

Production of Filled Hydrogels by Mechanochemically Induced Polymerization

C. Damm,¹ M. R. Mallembakam,¹ A. Voronov,² W. Peukert¹

¹*Institute of Particle Technology, Friedrich-Alexander University of Erlangen–Nuremberg, Cauerstrasse 4, D-91058 Erlangen, Germany*

²*Department of Coatings and Polymeric Materials, North Dakota State University, 1735 NDSU Research Park Drive, Fargo, North Dakota 58105*

Received 10 June 2010; accepted 27 July 2010

DOI 10.1002/app.33102

Published online 3 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Silica nanoparticles functionalized with polyvinylpyrrolidone (PVP) were obtained by the grinding/mechanical activation of quartz or nonfunctionalized silica nanoparticles in a stirred media mill in the presence of 1-vinyl-2-pyrrolidone, as proven by Fourier transform infrared spectroscopy. The polymer layer thickness formed on the silica nanoparticles after 8 h of mechanical activation in the absence of polymerization initiators amounted to about 10 nm, as derived from shear rheology. The silica nanoparticles functionalized with the hydrophilic PVP by mechanochemical polymerization reaction were used as fillers for hydrogels based on poly(hydroxyethyl methacrylate) (polyHEMA). The water absorption, release properties, and mechanical properties of the polyHEMA–silica composites were measured as functions of the filler content and particle size of the filler. PolyHEMA samples containing 20 wt % of the functionalized silica particles

exhibited a higher maximum water absorption than the unfilled polymer; this showed that the hydrophilic interface between the filler and the matrix improved the water absorption. The release of methylene blue from the polyHEMA–silica composites was governed by diffusion and was almost unaffected by the silica particles. The values for the storage modulus and loss modulus of the polyHEMA–silica composites increased with growing filler content. For constant filler content, the storage modulus increased with decreasing particle diameter of the filler; this showed that the reinforcing effect increased with the interface between the filler particles and the matrix polymer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 799–807, 2011

Key words: composites; hydrophilic polymers; silicas; swelling

INTRODUCTION

The mechanical activation of silica particles can result in the formation of free radicals at the surface of the particles.^{1–5} The reactive free radicals may initiate covalent grafting of functional components onto the surface of the silica particles.^{6–9} Mechanochemical polymerization reactions are promising both for particle functionalization and the formation of polymer nanocomposites. The grinding of quartz particles in a stirred media mill in the presence of styrene, methyl methacrylate, or acrylonitrile indeed leads to the formation of polystyrene, poly(methyl methacrylate), or polyacrylonitrile on the quartz particles, even in the absence of polymerization initiators.^{10–12} If quartz is ground in a mixture of styrene and methyl methacrylate, a poly(styrene–methyl methacrylate) copolymer will be formed on the quartz particles.¹³ The mono-

mer conversion and radical formation have been found to increase with growing total surface area of the quartz particles; this showed that the monomer conversion correlates with the amount of mechanochemically formed free radicals.^{10,13}

The mechanochemical polymerization initiation of hydrophilic monomers during the wet grinding of inorganic materials is promising because it offers a new method for the preparation of nanoparticles functionalized with hydrophilic polymers. In previous studies, it has been shown that the grinding of quartz in aqueous solutions of 1-vinyl-2-pyrrolidone (VP) or various acryl amides yields quartz particles functionalized with polyvinylpyrrolidone (PVP) or poly(acryl amides).^{11,14–16} These materials are interesting for the preparation of hydrogels.

Hydrogels are crosslinked polymers that are not soluble but highly swellable in water. These materials are useful for applications in biomedicine, such as drug-delivery devices or scaffolds for tissue engineering.¹⁷ These applications require a high water absorption by the hydrogels in combination with suitable release and mechanical properties.

Most hydrogels are too fragile to be used as replacements for load-bearing tissues.¹⁷ Thus, many

Correspondence to: C. Damm (c.damm@lfg.uni-erlangen.de).

Contract grant sponsor: German Science Foundation.

strategies have been developed to improve the mechanical strength of hydrogels: a high crosslink density, copolymerization, or the formation of double networks.^{17,18} Modifications of the hydrogel network that lead to advanced mechanical properties are often detrimental for the hydrophilicity, release properties, or transparency of the hydrogel material.¹⁷ Frequently, hydrogels are reinforced by filler particles, in particular, by fibers or layered silicates.^{17,19–21} The filler particles, however, must be well distributed in the hydrogel matrix to achieve the maximum reinforcing effect. This requires good compatibility between the surface of the filler particles and the hydrogel matrix. Inert inorganic filler particles functionalized with hydrophilic polymers are promising fillers for hydrogels because the interactions between the hydrophilic polymer chains on the particles with the chains of matrix polymer should facilitate a proper distribution of the fillers. Sarvestani et al.²² showed that enhanced interactions between the filler surface and the hydrogel matrix by suitable functionalization of the fillers indeed improved the reinforcing effect of filler particles.

In this article, we present a new approach for the functionalization of silica nanoparticles with PVP by mechanochemical polymerization initiation. The functionalized silica particles were used as fillers for hydrogels based on poly(hydroxyethyl methacrylate) (polyHEMA). The water absorption, release behavior, and mechanical properties of the polyHEMA–silica composites were investigated as functions of the filler concentration and particle size of the filler. We demonstrated that our filler particles yielded reinforced polyHEMA samples without any detrimental effect on the maximum water absorption and release properties.

EXPERIMENTAL

Materials

Quartz powder was purchased from Carl Roth GmbH (Karlsruhe, Germany). It contained 0.3 wt % alumina, 0.3 wt % iron(III) oxide, 0.1 wt % calcium and magnesium oxides, and 0.2 wt % sodium and potassium oxides as impurities (specifications from the supplier). According to our own analysis, the specific surface area of this commercial quartz powder amounted to 0.5 m²/g. Aqueous suspensions of the spherical silica nanoparticles Ludox TM50 (particle diameter \approx 30 nm, silica content = 50 wt %) and Ludox PW30 (particle diameter \approx 70 nm, silica content = 30 wt %) were supplied by Grace Davison (Columbia, MD). The silica nanoparticles were stabilized electrostatically and did not contain any organic additive. VP, hydroxyethyl methacrylate (HEMA), potassium persulfate, triethanol amine, and

methylene blue were supplied by Sigma Aldrich (Taufkirchen, Germany). The inhibitors present in VP and in the HEMA were removed by adsorption to alumina immediately before use. All of the other materials were used as supplied. Millipore water (specific resistivity = 18 M Ω cm) was used for the preparation of all of the solutions.

Mechanochemical polymerization experiments using a stirred media mill

A laboratory stirred media mill PE075 (Netzsch, Selb, Germany) was used to functionalize the silica nanoparticles with PVP by mechanochemical polymerization initiation. The grinding chamber (volume = 650 mL) was loaded with 250 mL of a 3M aqueous solution of VP containing 20 wt % silica particles. The pH of the suspension was about 7.400 mL of yttria stabilized zirconia beads (diameter = 0.5–0.63 mm) were used as grinding media. The stirrer tip speed was 4 m/s. The grinding experiments were carried out at 15°C. Quartz powder was ground under the same conditions as the Ludox particles to demonstrate that nanoparticles functionalized with PVP could be prepared by the breakage of coarser particles.

Normally, no polymerization initiator was used in the grinding experiments. For comparison, one polymerization experiment using Ludox TM50 particles was performed in the presence of potassium persulfate as the polymerization initiator. The concentration of potassium persulfate was 1 mol % in relation to the monomer VP.

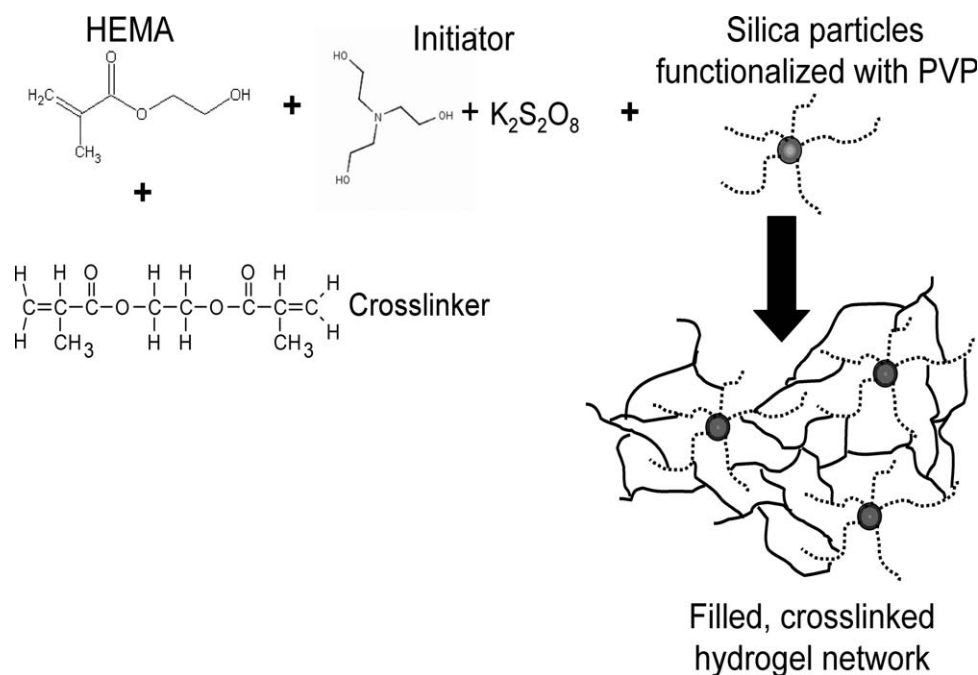
Characterization of the ground particles

The particle size distribution of the suspensions was measured by dynamic light scattering (DLS) with a Zeta-Sizer Nano (Malvern Instruments, Herrenberg, Germany). For DLS measurements, the silica suspensions were diluted with the dispersing medium by a factor of 100.

The flow curves of the purified silica suspensions were measured for shear rates in the range 0.1–2000 s⁻¹ with a double-gap shear rheometer (Physica UDS200, Paar Physica, Ostfildern, Germany).

The specific surface area of the powders was measured by nitrogen adsorption at 77 K [Brunauer–Emmett–Teller (BET) method] with a BET analyzer (Nova 2000, Quantachrome, Odelzhausen, Germany). Before BET analysis, the powders were heated to 300°C in air for 2 h to remove the polymer from the particle surface.

PVP on the silica particles was detected qualitatively by Fourier transform infrared (FTIR) spectroscopy in diffuse reflection mode (diffuse reflectance IR Fourier transform) with an FTIR spectrometer



Scheme 1 Principle of the formation of a filled hydrogel network through the polymerization of HEMA containing EDGMA in the presence of silica particles functionalized with PVP.

(Digilab Excalibur HE series, Varian, Darmstadt, Germany).

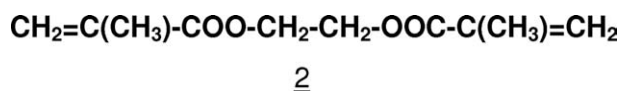
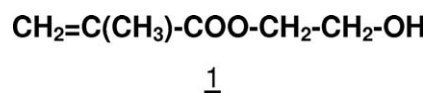
The amount of PVP grafted onto the silica particles was measured by thermogravimetric analysis (TGA; TGA Q50, TA instruments, Eschborn, Germany; nitrogen atmosphere, heating rate = 10 K/min). Before FTIR spectroscopy and TGA, the particles were separated by centrifugation (14,000 rpm, 10 min), washed five times with Millipore water, and dried *in vacuo* at 60°C. A scanning electron microscope (Gemini Ultra 55, Zeiss, Oberkochen, Germany) was used to visualize the morphology of the ground quartz particles. For the preparation of samples for scanning electron microscopy (SEM) investigation, one droplet of a diluted aqueous quartz suspension was deposited onto a silicon wafer. The coated wafers were dried at ambient temperature.

Preparation of the polyHEMA–silica composites

After milling, we purified the suspensions of the silica particles functionalized with PVP by centrifuging, washing, and redispersing the particles in Millipore water before using them as fillers to remove nongrafted PVP and nonreacted VP. HEMA (2 mL) and the purified silica suspension (2 mL) were mixed, and triethanol amine (100 μ L) was added as an accelerator. Finally, 10 mg of potassium persulfate was added as a polymerization initiator. The

mixture was cast into a mold immediately after mixing and cured at room temperature for 12 h.

According to the supplier, HEMA contained about 2% ethylene glycol dimethacrylate (EGDMA), which acted as a crosslinker because it was a bifunctional monomer:



Thus, curing of the HEMA silica mixtures resulted in the formation of filled crosslinked hydrogel networks. The principle of the network formation is shown in Scheme 1.

The silica content of the polyHEMA–silica composites was varied by dilution of the purified original silica suspension with Millipore water before it was mixed with HEMA and the initiators. The polyHEMA samples were dried at room temperature in a desiccator over molecular sieves until their weight remained constant before further investigation.

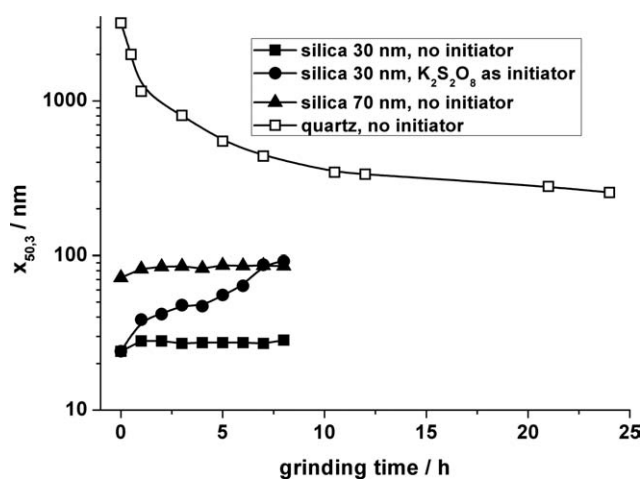
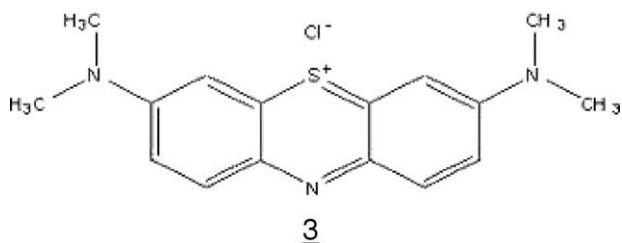


Figure 1 Median particle diameter of the silica particles ($x_{50,3}$) as a function of the stressing time in a stirred media mill in the presence of a 3M aqueous solution of VP. The dispersing medium had a pH value of 7, and the silica concentration was 20 wt % in all cases.

Characterization of the polyHEMA–silica composites

To investigate the water absorption, the dried polyHEMA–silica composite samples were weighed and then immersed in water. The weight of the samples was recorded as a function of the immersion time until the weight remained constant. Methylene blue was used to investigate the release properties of the polyHEMA–silica composites. To prepare samples for the investigation of the release properties, polyHEMA–silica composites containing 1 wt % methylene blue were prepared as described in the Preparation of the PolyHEMA–Silica Composites section.



A rectangular polymer specimen with the dimensions $3 \times 2 \times 0.2 \text{ cm}^3$ containing 1 wt % methylene blue was immersed in 20 mL of Millipore water at 293 K to investigate the release properties. The absorbance of the immersion liquid was recorded in the range 300–800 nm as a function of the immersion time with an ultraviolet–visible spectrophotometer (Cary 100 Scan, Varian). The released methylene

blue concentration was calculated from the absorbance of the immersion liquid at 660 nm.

The mechanical properties of the polyHEMA–silica composites were measured by dynamic mechanical analyses (DMA; instrument supplied by TA Instruments) with rectangular samples having the dimensions $2.0 \times 1.1 \times 0.2 \text{ cm}^3$. For DMA, three-point-bending experiments with a frequency of the mechanical load of 1 Hz and a maximum sample deformation of 0.5% were performed in the temperature range 35–100°C.

RESULTS AND DISCUSSION

Mechanochemical polymerization initiation of VP

Figure 1 shows the evolution of the volume-average median particle size of the silica particles with the time of stressing in the stirred media mill in the presence of a 3M aqueous solution of VP.

The median size of the quartz particles decreased with increasing grinding time because of the breakage and deagglomeration of the particles. After 24 h of grinding, the quartz particles reached a median size of about 250 nm. The SEM micrograph of the ground quartz particles (Fig. 2), however, showed that in addition to the coarse particles having diameters in the submicrometer range, a fraction of very fine particles was also present.

DLS was not able to detect small particles in the presence of coarse ones because the coarse particles contributed much more to the light scattering than the fine ones. Thus, the suspension was centrifuged to remove the coarse fraction and analyzed again by DLS. The volume-based particle size distributions q_3 obtained before and after centrifugation are shown in Figure 3.

The modal value for the particle size decreased from about 200 to about 55 nm because of the centrifugation; this proved that the grinding of quartz

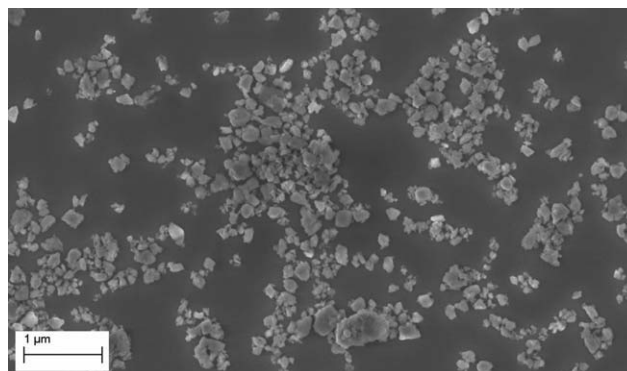


Figure 2 SEM micrograph of quartz particles ground for 24 h in a 3M aqueous solution of VP in a stirred media mill.

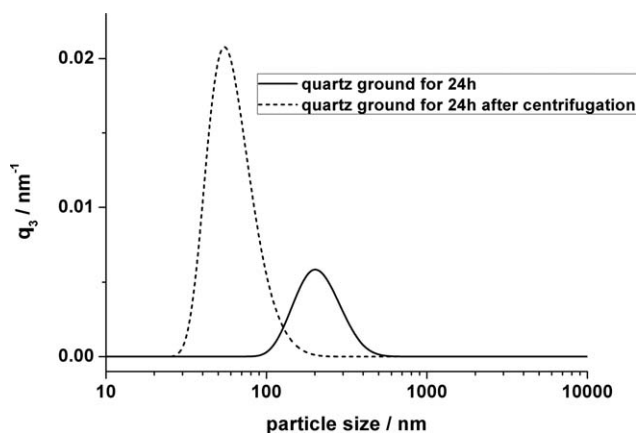


Figure 3 q_3 particle size distribution of quartz particles ground for 24 h in a 3M aqueous solution of VP before and after centrifugation (5 min at 14,000 rpm).

particles in the presence of VP indeed yielded nanoparticles. From the results mentioned previously, we concluded that the grinding of the quartz led to suspensions with broad particle size distributions. When this suspension was used as a filler for the hydrogels, an investigation of the influence of the filler particle size on the properties of the polymer was not possible. For such investigations, suspensions of functionalized silica particles with well-defined shapes and sizes are necessary. Thus, Ludox silica particles were stressed in a stirred media mill in the presence of the monomer VP. When the Ludox silica nanoparticles were stressed in the absence of any polymerization initiator, the median particle size did not change markedly with dispersion time; this showed that neither particle breakage nor agglomeration occurred. In comparison to the size of the original Ludox particles, the diameter of the stressed ones was about 15% larger; this hinted at the formation of a thin polymer layer around the particles. When the 30-nm silica particles were stressed in the presence of the polymerization initiator potassium persulfate (1 mol % in relation to VP), the size of the particles increased with stressing time; this indicated agglomeration (see Fig. 1). After washing and redispersion of these particles in water, again, particle sizes around 30 nm were observed; this showed that in the presence of polymerization initiators, depletion flocculation of the particles occurred because a large amount of polymer was formed in the free solution.

After they were stressed in the mill, the particles were separated from the dispersion medium, purified, dried, and investigated by FTIR spectroscopy to prove the formation of PVP on the particles. In Figure 4, the results found for the ground quartz particles are shown as an example. The FTIR spectra of the stressed Ludox silica nanoparticles (not shown) exhibited the same IR absorption peaks as the ground quartz particles.

The upper diagram in Figure 4 shows the well-known FTIR spectrum of PVP. This spectrum exhibited one characteristic peak at 1670 cm^{-1} , which could be assigned to the C=O valence vibration. In contrast, the FTIR spectrum of the monomer VP (Fig. 4, diagram in the middle) exhibited two absorption peaks in this spectral range: one at 1630 cm^{-1} , which was assigned to the C=O valence vibration, and another one at 1700 cm^{-1} , which was assigned to the C=C valence vibration. The spectrum of the ground quartz particles (lower diagram in Fig. 4) exhibited one IR absorption peak at 1670 cm^{-1} (C=O valence vibration).

From these results, we concluded that mechanical stressing of silica particles in a stirred media mill in the presence of VP indeed led to the formation of PVP on the particles, even when no polymerization initiator was added to the suspension. The grafted amount of PVP on the stressed particles was measured by TGA and measurements of the specific surface area. After 24 h of grinding, the PVP content of the quartz particles amounted to 0.39 mg/m^2 . On the 30 and 70-nm silica nanoparticles, PVP contents of 0.36 and 0.31 mg/m^2 , respectively, were formed after 8 h of mechanical activation in the absence of a polymerization initiator. When the 30-nm silica particles were stressed for 8 h in the presence of 1 mol % of the initiator potassium persulfate (in relation to VP) under the same conditions as mentioned previously, the grafted amount of PVP increased to 0.95 mg/m^2 .

For the steric stabilization of the silica particles and their interaction with the polyHEMA matrix, the thickness of the hydrophilic PVP layer on the silica particles was important. According to Ponton et al.,²³ the thickness of a polymer layer on monodisperse spherical particles can be determined from the dependence of the relative shear viscosity (η_{rel}); the

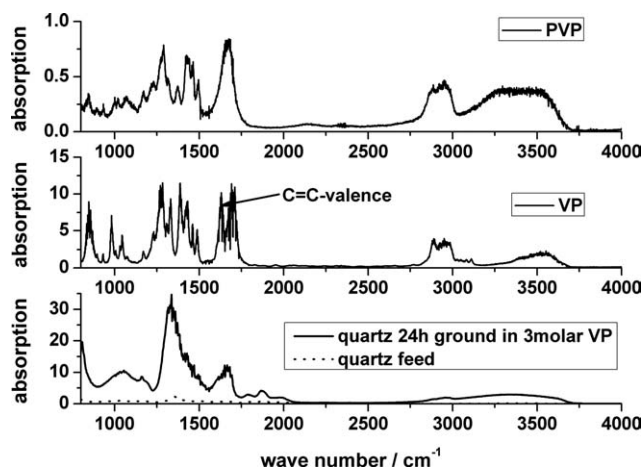


Figure 4 FTIR spectra of PVP, VP, quartz particles ground for 24 h in a 3M aqueous solution of VP, and quartz feed particles.

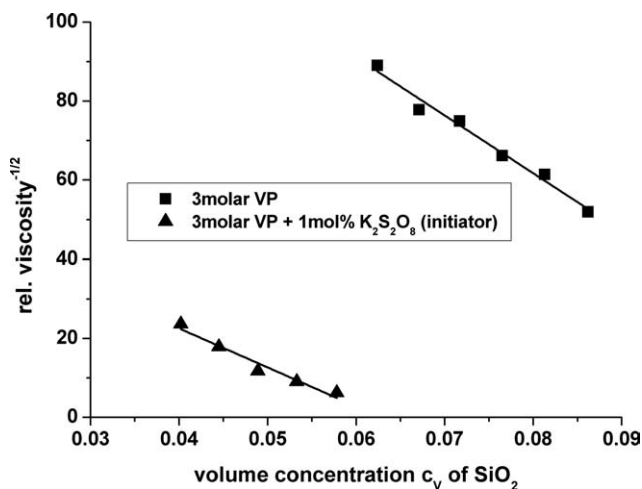


Figure 5 Evaluation of the η_{rel} data for aqueous suspensions of spherical silica nanoparticles functionalized with PVP according to the model suggested by Ponton et al.²³ Shear viscosity data recorded at a shear rate of 50 s^{-1} were used.

ratio of suspension and solvent viscosity) on the volume concentration (c_v) of the particles in the suspension according to eq. (1):

$$\eta_{\text{rel}}^{-1/2} = 1 - \frac{c_v \left(1 - \frac{\delta}{a}\right)^3}{\Phi_m} \quad (1)$$

where Φ_m is the maximum random packing density (0.64), a is the radius of the core particles (15 and 35 nm for the silica nanoparticles used), and δ is the thickness of the polymer layer. As an example, in Figure 5, the data for the relative viscosity at a shear rate of 50 s^{-1} obtained for the 30-nm silica particles stressed for 8 h in the presence of VP are shown, as evaluated according to eq. (1).

The plotting of $\eta_{\text{rel}}^{-1/2}$ versus c_v of the silica particles indeed led to straight lines (see Fig. 5); this proved that Ponton's model was valid for the spherical silica nanoparticles used in this study. From the

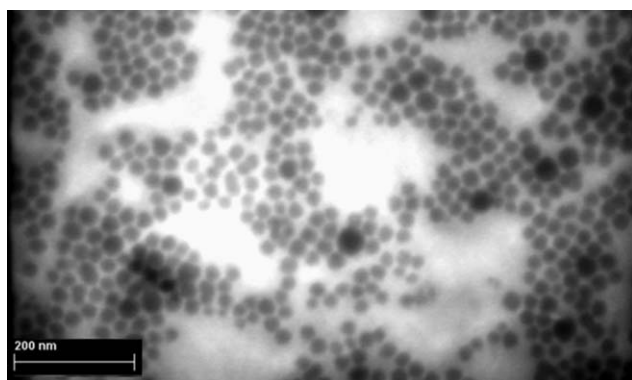


Figure 6 SEM micrograph of the 30-nm silica nanoparticles (Ludox TM50).

slopes of the straight lines, a polymer layer thicknesses of 10 nm on the silica particles was calculated for both the 30- and 70-nm silica particles stressed in the mill for 8 h in the absence of a polymerization initiator. The mechanical activation of the 30-nm silica particles in the stirred media mill in the 3M VP solution in the presence of 1 mol % (in relation to VP) of the polymerization initiator potassium persulfate for 8 h led to the formation of a 17 nm thick PVP layer. The model of Ponton did not yield reliable values for the thickness of the PVP layer on the ground quartz particles because the ground particles were irregularly shaped and not monodisperse (see Fig. 2), whereas the Ludox silica nanoparticles were spherical and quite narrowly distributed in size (particle size = 23 ± 7 and 65 ± 21 nm; see Fig. 6).

Accordingly, the thickness of the PVP layer on the quartz particles ground for 24 h in 3M aqueous VP solution in the absence of any polymerization initiator should also have been around 10 nm because the surface concentration of PVP was almost the same as in the case of the silica nanoparticles stressed for 8 h in the absence of the polymerization initiator. That means, on the LUDOX silica nanoparticles, the polymer layer seemed to grow faster than on the quartz particles.

Properties of the polyHEMA–silica composites

The silica particles functionalized with PVP mentioned in the Mechanochemical Polymerization Initiation of VP section were incorporated in polyHEMA according to the procedure described in the Preparation of the PolyHEMA–Silica Composites section. The water absorption, release of methylene blue dye, and mechanical properties of the polyHEMA–silica

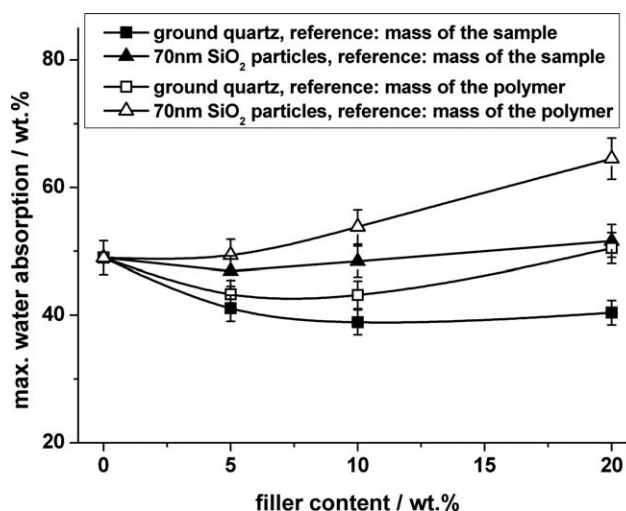


Figure 7 Maximum water absorption of the polyHEMA–silica composites as a function of the filler content. The silica particles used as fillers were functionalized with PVP.

composites were investigated as functions of the filler content and size of the silica particles used as filler. The results of these investigations are discussed later.

Water absorption

The maximum water absorption of the polyHEMA samples decreased slightly with growing silica content when the weight increase of the samples due to swelling was related to the initial weight of the whole composite (see Fig. 7, solid symbols). With increasing filler content, an increasing amount of swellable polymer was replaced by inert silica particles.

Taking this into account by relating the weight increase of the samples due to swelling to the initial weight of the polymer (see Fig. 7, hollow symbols), for the samples filled with the 70-nm silica particles, we observed a slight increase in the maximum water absorption at high filler content. This result was explained by an improved water uptake due to the hydrophilic PVP layer between the silica particles and the polyHEMA matrix. Comparing the results obtained for the polyHEMA samples filled with ground quartz particles (broad size distribution, irregular shape) and for the samples filled with 70-nm silica particles, we observed that the samples filled with the small silica particles exhibited a higher maximum water absorption than the polyHEMA samples filled with the same amount of ground quartz particles (see Fig. 7). This result was explained by the total area of the hydrophilic interface between the filler particles and the polyHEMA: The surface concentration of PVP was nearly the same for all of the silica particles functionalized in the absence of polymerization initiators, see the Mechanochemical Polymerization Initiation of VP section. The specific surface area of the 70-nm silica particles ($59 \text{ m}^2/\text{g}$), however, was larger by a factor of 1.4 than that of the ground quartz particles ($42 \text{ m}^2/\text{g}$). Thus, the total area of the PVP-containing interface was larger when the same amount of 70-nm silica particles instead of ground quartz particles was used as filler.

According to Serra et al.,²⁴ the diffusion coefficient of water in a polymer can be determined from the early time kinetics of the water absorption with eq. (2):

$$\frac{\Delta m_t}{\Delta m_\infty} = \frac{4}{l} \sqrt{\frac{Dt}{\pi}} \quad (2)$$

where Δm_t is the weight increase of the sample at the time t , Δm_∞ is the weight increase of the sample in equilibrium state, l is the thickness of the polymer sample, D is the diffusion coefficient of water in the

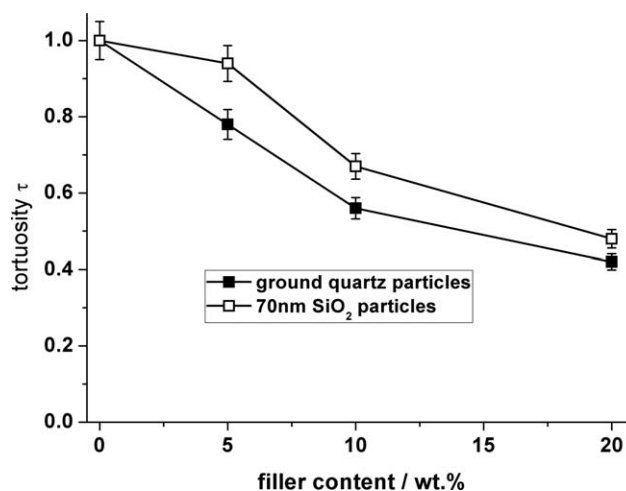


Figure 8 τ for the diffusion of water in the polyHEMA-silica composites as a function of the filler content. The silica particles were functionalized with PVP.

polymer, and t is the immersion time. From the values for the diffusion coefficient of water in the polyHEMA samples obtained by evaluation of the data for the water absorption according to eq. (2), the tortuosity (τ) could be calculated by eq. (3) with the diffusion coefficient of water in the polyHEMA-silica composite samples (D_{filled}) and the diffusion coefficient of water in the neat polyHEMA sample (D_{neat}):

$$\tau = \frac{D_{\text{filled}}}{D_{\text{neat}}} \quad (3)$$

where τ is a measure for the prolongation of the diffusion pathway due to the filler particles.

τ decreased with growing filler content (see Fig. 8). The filler particles prolonged the diffusion pathway of the water molecules and acted as diffusion barriers. Moreover, polymer chains could be immobilized by the filler particles. The reduced chain mobility also resulted in a decrease of the diffusion coefficient of the permeate in the polymer.

In comparison to the 70-nm silica particles, the ground quartz particles caused a stronger decrease of τ (see Fig. 8). Because of their larger diameter and anisotropic shape in comparison to the LUDOX silica nanoparticles (see Figs. 2 and 6), the quartz particles acted as a more effective diffusion barrier.

Release of methylene blue

In Figure 9, the cumulative release of methylene blue from a neat polyHEMA sample and from polyHEMA-silica composites containing the 70-nm silica particles is plotted versus the square root of the immersion time. For the neat polyHEMA sample and for all of the polyHEMA-silica composite

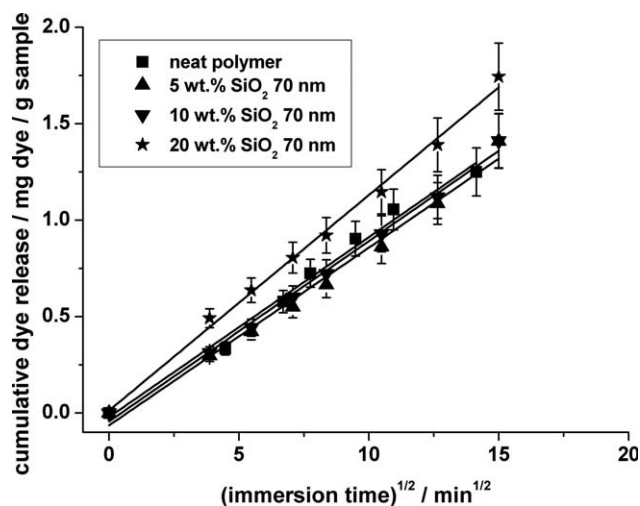


Figure 9 Cumulative release of methylene blue from a neat polyHEMA sample and from polyHEMA–silica composites as a function of the square root of the immersion time for different filler concentrations. The 70-nm silica particles functionalized with PVP were used as fillers.

samples investigated in this study, this plot led to straight lines; this proved that the release of the dye was governed by diffusion.²⁴

The 70-nm filler particles and the ground quartz particles (not shown) did not have a remarkable influence on the dye release from the polyHEMA samples (see Fig. 9). Thus, the effect of the filler particles on the water diffusion was not reflected in the diffusion of the dye, although the release of the dye was triggered by the absorption of water. From these results, we concluded that the diffusion rate of water molecules did not govern the release of the dye. Thus, the diffusion rate of the dye molecules through the polymer must have been much slower than the diffusion rate of water molecules. The values for the diffusion coefficients confirmed this hypothesis: The diffusion coefficient of methylene blue in the polyHEMA samples was about $7 \times 10^{-9} \text{ cm}^2/\text{s}$, as derived from the slopes of the straight lines in Figure 9 with eq. (2). This value was about two orders of magnitude lower than the diffusion coefficient of water in the polymer samples, which amounted to about $2 \times 10^{-7} \text{ cm}^2/\text{s}$ for the neat polyHEMA sample. This result was in agreement with our expectations because the diffusion coefficient and, therefore, the diffusion rate of a solute in the polymer matrix decreased with increasing molecular weight of the solute and with increasing interactions between the solute molecules and the polymer chains.²⁴

Thermomechanical properties

The storage moduli of the neat polyHEMA samples and the polyHEMA–silica composites measured by DMA with a frequency of the mechanical load of 1 Hz decreased with growing temperature (see

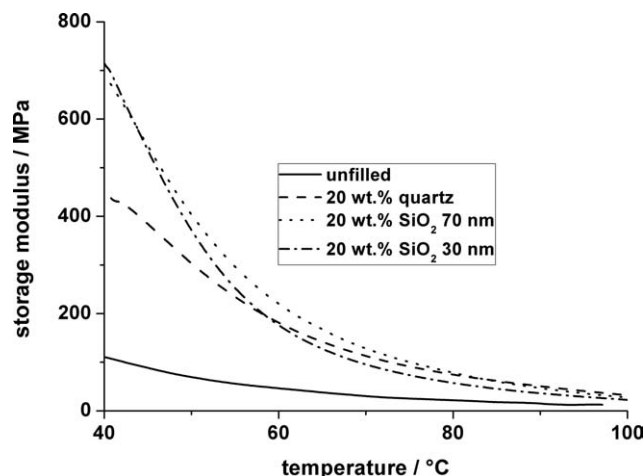


Figure 10 Storage moduli of a neat polyHEMA sample and polyHEMA–silica composites containing silica particles of different sizes as a function of the temperature. The silica concentration of the composite samples was 20 wt %. The silica particles were functionalized with PVP. The storage modulus was measured by DMA in a three-point-bending mode at a mechanical-load frequency of 1 Hz.

Fig. 10). Generally, the polyHEMA–silica composites exhibited larger values for the storage modulus than the neat polyHEMA. This reinforcing effect of the filler particles became more pronounced at lower temperatures (see Fig. 10).

In the following, the values for the storage modulus and loss modulus measured at a temperature of 40°C are compared to investigate the effects of size and concentration of the filler particles on the mechanical properties of the polyHEMA samples.

The storage modulus and loss modulus of the polyHEMA–silica composites increased with growing filler content, as Figure 11 shows for the ground

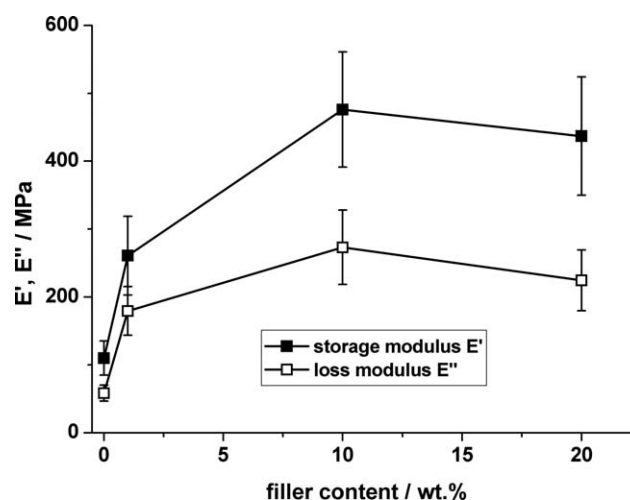


Figure 11 Storage and loss moduli of polyHEMA–silica composites as functions of the filler concentration. Ground quartz particles were used as fillers. The storage and loss moduli were measured at 40°C.

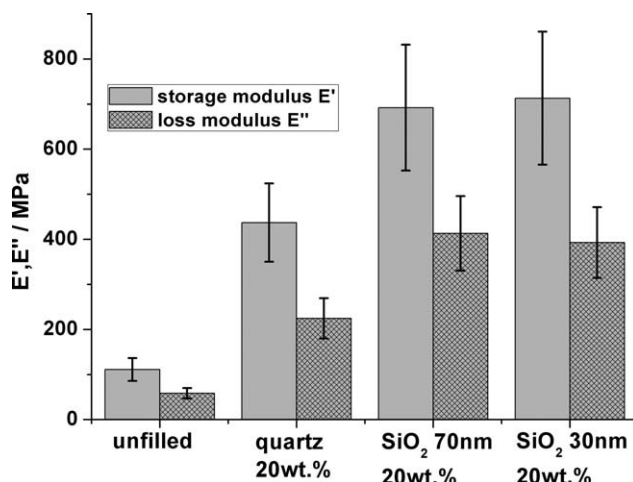


Figure 12 Storage and loss moduli of a neat polyHEMA sample and polyHEMA–silica composites containing silica particles of different diameters. The silica concentration of the composites was 20 wt %. The storage and loss moduli were measured at 40°C.

quartz particles. At high filler contents, both moduli seemed to reach a saturation value. When the filler content was kept constant, the storage modulus and loss modulus of the polyHEMA–silica composites increased with decreasing diameter of the filler particles (see Fig. 12).

Thus, the reinforcing effect and the increase in the viscosity due to the silica particles increased with decreasing particle diameter. From the results shown in Figures 11 and 12, we concluded that the storage modulus and loss modulus of the polyHEMA–silica composites increased with the total area of the hydrophilic interface of the filler particles.

In all cases, the value for the storage modulus was larger than the value for the loss modulus; this showed that the polyHEMA–silica composites and the neat polyHEMA sample behaved in a solidlike manner.

CONCLUSIONS

The mechanochemical polymerization initiation of VP due to stressing of silica particles in a stirred media mill was shown to be a suitable tool for functionalizing silica nanoparticles with PVP without the use of polymerization initiators. The silica nanoparticles did not agglomerate during stressing in the mill. The thickness of the PVP layer on the silica nanoparticles was about 10 nm, as derived from shear rheological investigations with the model suggested by Ponton et al.²³

The silica particles functionalized with PVP were used as fillers for polyHEMA. The filler particles allowed the preparation of reinforced polyHEMA samples with improved water absorption properties because the hydrophilic PVP-containing interface

between the filler particles and the polyHEMA matrix facilitated the water uptake. The reinforcing properties of the functionalized silica particles increased with decreasing particle diameter.

The size and shape of the filler particles affected both the mass transfer into and out of the hydrogel and their thermomechanical properties. The results given in this article may serve as a design guideline for generating the best hydrogel for a specific application.

Many thanks go to Amit Agrawal for his support with the grinding experiments and the preparation of the filled polymer samples. The authors are grateful to the German Science Foundation (DFG) for the financial support of this work.

References

1. Radtsig, V. A. *Defects in SiO₂ and Related Dielectrics: Science and Technology*; NATO Science Series; Springer: Berlin, 2000; 339.
2. Steinicke, U.; Ebert, I.; Geissler, H.; Hennig, H. P.; Kretzschmar, U. *Cryst Res Technol* 1978, 13, 597.
3. Steinicke, U.; Hennig, H. P.; Richter-Mendan, J.; Kretzschmar, U. *Cryst Res Technol* 1982, 17, 1585.
4. Steinicke, U.; Kretzschmar, U.; Ebert, I.; Hennig, H. P.; Barsova, L. I.; Jurik, T. K. *React Solids* 1987, 4, 1.
5. Damm, C.; Peukert, W. *Langmuir* 2009, 25, 2264.
6. Governa, M.; Fenoglio, I.; Amati, M.; Valentino, M.; Bolognini, L.; Coloccini, S.; Volpe, A. R.; Carmignani, M.; Fubini, B. *Toxicol Appl Pharmacol* 2002, 179, 129.
7. Shi, X.; Dalal, N. S.; Vallyathan, V. *Toxicol Environ Health* 1988, 25, 237.
8. Fenoglio, I.; Fonsato, S.; Fubini, B. *Free Radical Biol Med* 2003, 35, 752.
9. Fubini, B.; Fenoglio, I.; Ceschino, R.; Ghiazza, M.; Martra, G.; Tomatis, M.; Borm, P.; Schins, R.; Bruch, J. *Int J Environ Health* 2004, 207, 89.
10. Hasegawa, M.; Kimata, M.; Kobayashi, S.-I. *J Appl Polym Sci* 2001, 82, 2849.
11. Kaupp, G. *Cryst Eng Commun* 2009, 11, 388.
12. Vasiliu-Oprea, C.; Badiu, S.; Marcu, M.; Rotaru, A. *Mater Plast* 1998, 32, 102.
13. Hasegawa, M.; Kimata, M.; Kobayashi, S.-I. *J Appl Polym Sci* 2002, 84, 2011.
14. Voronov, A.; Kohut, A.; Synytska, A.; Peukert, W. *J Appl Polym Sci* 2007, 104, 3708.
15. Damm, C.; Mallembakam, M. R.; Peukert, W. *Adv Powder Technol* 2010, 21, 50.
16. Hasegawa, M.; Akiho, Y.; Kanda, Y. *J Appl Polym Sci* 1995, 55, 297.
17. Myung, D.; Waters, D.; Wiseman, M.; Duhamel, P.-E.; Noolandi, J.; Ta, C. N.; Frank, C. W. *Polym Adv Technol* 2008, 19, 647.
18. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv Mater* 2003, 15, 1155.
19. Qin, Y. *J Appl Polym Sci* 2008, 108, 2756.
20. Jukola, H.; Nikkola, L.; Gomes, M. E.; Chiellini, F.; Tukiainen, M.; Kellomäki, M.; Chiellini, E.; Reis, R. L.; Ashammakhi, N. *J Biomed Mater Res B* 2008, 87, 197.
21. Agrawal, S. K.; Sanabria-DeLong, N.; Tew, G. N.; Bhatia, S. R. *Langmuir* 2008, 24, 13148.
22. Sarvestani, A. S.; He, X.; Jabbari, E. *J Nanomater* 2008, 2008, 1.
23. Ponton, A.; Quemada, D.; Lafuma, F.; Neel, O. *Colloids Surf A* 1996, 119, 255.
24. Serra, L.; Domenech, J.; Peppas, N. A. *Biomaterials* 2006, 27, 5540.