size distribution of silica modified with 50 cm^3 0.1% latex milk, as affected by the concentration, (a) intensity (b) volume

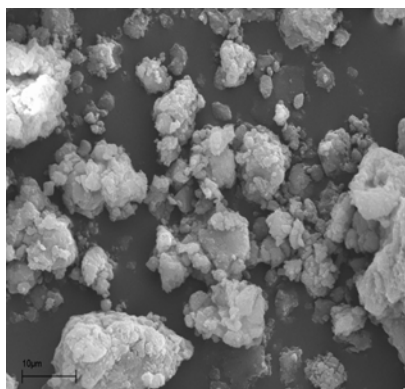


Fig. 10. SEM microphotograph of silica impregnated with 50 cm^3 0.1% latex milk

The first band was linked to the presence of particles of low diameters, in the range of 295–396 nm (maximum intensity of 2.5 corresponded to particles of 342 nm in diameter). The two remaining bands of higher intensities corresponded to particles of higher diameters and to secondary agglomerates in the range of 1480–5560 nm, with maximum intensity of 22.3 for particles of 1720 nm in diameter. The polydispersity index amounted to 0.530. Taking, on the other hand, the volume into account, the particle size distribution manifested the presence of two bands, of which the first manifested minimum intensity in the particle diameter range of 342–396 nm while the other band, spanning the range of 1280–6440 nm, corresponded to particles of higher diameters with maximum volume of 18.0 for the particles of 1990 nm in diameter. The SEM microphotograph (Fig. 10) confirmed the presence of secondary agglomerates.

The rates of wetting with water for silicas modified with 5% latex milk and the unmodified silica are compared to each other in Fig. 11.

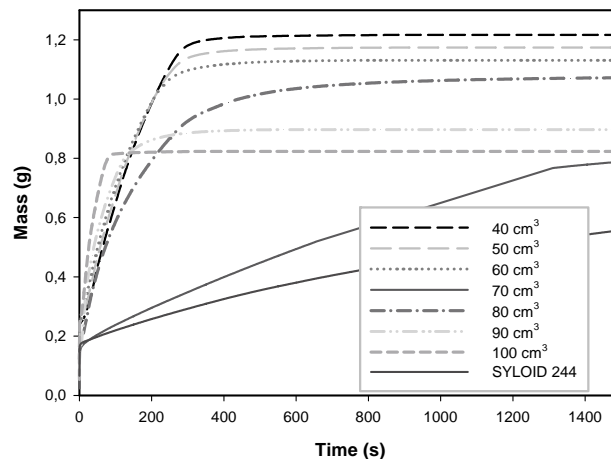


Fig. 11. Rate of wetting with water of the unmodified silica and silica modified with 5% latex milk

The studies documented that increasing bulk density of silica was accompanied by decreasing increments in silica weight in time, reflecting decreasing rates of wetting of the silica sample. For the sample modified with 40 cm³ 5% latex milk bulk density amounted to 246 g/dm³ and the silica demonstrated the highest increments in weight in time. For silicas modified with 60 cm³ and 100 cm³ latex bulk density values amounted to, respectively, 277 g/dm³ and 488 g/dm³. The relationship did not hold in the case of sample modified with 70 cm³ latex milk, which manifested the lowest weight increase but the sample showed higher wettability as compared to that of the original, pure SYLOID[®]244 silica.

Rates of wetting with water of the unmodified silica and silicas modified with 1% latex milk are compared in Fig. 12.

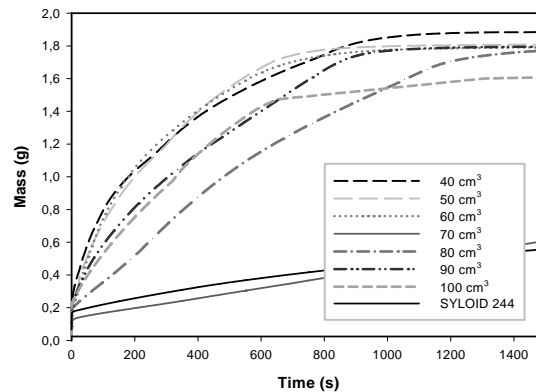


Fig. 12. Rate of wetting with water of the unmodified silica and silica modified with 1% latex milk

In the analysis of wettability with water of silicas modified with 1% latex milk and those modified with 5% latex milk a similar character of their surface could be disclosed. The weight increments in time, determined by the rates of wetting the samples decreased with increase in their bulk density. For the sample modified with 40 cm^3 1% latex milk bulk density amounted to 128 g/dm^3 , while bulk densities of silica samples modified with 80 cm^3 and 100 cm^3 latex amounted to, respectively, 151 g/dm^3 and 184 g/dm^3 . Similarly, the sample modified with 70 cm^3 latex milk manifested the lowest weight increment but the sample showed better wettability as compared to the original SYLOID[®]244 silica.

Rates of sedimentation in water of silicas modified with 1%, 0.1% latex milk and of unmodified silica are compared in Fig. 13, respectively.

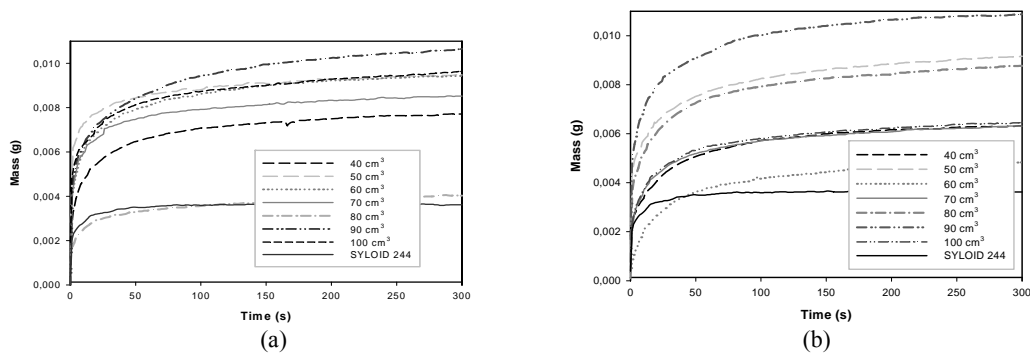


Fig.13. Rates of sedimentation in water of unmodified silica and silica modified with 1% latex milk (a), 0.1% latex milk (b)

The results showed that silicas modified with latex milk manifested sedimentation rates which decreased with increasing amounts of latex milk used for modification and with increasing hydrophobic character of the silica. For the sample modified with 1%

latex milk the situation was as follows: the capacity to absorb water amounted to 400 cm³/100g when silica was modified with 50 cm³ latex milk, 383 cm³/100g when it was modified with 70 cm³ latex milk, 363 cm³/100g when it was modified with 80 cm³ latex milk. As demonstrated by the above values, an increase in silica surface hydrophobicity resulted in decreasing weight increments in time, which determined the rate of sample sedimentation in water. A similar situation was in the case of the sample modified with 0.1% latex milk: the capacity to absorb water amounted to 433 cm³/100g when the sample was modified with 50 cm³ latex milk, 367 cm³/100g when it was modified with 60 cm³ latex milk, 333 cm³/100g when it was modified with 70 cm³ latex milk. The highest weight increment for the studied samples was observed at the beginning of the measurements and the increments decreased in time when the weight of the samples increased.

CONCLUSIONS

The proposed method for silica surface modification using latex emulsions represents a simple technique, which leads to products of interesting physicochemical parameters. Present studies indicate that augmented concentration and amount of the latex milk used for alteration of silica surface increase bulk density and hydrophobicity of SiO₂. Silicas of lower particle diameters are obtained upon surface modification with 5% latex, as demonstrated by SEM microphotographs. The lowest polydispersity (0.357) has been manifested by the silica, which was modified using 1% latex milk.

The experiments have shown that augmented bulk density of the modified samples is accompanied by decreasing weight increments in time, determining the rate of wetting the samples with water. The exception involves samples modified with 70 cm³ latex which show lower weight increments in time but the weight remains more favourable than that of pure SYLOID[®]244 silica.

The rate of silica sedimentation in water measured by the weight increments in time is lower for the samples modified with latex milk (it decreases with increasing amount of latex emulsion used for the modification). The observed effect clearly proves for augmented hydrophobicity of silica following its modification using the polymer emulsion.

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Siwińska-Stefańska K., Krysztafkiewicz A., Jesionowski T., *Analiza fizykochemiczna krzemionek powlekanych naturalnym mleczkiem lateksowym*, Physicochemical Problems of Mineral Processing, 40, (2006), 275-286 (w jęz. ang.).

Przedstawiono badania nad sposobem zmiany charakteru powierzchni krzemionki koloidalnej SYLOID 244 z hydrofilowego na hydrofobowy, wykorzystując naturalne mleczko lateksowe. Badano wpływ stężenia oraz objętości użytej emulsji lateksowej LATEKS KAGETEX®FA na strukturę krzemionek hydrofobowych oraz na właściwości fizykochemiczne, takie jak: gęstość nasypowa, chłonności wody, ftalanu dibutyli i oleju parafinowego. Wykonano również pomiary sedimentacji i zwilżalności wodą modyfikowanych i nie modyfikowanych krzemionek.