

Dispersions of silica nanoparticles in ionic liquids investigated with advanced rheology

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Received: 29 June 2011 / Accepted: 15 November 2011 / Published online: 28 January 2012
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Abstract The colloidal stabilities of dispersions of unmodified and surface-functionalized SiO₂ nanoparticles in hydrophobic and hydrophilic imidazolium-based ionic liquids were studied with advanced rheology at three temperatures (25, 100, and 200 °C). The rheological behavior of the dispersions was strongly affected by the ionic liquids hydrophilicity, by the nanoparticles surface, by the concentration of the nanoparticles in the dispersion as well as by the temperature. The unmodified hydrophilic nanoparticles showed a better compatibility with the hydrophilic ionic liquid. The SiO₂ surface functionalization with hydrophobic groups clearly improved the colloidal stability of the dispersions in the hydrophobic ionic liquid. The temperature increase was found to lead to a destabilization in all studied systems, especially at higher concentrations. The results of this study imply that ionic liquids with tailored properties could be used in absorbers directly

after reactors for gas-phase synthesis of nanoparticles or/and as solvents for their further surface functionalization without agglomeration or aggregation.

Keywords Ionic liquids · Nanoparticles · Dispersions · Rheology · Colloids · Temperature effect

Introduction

The nanotechnology is dealing with the design, fabrication, characterization, and applications of nanostructures and nanomaterials (Gao 2004). In the definition given by Ramsden, a nanomaterial has at least one spatial dimension smaller than 100 nm. Deriving from here the nanoplates are objects with one dimension less than 100 nm, the nanofibers are objects with two dimensions under 100 nm and nanoparticles have all three dimensions under 100 nm (Ramsden 2009). The continuously increasing interest in nanomaterials and nanotechnology resides in the fact that nanoscale materials usually show very different properties compared with the bulk, enabling their use in unique applications in optics, electronics, nanobiology, medicine, etc. For example, opaque substances become transparent and can be used in the preparation of nanocomposite films with special optical properties.

A considerable part of the nanotechnology studies is focused on TiO₂-based nanomaterials (nanopowders, nanostructured films, nanocomposites) because of their

Electronic supplementary material The online version of this article (doi:10.1007/s11051-011-0651-1) contains supplementary material, which is available to authorized users.

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many potential applications as pigment (Pfaff and Reynders 1999), as photocatalyst (Hashimoto et al. 2005; Ryu and Choi 2008), for solar energy conversion (Mor et al. 2006; Hara et al. 2003; Nakade et al. 2003), as membranes (Albu et al. 2007; Onozuka et al. 2006) and in sensors (Wang et al. 2006). Besides titania, silica nanoparticles have also wide applications, for instance in the field of solar energy (Berginc et al. 2008; Xue et al. 2004; Prevo et al. 2007; Lee et al. 2009). Relatively facile and cheap, the flame processes are widely used for the industrial production of oxide nanoparticles like TiO₂ and SiO₂. Varying the process parameters such as precursor type, residence time, or precursor fluxes, the particles populations can be easily controlled (Briesen et al. 1998; Tsantilitis et al. 2002).

Most powdered oxide materials produced in flame reactors have extremely short life time as primary particles, and they usually form agglomerates and aggregates in which the primary nanoparticles are held together by bonds of different strength. The terms “agglomerates” and “aggregates” are used in different contexts and have different interpretations (Nichols et al. 2002). In this article, we follow Jiang et al.: The term “agglomerates” refers to collections of primary particles held together by weak Van der Waals forces and the term “aggregates” refers to tridimensional structures formed from primary particles held together by strong chemical bonds (i.e., sintered structures) (Jiang et al. 2009). The formation of aggregates is in most cases unwanted because it alters the nanoparticles unique physicochemical properties which make them interesting for different applications. Most of the aggregation takes place due to the long pathways of the particles in the reactor at high temperature. Several strategies have been developed to prevent this phenomenon; for instance, in situ functionalization of titania nanoparticles (Teleki et al. 2010) or modeling of the population balance based on the investigation of various particle formation pathways and subsequent reactor (re)design (Tsantilitis et al. 2002).

The motivation of this study was to find a liquid medium to collect the particles in the reactor or at its exit before they have time to aggregate. One condition is that this absorber solvent has to be stable up to the high temperatures imposed by the synthesis process. Ionic liquids have received much attention as environmentally friendly solvents for organic chemical reactions (Ye et al. 2001; Welton 1999; Chiappe and Pieracini 2005; Marsh et al. 2002; Lu et al. 2009; Zhang et al.

2002), in catalysis (Welton 1999; Zhao et al. 2002; Seddon 1997), in electrical applications (Hapiot and Lagrost 2008; Lu et al. 2002; Tsuda and Hussey 2007; Buzzeo et al. 2004), as well as for separation or dispersant media because of their unique properties such as negligible vapor pressure, thermal stability, and ionic conductivity. Those properties make them ideal candidates as the absorber medium at the flame reactor exit. “Ionic liquid” is the generic term that defines a class of materials constituted entirely of ions and being liquid below 100 °C. The most recent generations of ionic liquids include a large, poorly coordinated inorganic anion combined with a non-symmetric organic cation (Buzzeo et al. 2004).

There are previously published works that study the gelation of ionic liquids in the presence of SiO₂ nanoparticles, with possible applications in dye-sensitized solar cells (Wang et al. 2003; Shimano et al. 2007). The combination of ionic liquids and inorganic oxides like SiO₂ toward ionogels, as multi-purpose hybrid materials for different applications, has been reviewed recently (Le Bideau et al. 2011). We are only aware of one previous group of studies dealing with dispersions of silica particles in ionic liquids, but a different type of silica particles had been involved (larger particle size and different polymer modifications) and other ionic liquids had been used (Ueno et al. 2008a, b, 2009, 2010). The only review concerning the colloidal stability of nanoparticles in ionic liquids is of recent date and has been written by the same group (Ueno and Watanabe 2011). In this study we have studied two imidazolium-based ionic liquids (Fig. 1), one hydrophilic and one hydrophobic, as candidates for absorber media for inorganic nanoparticles. The dispersibility of unmodified commercial SiO₂ nanopowders and of home-made hydrophobically functionalized silica nanoparticles (Fig. 2) was studied for different concentrations at room temperature, 100 and 200 °C. The methodology

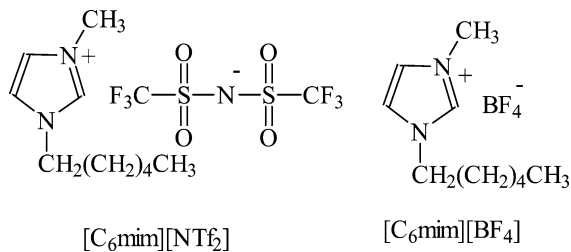
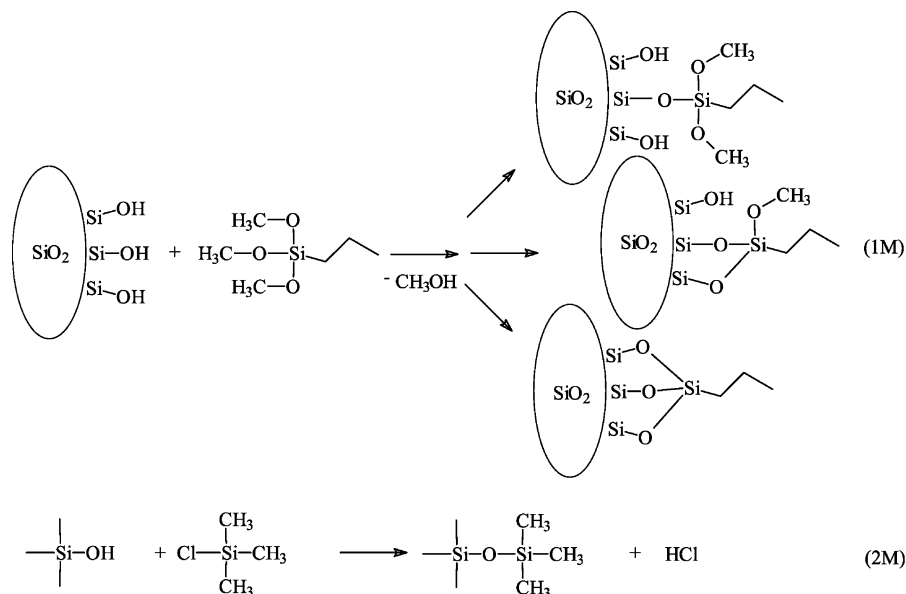


Fig. 1 Chemical structures of ionic liquids used in this study

Fig. 2 Reaction mechanisms for SiO₂ functionalization



used was the redispersion of SiO₂ nanoparticulate powders, which are already agglomerated/aggregated in pure form or after hydrophobic surface modification, in ionic liquids via ultrasound treatment. Thereafter the rheological behavior of the dispersions was investigated.

Materials and methods

Materials

SiO₂ nanopowder was purchased from Aldrich and had a primary particle domain size between 10 and 20 nm according to the producer specifications. The hydrophobic SiO₂ modifications were performed with trimethoxypropylsilane (TMPS) and chlorotrimethylsilane (CTMS), both purchased from Aldrich.

The ionic liquids 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₆mim][NTf₂] (hydrophobic), and 1-hexyl-3-methylimidazolium tetrafluoroborate, [C₆mim][BF₄] (hydrophilic), were purchased from Iolitech GmbH. The ionic liquids were dried overnight at 70 °C under vacuum conditions.

Particle functionalizations

For the first modification (1M), SiO₂ nanoparticles were dried under vacuum conditions at 120 °C overnight. The nanoparticles (0.603 g) were dispersed

in approximately 20 mL of dried toluene. To this dispersion 0.235 mL of TMPS was added. The mixture was refluxed overnight at 110 °C under Argon and then left to cool down for several minutes until most of the nanoparticles had precipitated. The precipitate was decanted and washed several times with toluene and ethanol to remove the non-reacted TMPS. The resulting nanoparticles were dried in an oven at 65 °C in vacuum.

The second modification (2M) was carried out in a similar way as described for 1M, but with 0.4 mL of CTMS. Due to the low boiling point of CTMS (57 °C), the temperature of the mixture was maintained at 50 °C and reaction was performed for 2 days in order to insure that the silane reacted completely with the nanoparticles. The nanoparticles were washed and dried as described above for sample 1M.

Preparation of nanoparticle dispersions in ionic liquids

Nanoparticle dispersions in ionic liquids were prepared at 0.1, 0.3, 0.5, 1, and 2 wt% by ultrasound treatment in a BANDELIN-Sonorex Digitec ultrasound bath. The ionic liquid and the desired powder amount were inserted in a snap-cap vial which was then suspended in the ultrasound bath and treated for 1 h at a power of 80 W. An ultrasound treatment with a Sonotrode finger was not feasible due to ionic liquids decomposition.

Characterization

The modified nanoparticles were characterized by nitrogen adsorption and BET analysis using a Beckmann Coulter SA 3100 Surface Area Analyzer, by ^{29}Si -NMR using a Bruker DPX 300 spectrometer, by transmission electron microscopy using a Philips CM 200 FEG equipment, by FTIR using a Varian 3100 Escalibur Series spectrometer and by elemental analysis using a Euro EA Elemental Analyzer.

The rheological characterization of the dispersions was performed with an Anton Paar Rheometer Physica MCR 301 at 25, 100, and 200 °C. Viscosity, storage modulus and loss modulus were measured. The cone-and-plate system with a diameter of 50 mm and a cone angle of 1° was used. To eliminate any previous shear histories and to allow the samples establish their equilibrium structures, a steady pre-shear was applied at a shear rate of 1 s⁻¹ for 60 s followed by a 120 s rest period before each dynamic rheological measurement. To determine the linear viscoelastic limit, a dynamic measurement as a function of strain amplitude was conducted before each dynamic frequency sweep measurement. The frequency sweep was performed at constant strain amplitude 0.1%.

Results and discussion

The synthesized SiO₂-1M and SiO₂-2M nanoparticles were characterized using transmission electron microscopy, BET surface area and elemental analysis, as well as by FTIR and ^{29}Si -NMR spectroscopy (see Table S1 and Fig. S1 in Supporting Information). The morphologies of the unmodified and functionalized SiO₂ nanoparticles are shown in Fig. 3.

The specific surface measurements revealed that the modified nanoparticles had lower BET surface area than the unmodified ones (Table 1). These results were in agreement with the powders structures observed by TEM showing an increase of the nanoparticles sizes from ~5 to ~20 nm after the functionalization. The higher loss of surface area for the SiO₂-1M powder suggests the formation of a more aggregated material than in case of the functionalization toward SiO₂-2M. The thickness of the added organic layer and decrease of surface roughness is probably the reason for the decrease of microporosity for the modified materials.

In the FTIR spectra of the unmodified SiO₂ and of the two functionalized nanopowders the characteristic Si–O–Si band at ~1,060 cm⁻¹ and a broad band between 3,750 and 3,000 cm⁻¹ corresponding to the coordinated water (3,400–3,000 cm⁻¹) and to the associated hydroxyl groups (3,750–3,470 cm⁻¹) were present (Harbeck et al. 2003). The functionalized powders presented additionally the following bands: at ~2,960 and 799 cm⁻¹ assigned to the –CH₂ functional group and at ~950 cm⁻¹ assigned to the –CH₃ functional group. For the sample SiO₂ 2M another band at ~850 cm⁻¹ was recorded and assigned to the –CH functional group (Tripp and Hair 1995; Chen et al. 2008) (see Fig. S2 in Supporting Information).

The contents of carbon and hydrogen in the modified nanoparticles were determined by elemental analysis (Table 1). Based on the BET result for the unmodified silica powder the number of the free Si–OH sites on the surface was calculated. Because the only sources of C in the modified powders, measured by elemental analysis, are the propyl and methyl groups, and assuming 3 C for each propyl group and 1 C for each methyl group it was possible to calculate the number of Si sites on which a coupling of silane was realized for each type of modification. From the difference it was possible to calculate an approximated degree of surface coverage. It was observed that the first modification had lead to a higher coverage degree. This can be related to the fact that with TPMS not only a 1:1 reaction with surface silanol but also condensation reactions are possible (Fig. 2).

The rheological characterization for the unmodified SiO₂ dispersions in the hydrophilic and hydrophobic ionic liquids was performed at three different temperatures: 25, 100, and 200 °C (Figs. 4, 5, and 6). Previous results published by Ueno and collaborators had revealed that gelation occurred upon addition of SiO₂ nanoparticles in a concentration ≥3 wt% (Ueno et al. 2008a). Because the aim was to prepare stable dispersions of SiO₂ nanoparticles in ionic liquids, the concentration interval 0.1–2 wt% was selected for our studies.

In the hydrophobic ionic liquid at room temperature, the dispersions at low concentrations (up to 1 wt%) behaved like Newtonian fluids where viscosity is independent of the shear rate. At higher concentrations (≥1 wt%) the dispersions were unstable; the viscosity depended strongly on the shear rate suggesting the presence of agglomerates. The curves showed a

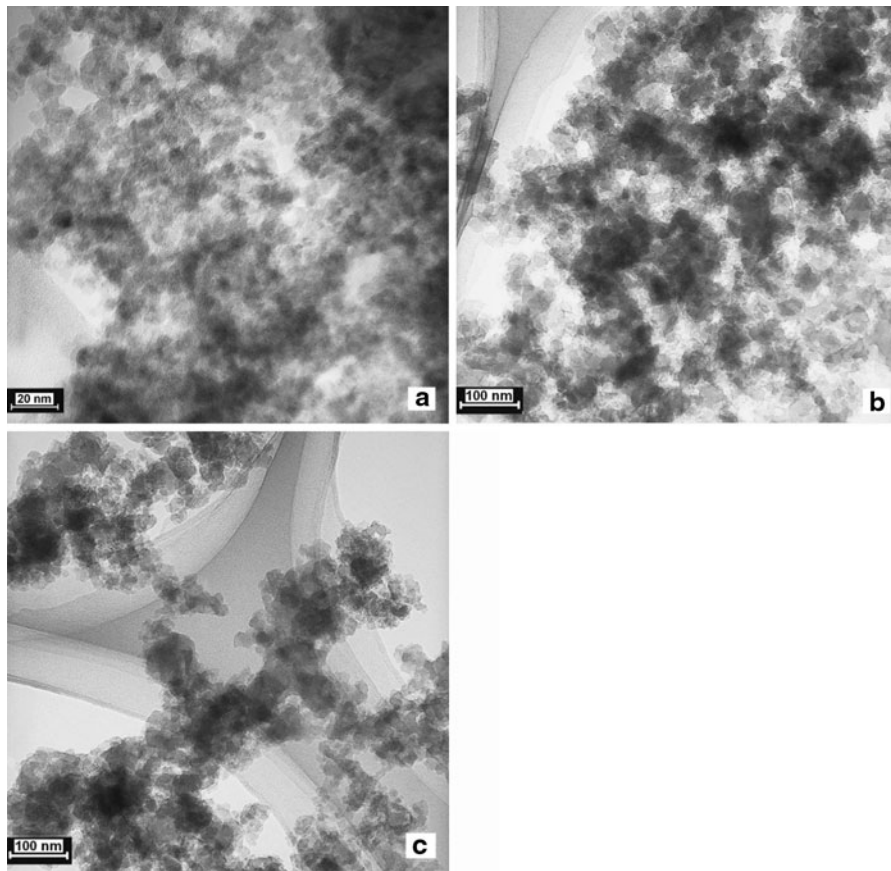


Fig. 3 TEM micrographs of the pure SiO₂ (a), SiO₂-1M (b), and SiO₂-2M nanopowders

Table 1 Results of BET measurements and elemental analysis for SiO₂, 1M and 2M nanoparticles

Sample	BET surface area (m ² /g)	Surface area fraction in micropores (%)	Elements		Surface coverage (%)
			C (%)	H (%)	
Unmodified SiO ₂	590	61.7	–	–	–
Modification 1M	288	42.4	3.40	1.34	69
Modification 2M	397	47.9	3.53	1.80	58

Fig. 4 Viscosity versus shear rate for the pure SiO₂ at 25 °C in a hydrophobic (left) and a hydrophilic (right) ionic liquid—concentration dependence

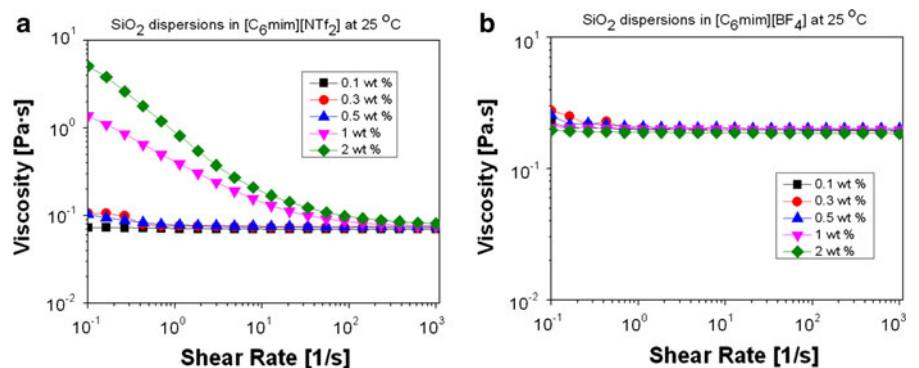


Fig. 5 Viscosity versus shear rate for the pure SiO₂ at 100 °C in a hydrophobic (left) and a hydrophilic ionic liquid—concentration dependence

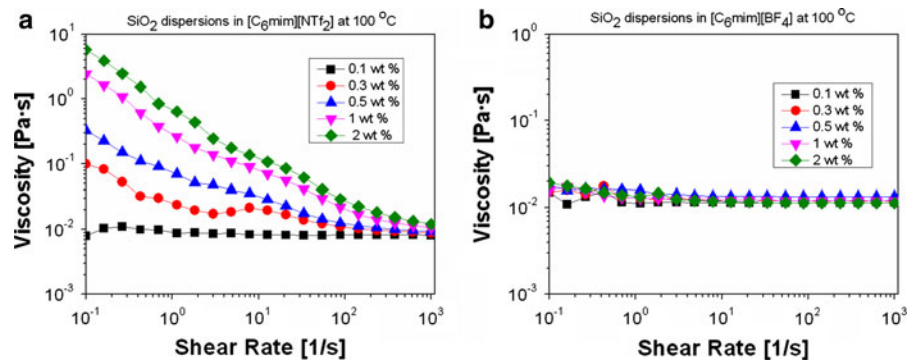
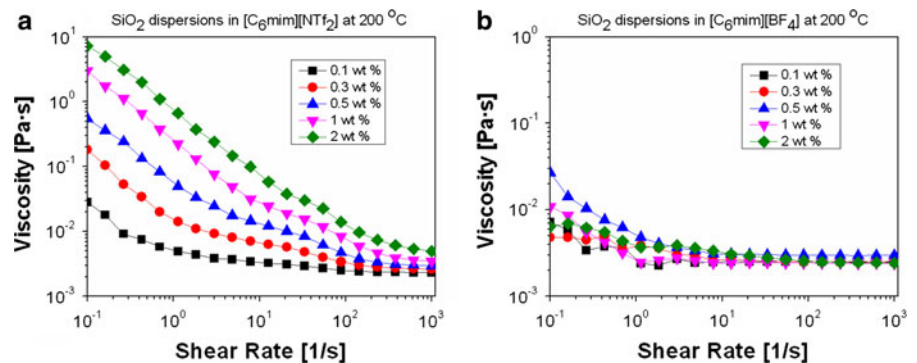


Fig. 6 Viscosity versus shear rate for the pure SiO₂ at 200 °C in a hydrophobic (left) and a hydrophilic ionic liquid—concentration dependence



clear “shear thinning” behavior (Metzger 2011), which indicates at higher shear rates the breaking of the agglomerates into primary particles.

With the increase of temperature the dispersions became unstable and the viscosities depended on the shear rate even for the lowest solid concentrations.

In case of the dispersions prepared in the hydrophilic ionic liquid, one could observe that the samples behaved like Newtonian fluids at room temperature and 100 °C even at higher concentrations, suggesting a better dispersibility in this ionic liquid.

The increase of temperature to 200 °C induced a destabilization of the dispersions but not so pronounced like in the case of the hydrophobic ionic liquid. This confirmed once more that the hydrophilic ionic liquid is a better dispersion medium for the unmodified nanoparticles than the hydrophobic one.

The better dispersibility of the pure SiO₂ powder in the hydrophilic ionic liquid can be easily explained by the presence of the –OH groups and coordinated water on the particles surfaces, confirmed by the FT-IR study. Consequently, the hydrophobic surface modifications of the particles, performed with the methods

1M and 2M, should lead to an improvement of the material’s dispersibility in the hydrophobic ionic liquid.

The rheological characterization was also used to evaluate the dispersibility of surface-modified nanoparticles in the hydrophobic ionic liquid (Figs. 7, 8). In both cases an improvement of the dispersion stability was observed when compared with the unmodified material. The first modification seemed to have a slightly better effect than the second one, probably because of a higher coverage degree (Table 1). This suggests that further improvement of dispersibility can be achieved by optimization of the modification processes in order to obtain a maximum coverage of the SiO₂ surface.

Oscillatory shear measurements were performed for the study of the viscoelastic behavior of the dispersions in the ionic liquids. Exemplaric results, determined for the 0.3 wt% samples in hydrophobic ionic liquid, measured under constant strain amplitude of 0.1% within a linear viscoelastic regime, are shown in Figs. 9 and 10.

For the unmodified SiO₂ nanoparticles in the hydrophobic ionic liquid, the oscillatory shear

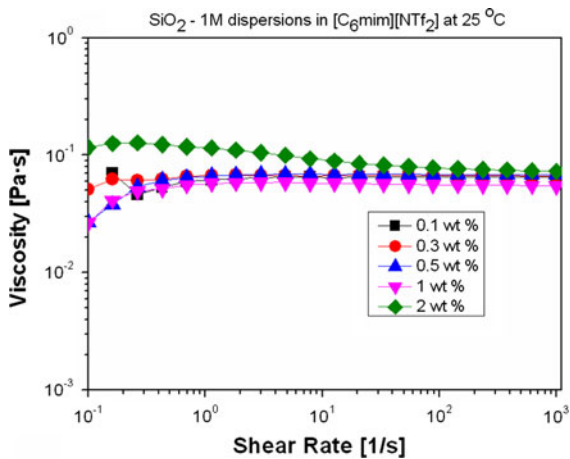


Fig. 7 Viscosity versus shear rate for the SiO₂–1M in a hydrophobic ionic liquid at 25 °C—concentration dependence

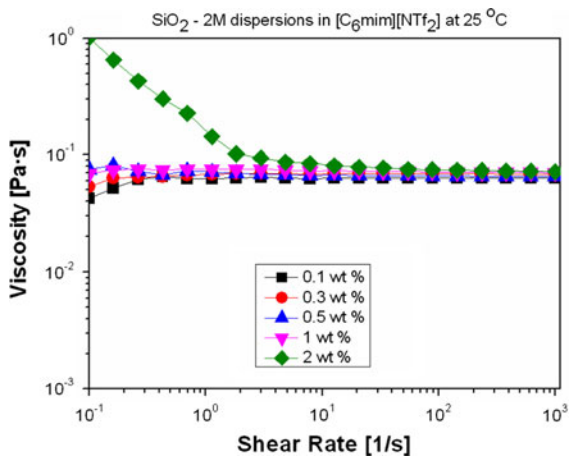


Fig. 8 Viscosity versus shear rate for the SiO₂–2M in a hydrophobic ionic liquid at 25 °C—concentration dependence

measurements at 25 °C showed that at low frequencies the storage modulus was higher than the loss modulus. This indicates that the particles are colloiddally unstable (flocculated into a 3D network). At higher frequencies (>10 rad/s) the loss modulus was higher than the storage modulus suggesting that the agglomerates were broken and a true liquid state was achieved (Ueno et al. 2008a, b).

Figure 10 presents the results of the oscillatory measurements for the two dispersions of surface-functionalized nanoparticles in the hydrophobic ionic liquid at 25 °C. In both cases the loss modulus was higher than the storage modulus for all angular frequencies suggesting the presence of stable dispersions over the whole interval. This result confirms

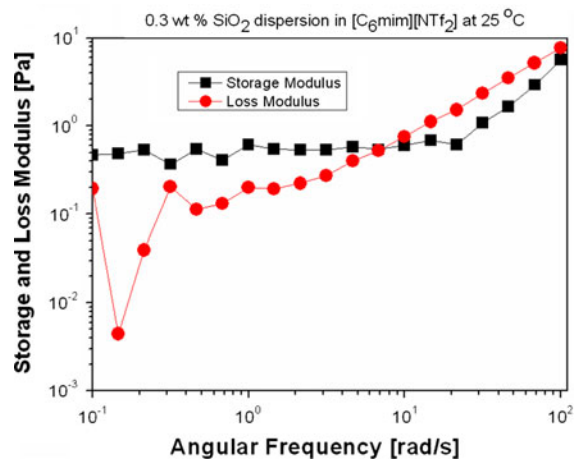


Fig. 9 Storage and loss modulus versus angular frequency for 0.3 wt% SiO₂ dispersion in hydrophobic ionic liquid at 25 °C

once more the improvement of the dispersibility in the hydrophobic ionic liquid by SiO₂ surface functionalization with hydrophobic groups. The colloidal stability of the hydrophilic silica in low concentrations may be explained by the formation of hydrogen bonding in the solvation layers (Ueno et al. 2009). In this case the repulsive solvation force derives from the coordinated ILs, increasing the colloidal stability. For the methyl and propyl substituted SiO₂ powders the key role for the improvement of the colloidal stability, especially in the hydrophobic ionic liquid, is the reduction of the inter-particle attractions (no hydrogen bonding is possible between particles but only Van der Waals attractions).

Analogous studies had been performed for all concentrations at 25 and 100 °C and for each sample the stability domains were determined (Tables 2, 3, and 4). Dispersions are considered “stable” when the nanoparticles do not show a tendency to agglomerate into a 3D network (i.e., to flocculate). In the cases where gelation occurred, the critical angular frequency was defined as the lowest frequency where the viscous behavior of a solution could be detected. Large values for critical angular frequency or even gelation over the entire frequency range clearly illustrated the trend that it was difficult or impossible to obtain stable dispersions at high-temperatures and/or -nanoparticle concentrations.

The nanoparticles functionalization with hydrophobic groups clearly improved their dispersibility in the hydrophobic ionic liquid. The superior properties of particles modified according to method 1M was seen again, because only for the combination of the

Fig. 10 Storage and loss modulus versus angular frequency for 0.3 wt% SiO₂-1M (*left*) and SiO₂-2M (*right*) dispersions in hydrophobic ionic liquid at 25 °C

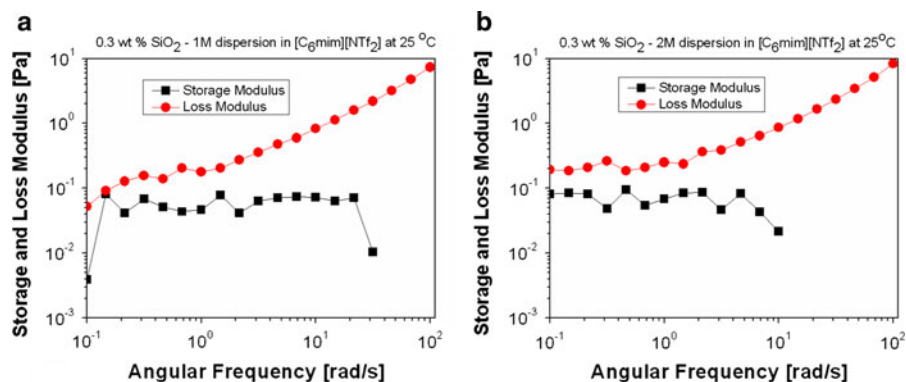


Table 2 Critical angular frequency for dispersions of SiO₂ in [C₆mim][NTf₂] at different temperatures

Concentration (wt%)	Critical angular frequency (rad/s) at 25 °C	Critical angular frequency (rad/s) at 100 °C
0.1	1	Unstable (gel)
0.3	10	Unstable (gel)
0.5	1	21.5
1	15	30
2	10	Unstable (gel)

Table 3 Critical angular frequency for dispersions of SiO₂-1M in [C₆mim][NTf₂] at different temperatures

Concentration (wt%)	Critical angular frequency (rad/s) at 25 °C	Critical angular frequency (rad/s) at 100 °C
0.1	7	0.2
0.3	Stable	Stable
0.5	Stable	Stable
1	3	Stable
2	0.5	Unstable (gel)

highest concentration and high temperature no stable dispersion could be achieved. For modification 2M, the stability domain was significantly smaller than for 1M, but still much larger than for the unmodified particles. These results correlated very well with the long-term stability of nanoparticles dispersions judged by visual inspection.

Conclusions

Rheology was proven to be a very powerful tool in the study of the colloidal stability of different

Table 4 Critical angular frequency for dispersions of SiO₂-2M in [C₆mim][NTf₂] at different temperatures

Concentration (wt%)	Critical angular frequency (rad/s) at 25 °C	Critical angular frequency (rad/s) at 100 °C
0.1	0.3	Stable
0.3	Stable	1.2
0.5	Stable	6.8
1	4.6	Unstable (gel)
2	68	Unstable (gel)

nanoparticles dispersions in hydrophilic and hydrophobic ionic liquids. The rheological behavior of the dispersions was strongly affected by the hydrophilicity of the ionic liquid, by the surface hydrophilicity of the nanoparticles, by the concentration of the nanoparticles in the dispersion as well as by the temperature. For all the systems a destabilization of the dispersion with the increase of the nanoparticles concentration was observed. The same effect was also induced by the increase of the temperature. The unmodified SiO₂ nanoparticles, which have a hydrophilic surface, yielded very stable dispersions in the hydrophilic ionic liquid. Their dispersibility in the hydrophobic ionic liquid was limited, stable dispersions being obtained only at small concentrations and low temperatures. Their surface functionalization with hydrophobic groups extended the dispersions stability domain to higher concentrations and in some cases to higher temperatures. It is expected that a further optimization of the functionalization process, in order to achieve a higher coverage with hydrophobic functional groups; will lead to further improvements of the powder dispersibility in the hydrophobic ionic liquid. The variation of the structure of the ionic

liquid, beyond the simple classification into hydrophilic and hydrophobic, offers also more potential when specific interactions of their constituents with the nanoparticles surface can be used. The results of this study imply that ionic liquids with tailored properties could be used in absorbers directly after reactors for gas-phase synthesis of nanoparticles or/and as solvents for their further surface functionalization without agglomeration or aggregation.

Acknowledgments The financial support through the Nano EnergieTechnikZentrum (NETZ), an application-focused research project partially financed by the state of North Rhine-Westphalia and the European Union, is kindly acknowledged. Thanks are also due to Khaled Anagreh who did several experiments during the work on his Bachelor thesis “Dispersion von Nanopartikeln in Ionischen Flüssigkeiten” at University Duisburg-Essen.

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