Mechanochemical Modification of Silica with Poly(1-vinyl-2-pyrrolidone) by Grinding in a Stirred Media Mill

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ABSTRACT: The polymerization of 1-vinyl-2-pyrrolidone (VP) mechanochemically initiated by grinding silica was investigated in a wet stirred media mill. The polymerization itself proceeds from the silica grinding without any additional initiator. We have found that the amount of grafted polymer increases with an increase in total ground silica surface. The suspension of polymer-modified silica nanoparticles showed high colloidal stability in water because of the appearance of grafted hydrophilic PVP on the surface during the reactive grinding. Because the nanoparticles SiO_2-*graft*-PVP are biocompatible, the developed polymer nanocomposite material can be of particular interest for the performance of membranes and for the fabrication of biocompatible hydrogels with enhanced mechanical properties and porosity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3708–3714, 2007

Key words: graft hydrophilic polymers; nanoparticles; reactive grinding

INTRODUCTION

Interest in surface modification of inorganic oxide substrates with covalently bonded polymers has grown for various applications as well as for the fundamental study of processes at interfaces. Grafted polymers offer good opportunities to manipulate interfacial properties. Applications of polymer-modified substrates include control of filler properties in composites,[1] biocompatible surfaces,[2] colloidal stability,[3] and inorganic membranes.[4] It was shown that surface-radical polymerization is an efficient and controllable method for the creation of a dense grafted polymer layer.[5,6] It is well known that solids with an activated surface induce various mechanochemical phenomena.[7] The degree of mechanochemical polymerization of styrene and methylmethacrylate, initiated by grinding on solid inorganic substrate, was found to be closely related to the total surface area of the ground material.[8–15] This technique is very promising because of the new application possibilities developed during grinding of nanomaterials; for example, the fabrication of nanocomposites.[15,16]

The freshly formed surface of many inorganic solids can be activated during grinding. There are two types of polymerization mechanisms, radical and ionic, depending on monomer nature.[1,9–11,15,16] EPR spectroscopy data showed that during mechanical loading of silica, Si—O—Si bonds break with the formation of paramagnetic centers (radicals) $\equiv$Si—O•.[17,18] These short-lived active centers in the chemically active medium can interact with surrounding molecules and initiate polymerization on the fresh solid surface.[8,12,13] The results showed that the degree of polymer grafting depends linearly on the increase of the activated solid surface.[13,15] The process of mechanochemical grafting was effectively performed in water dispersions as well as in organic media.[19] A range of grafted and crosslinked polymers was prepared with the participation of macroradicals initiated at the expense of the radical reaction of initiation, chain transfer, and recombination.[20–22] However, only mechanochemical grafting of the vinyl monomers styrene and methylmethacrylate had previously been investigated,[8,12,14] as well as the mechanical activation of silica in the ethylene atmosphere resulting in a grafting polymerization of polyethylene on the silica's surface.[23]

These results encouraged our interest in the possibility of mechanochemical polymerization of 1-vinyl-2-pyrrolidone (VP) onto silica initiated by reactive grinding. The VP polymerization that has been found typically proceeds by a radical mechanism.[24] This procedure is of particular interest because poly(1-vinyl-2-pyrrolidone) (PVP) is nontoxic and has excellent hydrophilic and biocompatible properties.[25,26] Surface-bonded PVP can be useful for

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enhancing the performance of membranes[27] and biocompatible hydrogels.[25,26] To effectively utilize the mechanical energy in the grinding operations and to simultaneously modify the surface properties of fine inorganic silica, we investigated the mechanochemical radical polymerization of VP initiated by mechanical grinding in water. Additionally, we performed the grinding polymerization in the presence of a radical initiating system.

EXPERIMENTAL

Materials and methods

The graft polymerization of VP (Aldrich) onto silica (quartz powder with $X_{50,3} = 2.65$ μm) was carried out via a one-step process of wet grinding the powder in a stirred media mill, described elsewhere.[28] Distilled VP was mixed with millipore water to form 3 mol/L monomer solution. The solution was added to the milling pot in which grinding balls and the silica suspension (solid concentration 20%) were charged. The grinding medium used was Yttria stabilized ZrO_2 beads 0.4–0.5 mm in size. The ball loading volume was 75% of the free volume inside the mill. The reaction mixture was kept under nitrogen atmosphere, with the reaction temperature controlled to within 0.1°C by a circulating water bath. All the experiments were conducted in a batch-wise closed system at 20°C. During the reaction, aliquots of the reaction mixture were withdrawn at various time intervals and copious amounts of water were added to each sample to quench the reaction. For certain experiments, the free-radical polymerization of VP onto silica was performed in the presence of 0.8% of a mixture of 3% hydrogen peroxide and 25% ammonium hydroxide (1 : 1 (w/w) and 2 : 1 (w/w)). The withdrawn samples were centrifuged, thoroughly washed with water by Soxhlet extraction overnight, and dried in vacuum at 110°C.

Characterization

The polymer graft yield (milligram of polymer/gram of silica) was determined by measuring the weight loss that occurred upon heating the polymer-grafted nanoparticles from 200 to 900°C in thermogravimetry measurements at the rate of 10°C/min (Q50 Thermoanalyser, TA Instruments). For the experiment without initiating mixture, the amount of grafted polymer was additionally calculated in milligram (graft polymer) per meter square (ground silica). Specific area of ground particles was determined in BET measurements. Each of the polymer-modified samples was heated at 350°C during 5 h before surface-area measurements.

The PVP-modified silica's FTIR spectra in KBr powder were recorded on a Varian Excalibur Spectrometer FTS 3100 with a resolution of 4 cm^{-1} using the Easy Diff diffuse reflectance accessory.

The composition of the grafted polymer coating was examined with a Euro EA 3000 organic elemental analyzer.

The particle size distribution was determined for mixtures of a selected amount of modified SiO_2 and 5 mL of water. Both particle size distribution and ζ-potential of modified silica samples were determined via light scattering using a Malvern Nano ZS Instrument with a 633-nm ''red'' laser.

The rate of change of water penetration through nonmodified ground quartz silica and the selected samples of ground modified powders were estimated by capillary penetration experiments.

The colloidal stability of the polymer-coated silica and of the nonmodified ground quartz in water were monitored by UV-spectral analysis over time (Cary 100 Scan Spectrophotometer, Varian).

RESULTS AND DISCUSSION

Figure 1(a) shows the change in the silica's particle size in time during the reactive grinding. Simultaneous graft yield of PVP onto the silica's freshly formed particular surface is monitored at the Figure 1(b). Each group of symbols represents an independent experiment. A continuous decrease in the silica average particle size has been observed after 6 h of the reactive grinding. Similar particle size may be reached in each of the experiments, regardless of the presence and concentration of a radical polymerization initiator in the stirred media mill.

To investigate the effect of an additional initiator on the graft polymer yield, we ground silica dispersion at constant initial VP concentration and (i) without additional initiator, (ii) with the addition of hydrogen peroxide water solution and ammonium water (1 : 1) mixture, and (iii) with the addition of hydrogen peroxide water solution and ammonium water (2 : 1) mixture. The nongrafted PVP macromolecules were removed from the graft PVP layer by extraction in Soxhlet with a hot water. The presented data [Fig. 1(a)] indicate that grinding and surface modification of silica nanoparticles proceed simultaneously in a reactive stirred media mill in each of the performed experiments.

We observed a continuous decrease in the size of silica particles in time, as well as the appearance of a grafted PVP layer with covalently bonded chains on the particles' surface in each experiment. The measurements were performed after the extraction of the samples with a hot water to prevent the influence of nongrafted polymer chains on the amount of the attached polymer.

It is worth to note that the monomer conversion was lower than 3% and the grafted value was close

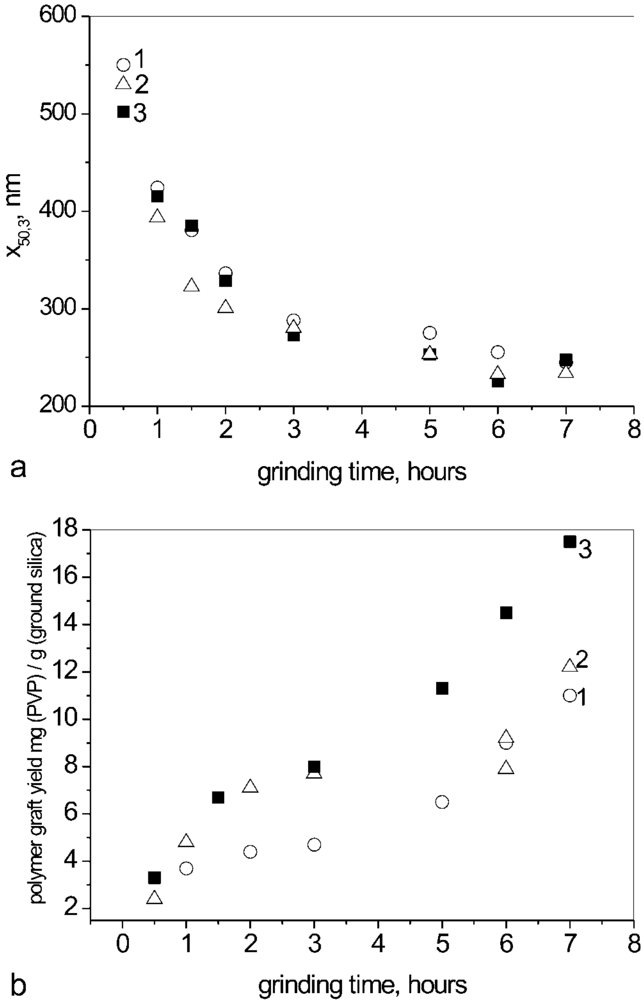


Figure 1 (a) Change in the silica's particle size in time during the reactive grinding ((1) grinding without initiator, (2) initiating mixture 1 : 1, (3) initiating mixture 2 : 1). (b) Graft values of poly-1-vinyl-2-pyrrolidone onto the silica's freshly formed particular surface ((1) grinding without initiator, (2) initiating mixture 1 : 1, (3) initiating mixture 2 : 1).

to zero after 8 h only in the presence of initiator in similar conditions without the silica grinding.

The surface area and the volume of one particle can be calculated in first approximation according to equations:

$$S_p = \pi d^2 \tag{1}$$

$$V_p = 1/6\pi d^3 \tag{2}$$

where d is the diameter of particle.

The number of particles formed from unit mass of silica can be calculated according to equation:

$$N = 1/(\rho V_p) \tag{3}$$

where $\rho = 2.65$ g/cm^3 is the silica density.

Therefore, the overall surface of particles formed from unit mass of silica equals to:

$$S = NS_p \tag{4}$$

Figure 2(a) shows the dependence of the grafted value per 1 g of silica on the surface of particles in 1 g silica during 7 h of grinding in the presence of VP and initiator (plots 2,3) as well as in the absence of the initiator (plot 1). All presented data lie on a straight line with a correlation coefficient of 0.8825. Therefore, we may assume that the initiator did not influence the grafting initiation at the experimental initiator concentrations.

The tangent of slope angle of the straight line equals to 1.30 ± 0.08 mg/m^2 showing that the formation of 1 m^2 of fresh silica surface-initiated grafting of 1.3 mg PVP at the silica grinding.

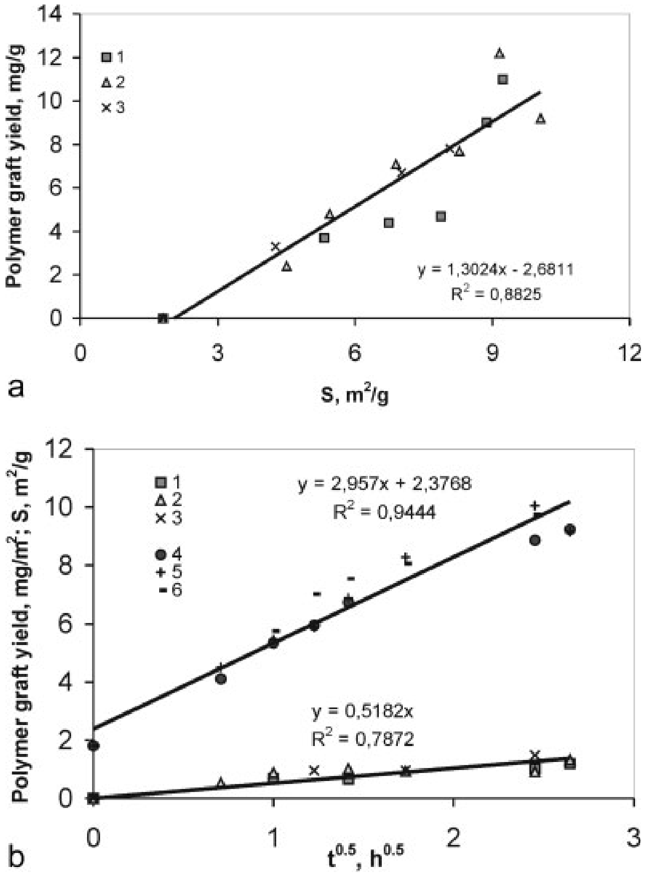


Figure 2 (a) Dependence of graft values of poly-1-vinyl-2-pyrrolidone per 1 g of silica on the overall particle surface of 1 g silica during 7 h of grinding. Number of curves corresponds to number of curves of the Figure 1. (b) Dependence of the graft values of 1-vinyl-2-pyrrolidone onto the 1 g of silica (1–3) and overall particle surface of 1 g silica (4–6) on time. The number of curves (1, 4; 2, 5; and 3, 6) corresponds to number of curves (1, 2, and 3) of Figure 1.

The kinetics of fresh surface-area formation during the grinding can be described by equation:

$$S = S_o + k_1 t^{0.5} \tag{5}$$

where S_o is the overall surface of 1 g of initial silica particles and k_1 is rate constant of surface-area formation during the grinding.

Experimental data on the surface-area formation during the silica grinding lie on the straight line according to eq. (5) [Fig. 2(b), plots 4–6)]. The correlation coefficient is equal to 0.944 and the rate constant of $k_1 = 0.518 \pm 0.04$ m^2 g^{-1} h$^{-0.5}$. The rate of the surface-area formation does not depend on the presence of the initiator.

Dependence of the amount of grafted polymer on time during the grinding can be described by eq. (6) obtained according to eq. (5) if new silica surface initiates grafting:

$$\text{Grafting} = k_2 t^{0.5} \tag{6}$$

where k_2 is rate constant of grafting.

Figure 2(b) (plots 1–3) shows that experimental data of the grafted value of VP in time lie on the straight line running through the origin of coordinates according to eq. (6). Correlation coefficient is equal to 0.787. The rate constant of $k_2 = 0.52 \pm 0.08$ mg m^{-2} h$^{-0.5}$. The grafting rate does not depend on the presence of peroxide initiator.

Therefore, we may assume that the initiator does not evidently treats with radicals on the silica surface and can be the chain transfer reagent from the grafted chains onto the monomer in solution.

We confirmed the formation of the polymer covalently attached to the silica's surface via FTIR spectroscopy and elemental analysis. There is an appreciable difference between the spectra of bare silica and silica with grafted PVP (Fig. 3). When compared with the spectrum of bare silica, in the PVP-modified silica, spectrum appears in the following new characteristic absorption bands. We observed the bands at 1660 cm^{-1} attributed to the valence oscillations of the C=O bonds in tertiary amides (amide I band) at 1462, 2893, and 2960 cm^{-1} resulting from deformation and valence (symmetric and antisymmetric) oscillations of the CH$_2$ groups, respectively, at 1423 cm^{-1}, which may be ascribed to the deformation oscillations of the CH$_2$ groups adjacent to the carbonyl group in pyrrolidone ring. The absence of any absorption band in the ranges 1725–1700 and 1610–1550 cm^{-1} that could be attributed to the valence oscillations of the C=O bonds in carboxyl groups and COO$^-$ groups in carboxylate anions, respectively, indicates that the hydrolysis of pyrrolidone ring has not occurred under VP polymerization conditions as well as during the extraction of nongrafted PVP in a Soxhlet apparatus.

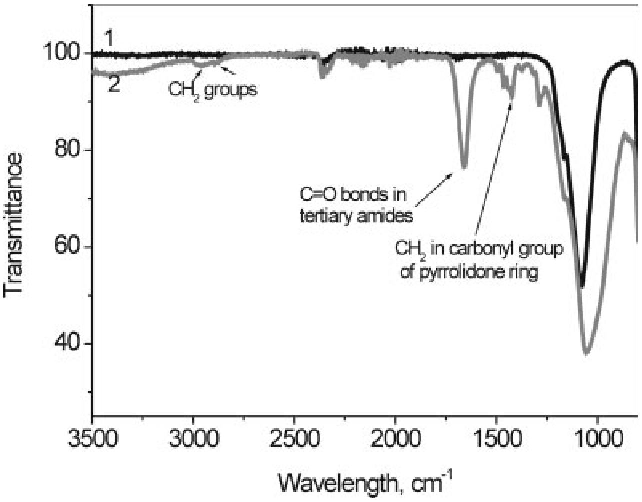


Figure 3 FTIR spectra of bare silica (1) and SiO$_2$-*graft*-poly(1-vinyl-2-pyrrolidone) (2).

The elemental analysis measurements yielded nitrogen and carbon values in the ground in the presence of VP silica nanoparticles (we recorded 0.19% w/w nitrogen and 0.95% w/w carbon after 7 h of reactive grinding as in Experiment 3 as well as 0.1% w/w nitrogen and 0.55% carbon after 6 h of reactive grinding as in Experiment 1). The amount of PVP grafted to the silica surface during grinding in a stirred-media mill has been estimated with the aid of equations given below:

$$\text{Grafted PVP } (\%) = \frac{N_{\text{sample}}(\%)}{N_{\text{PVP}}(\%)} \times 100\% \tag{7}$$

$$\text{Grafted PVP } (\%) = \frac{C_{\text{sample}}(\%)}{C_{\text{PVP}}(\%)} \times 100\% \tag{8}$$

where N_{sample} and C_{sample} are the content of nitrogen and carbon in the analyzed sample (%); N_{PVP} and C_{PVP} are the theoretical content of nitrogen (12.6% w/w) and carbon (64.8% w/w) in poly(1-vinyl-2-pirrolidone), calculated from the polymer molecular formula $(C_6H_9NO)_n$ (%).

The calculated according to eqs. (7) and (8) values are in good agreement (1.51 and 1.47% w/w, respectively, for Experiment 3 and 0.79 and 0.84% w/w, respectively, for Experiment 1). As it is seen, the amount of graft PVP calculated from both carbon and nitrogen content correspond to the TGA analysis data.

Figure 4 presents the change in surface charge of SiO$_2$-*graft*-PVP for each of the performed experiments after the extraction. The ζ-potential of unwashed modified silica remains stable regardless of grinding time, and increases with an increase in the

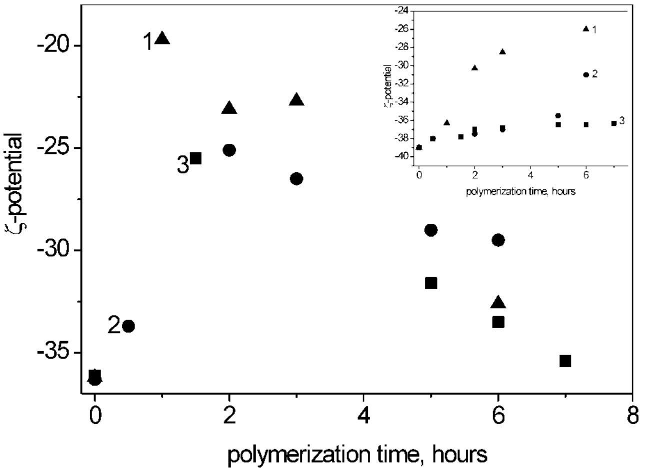


Figure 4 Change in surface charge of SiO_2-*graft*-poly(1-vinyl-2-pyrrolidone) water suspensions (washed samples) over time of reactive grinding ((1) without initiator, (2) initiating mixture 1 : 1, and (3) initiating mixture 2 : 1). The surface charge of unwashed SiO_2-*graft*-polymer is presented at the inset.

amount of grafted polymer (data are presented at the inset). However, the surface-charge measurements of washed modified silica samples show the nonlinear character of the charge's change over time (Fig. 4). ζ-Potential values for the washed silica reach the maximal value after 1–2 h of mechanochemical polymerization and then drop over the time during grinding. It obviously indicates that graft polymer macromolecules are able to change surface properties during the reactive grinding.

We assume that with an increase in the amount of grafted polymer, the macromolecules may change their orientation from ''flat'' (obviously, typical in the earlier stages of the polymerization) to ''dense.'' Therefore, the orientation change results in a reopening of initial noncoated silica surface and increases the surface charge. To confirm this assumption, we performed capillary penetration rate experiments of the some selected polymer-grafted silica samples. The nonlinear change of surface properties was also observed for the SiO_2-*graft*-PVP in wetting measurements (Fig. 5). With an increase in the amount of grafted polymer, the penetration rate initially decreases indicating the appearance of more hydrophobic polymer chains at the surface. When the amount of grafted polymer reached some certain value, obviously the polymer chains change the orientation at the surface and reopen the more hydrophilic silica surface that increases the water penetration rate.

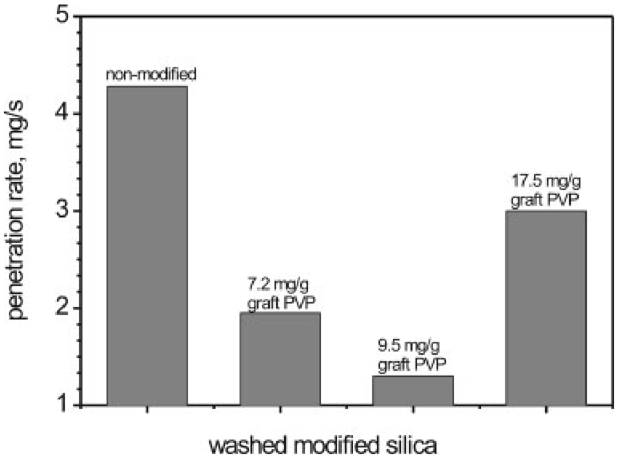


Figure 5 Water penetration rates through the coated and initial ground silica.

The effect of graft poly(1-vinyl-2-pyrroldione) chains on the colloidal stability of modified silica nanoparticles in water is presented in Figure 6. Before we start settling kinetics measurements, the maximum absorption intensity was determined for each of the experimental silica dispersions. This value was used for the kinetics measurement that was performed at the experimental wavelength corresponding to the maximum absorption intensity.

The suspension of nonmodified silica in water is unstable. We observed that the initial silica settles immediately after the beginning of the experiment. In turn, each of grafted poly(1-vinyl-2-pyrroldione) silica suspensions remains stable over time. It is well known that the PVP macromolecules interact readily with water. Thus, solvated macromolecules of grafted polymer provide for high colloidal stability of modified silica nanoparticles as a result of their steric stabilization in water.[29] It confirms once again that PVP grafts to the silica's surface by reactive grinding and forms SiO_2-*graft*-PVP nanocomposite particles according to Scheme 1.

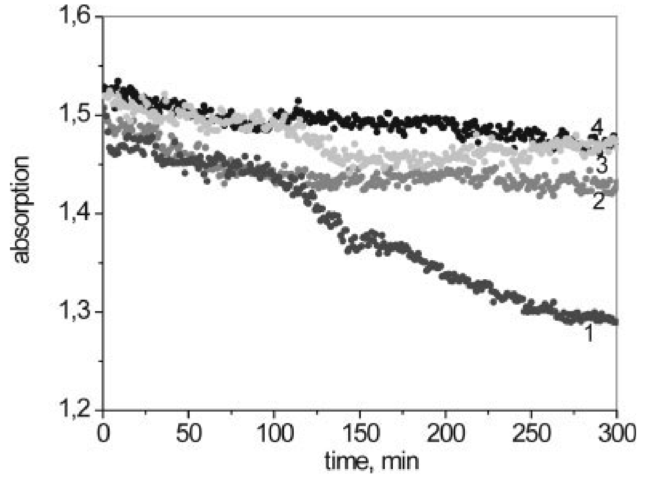
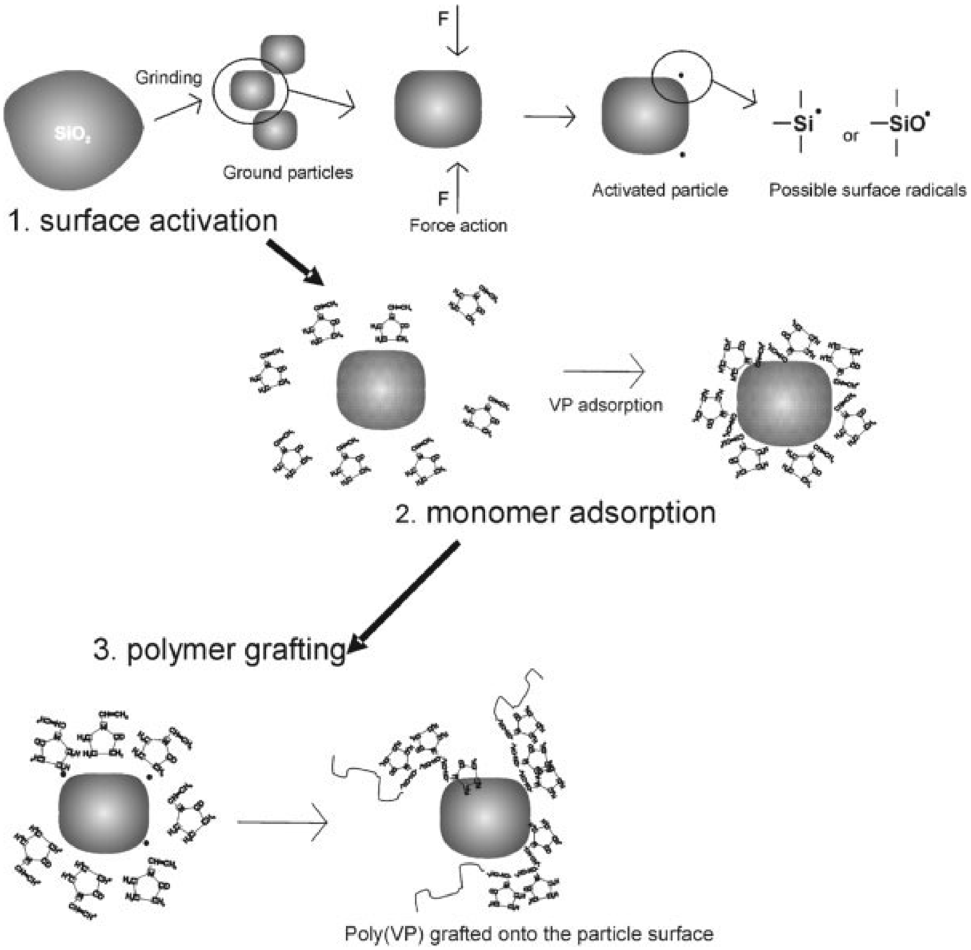


Figure 6 Effect of graft poly(1-vinyl-2-pyrroldione) on the colloidal stability of modified silica nanoparticles in water ((1) nonmodified sample, (2) 7.2 mg/g graft PVP, (3) 9.5 mg/g graft PVP, and (4) 17.5 mg/g graft PVP).



Scheme 1 Grafting of PVP onto the silica particles' surface.

Some selected samples of mechanochemically polymer-modified silica nanoparticles were investigated with scanning electron microscopy measurements. We observed mainly round particles with a size under 100 nm (Fig. 7) that confirms decrease in average particle size during reactive grinding occurred together with a graft polymerization.

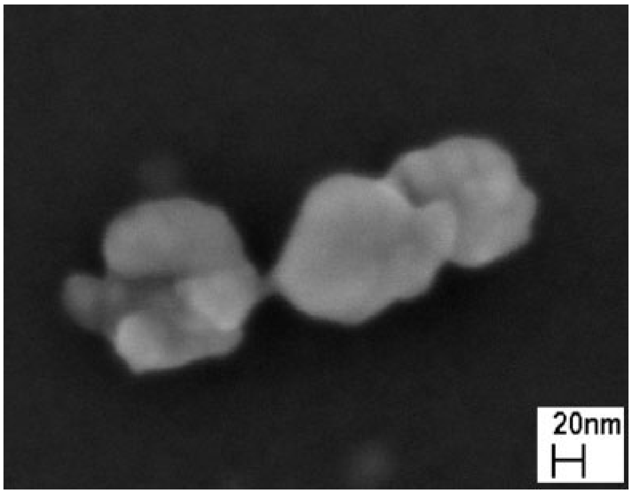


Figure 7 Scanning electron microscopy of mechanochemically modified silica nanoparticles with graft PVP.

CONCLUSIONS

The mechanochemical polymerization of VP was performed by grinding silica in a water monomer solution. The results show that polymerization of VP occurs on the mechanically activated solid surface of the silica during the grinding. FTIR measurements and elemental analysis confirmed the mechanochemical polymerization of VP on silica. An increase in the silica's total surface area leads to an increase of the amount of grafted polymer. This confirms that the polymerization is initiated by mechanical activation of the solid surface. Polymer-modified silica nanoparticles have essentially improved colloidal stability in water. It may be explained by the steric stabilization of coated silica particles with grafted polymer chains interacting with an aqueous medium. We believe that reactive grinding is a promising technique to tailor and manipulate the interfacial properties of solid materials with a variety of surface-bonded polymers.

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References

1. Yablokova, N. V.; Aleksandrova, Y. A.; Titola, O. M. Polym Sci USSR 1986, 28, 2122.
2. Cohn, D.; Hoffmann, A. S.; Ratner, B. D. J Appl Polym Sci 1984, 29, 2645.
3. Labile, R.; Hamann, K. Adv Colloid Interface Sci 1980, 13, 63.
4. Castro, R. P.; Cohen, Y.; Monboquette, H. G. J Membr Sci 1993, 84, 151.
5. Luzinov, I.; Senkovsky, V.; Minko, S.; Voronov, A.; Hild, S.; Marti, O.; Wilke, W. Macromolecules 1998, 31, 3945.
6. Voronov, A.; Shafranska, O. Langmuir 2002, 18, 4471.
7. Kubo, T. Mukibuts no Mechanochemistry; Sogo Gijutu Shuppan: Tokyo, 1987.
8. Kargin, V. A.; Plate, N. A. Polym Sci 1959, 1, 330.
9. Arnett, L. M.; Bechtold, M. F.; Benson, R. E. U.S. Pat. 2,728,732 (1955).
10. Deuel, H. Makromol Chem 1959, 34, 206.
11. Benson, R. E.; Castle, I. E. J Phys Chem 1958, 62, 840.
12. Hasegawa, M.; Sato, M.; Sakuyama, S.; Kimata, M. J Soc Powder Technol Jpn 1997, 34, 10.
13. Hasegawa, M.; Kimata, M.; Kobayashi, S. J Appl Polym Sci 2001, 82, 2849.
14. Hasegawa, M.; Kimata, M.; Kobayashi, S. J Appl Polym Sci 2001, 84, 2011.
15. Bryk, M. T. Polymerization on the Solid Inorganic Surface; Naukova Dumka: Kiev, 1981.
16. Pomogailo, A. D.; Kestelman, V. N. Metallopolymer Nanocomposites; Springer: Berlin, 2005.
17. Radtsyg, V. A.; Bystrikov, A. V. Kinet Katal 1978, 19, 713.
18. Vlasova, M. V.; Kakazey, N. G. Electronic Paramagnetic Resonance in Mechanically Destroyed Solids; Naukova Dumka: Kiev, 1979.
19. Taubman, A. B.; Blyskosh, G. S.; Yanova, L. P. Lakokrasochnye materialy i primenenie 1966, 3, 10.
20. Heinicke, G. Tribochemistry; Akademie-Verlag: Berlin, 1984.
21. Beyer, M. K.; Clausen-Schaumann, H. Chem Rev 2005, 105, 2921.
22. Prut, E. V. Vysokomol Soedin 1994, 36, 601.
23. Schoenherr, S.; Schrader, R.; Steinert, K. H. Z Anorg Chem 1977, 432, 21.
24. Sidelkovskaya, F. P. Chemistry of *N*-vinylpyrrolidone and its polymers; Nauka: Moscow, 1970.
25. Hefferman, J. G.; Sherrington, D. C. J Appl Polym Sci 1984, 29, 3013.
26. Inoue, H.; Kohama, S. J Appl Polym Sci 1984, 29, 877.
27. Castro, R. P.; Cohen, Y.; Monboquette, H. G. J Membr Sci 2000, 179, 207.
28. Stenger, F.; Mende, S.; Schwedes, J.; Peukert, W. Chem Eng Sci 2005, 60, 4557.
29. Napper, D. H. Stabilization of Colloidal Dispersions; Academic Press: London, 1986.