Rheology of UV curable colloidal silica dispersions for rapid prototyping applications

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Abstract

Silica is a very promising material for micro-devices produced by rapid prototyping techniques due to its high transparency, thermal and chemical resistance. UV curable dispersions for rapid prototyping methods such as stereolithography should posses specific rheological properties which are crucial for such applications. We developed highly filled, low viscosity silica dispersions (up to 60 vol%) in UV curable, acrylate based systems. The influence of silica particle size, solid loading, temperature and shear rate on the viscosity of dispersions was investigated. The dispersions exhibited different types of shear thickening depending mainly on the size of particles. The critical shear rate defined as the onset of shear thickening, was found to be dependent on temperature, particle size, solid loading of the dispersions. The understanding of these rheological properties enables the design of new dispersions that meet rapid prototyping process requirements.
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1. Introduction

The general purpose of rapid prototyping (RP) is producing complex freeform solid objects directly from a computer model of an object without part-specific machinery. This approach allows reduction of product development time by shortening the period between design and testing. At first, RP was used for making different types of prototypes. Through the years the concept of RP applications has evolved into "rapid manufacturing" and today these techniques are used for making fully functional components.[1,2] RP techniques are very convenient for building microcomponents, e.g. microreactors. Micro-channeled devices can make a revolution in chemical or pharmaceutical laboratories and industries in the nearest future.[3] The smaller the

dimensions of microreactors the shorter residence times and higher heat transfer rates are, thus improving efficiency of such devices. In microsystem technology, small and microsized components made from ceramic or glass materials become more and more important due to their outstanding thermomechanical properties and stability against most chemicals.[4] Additionally transparency of glass microreactors into the ultraviolet (UV) spectrum allows performance of photochemistry as well as observation of crucial parameters such as flow patterns, catalyst packing and mixing of the reactants.[5]

Amorphous silica is cheap, has high transparency in the UV–vis spectrum, high melting point, chemical and structural stability and excellent thermal shock resistance.[6–9] These characteristics make silica a very promising material for micro-devices produced from colloidal techniques such as specialty casting and fiber draw[7,8] or by rapid prototyping techniques relying on UV curable dispersions.[6,9] In order to make high resolution objects by RP techniques such as stereolithography (SLA), stable, UV transparent dispersions with viscosity lower than ∼3 Pa s is prerequisite in order to ensure satisfactory layer recoating.[10]

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Table 1
Particle size and surface area of powders used in the study.

Name	D10 (µm)	D50 (µm)	D90 (µm)	Specific surface area (m^2/g)
OX50 – "nano"	0.07	0.12	0.21	54
Alfa – "submicron"	0.17	0.23	0.30	22.90
Excelica – "micron"	2.20	3.9	6.5	0.60

The rheological properties play a key role in controlling the shape forming behavior and optimizing the properties of the green body.[11,12] Stable dispersions with high solid loadings are required for the colloidal forming of ceramics which offers a potential way to eliminate structural defects and anisotropy of the stress centers in sintered ceramics.[12] Next cannot be neglected for any slurry ceramic processing is the maximum shear rate of process. High shear rates that occur during shaping process may induce shear thickening behavior.

Shear thickening refers to the increase in apparent viscosity when the applied shear rate is increased.[13] The mechanics of such behavior is not yet fully understood despite an extensive research.[11,13–15] The most popular explanation of shear thickening is still the Hoffman's *order–disorder transition* theory. It assumes transition from an easy flowing state where the particles are ordered into layers to a disordered state where this ordering is absent.[13] It is strongly believed that the reversible shear thickening in colloidal dispersions is a result of the formation of stress-bearing transient aggregates of "clusters" organized in the compressive axis flow. The increase in viscosity is a result of lubrication squeeze forces in the thin fluid layer that separates the particles within this structure.[14]

This work is focused on the rheological characterization of silica dispersions in mildly polar UV curable acrylate monomers. The influence of powder size (nano, submicron, micron), solid loading and temperature on the rheological behavior of the dispersions was investigated.

2. Experimental

2.1. Materials

Three types of commercially available amorphous silicas were chosen for this study. "Nano", Aerosil OX50, with average particle size of 0.04 µm (Evonik, Germany), "submicron", 0.25 µm (Alfa Aesar, USA) and "micron", Excelica 3 µm (Tokoyama, Japan). The specific surface area and particle size distribution were measured with ASAP 2010 Micromeritics (USA) and LS230 (Beckman Coulter, USA), respectively (Table 1). Fig. 1 presents electron micrographs of the three powders. Fig. 1a shows TEM and b, c SEM pictures of powders, respectively. The particles of all types of silica have spherical shape. "Nano" is in the range of 40–80 nm. It should be noted, however, that initial nano particle dispersion contains a certain fraction of coarser particles, probably aggregates on the level of 120 nm. Particles of "micron" are on the level of 3 µm but as seen from Fig. 1c some grains can be much bigger, even 15 µm. XRD analysis was made using Philips X'pert Pro MPD, X-ray diffractometer and from that is known that all used pow-

ders have amorphous phases. Based on a previous study[9] three types of monomers were chosen as dispersing media for silica powders (4-HBA, 2-HEA and PEG200DA). Table 2 shows the structure of the monomers used in this study.

The monomers were selected since they have refractive indices similar to amorphous silica (Table 1) in order to reduce the Van der Waals attraction. Additional benefit is the transparency of the slurries.[9] The monomers used in this study are low molecular weight, Newtonian liquids and their viscosity varies between 0.01 (2-HEA) and 0.025 Pa s (PEG200DA) at 23 °C. As demonstrated in Wozniak et al.,[9] the usage of refractive index matched, but non-hydroxy terminated acrylates as for example PEG200DA results in highly viscous dispersions which exceed the maximum viscosity limit for stereolithography applications (5 Pa s at 30 s^{-1}) even at solid loading below 15–18 vol% of nanosilica. On the other hand the usage of OH terminated monofunctional by the formation of hydrogen bonding between OH terminated monomers and silanol groups present on the silica surface and the formation of solvation layers. On the other hand, the use of these monofunctional UV curable monomers results after UV curing in elastic sheets of low durability. Because of that difunctional monomer should be added to the monomer mixture in order to provide sufficient crosslinking density. An addition of 7 vol% difunctional acrylate such as PEG200DA to the monomer mixture containing the monoacrylate (4-HBA or 2-HEA) was found sufficient to produce sheets with good mechanical properties while maintaining acceptable dispersion viscosity.[9] The monomer mixtures used in this study were either 7 vol% PEG200DA/93 vol% 2-HEA (PEG200DA/2-HEA) or 7 vol% PEG200DA/93 vol% 4-HBA (PEG200DA/4-HBA).

2.2. Dispersion preparation and characterization

The silica dispersions in the monomer mixtures were prepared using a laboratory dissolver, Ultra Turrax T 50 (USA). The silica powders were slowly and incrementally added to the monomer mixture. Each addition was followed by a homogenization step. When all powder was added, the dispersions were mixed for 2 h at 800 rpm. Dispersions with maximum solid loadings of 43 vol% ("nano"), 54 vol% ("submicron") and 60 vol% ("micron") were prepared. These dispersions were diluted with monomer mixture to obtain dispersions with lower solid loading. Mixed "nano" and "micro" particle dispersions were prepared by the addition of "micron" powder to the "nano" dispersions with a given "nano" powder concentration. The mixed dispersions were homogenized for 2 h at 800 rpm. The rheological measurements were conducted using a rotational viscosimeter (Rheolab MC120, Physica Messtechnik GmbH, Germany) equipped with a thermostat (VT 100, Physica). The experiments were run at
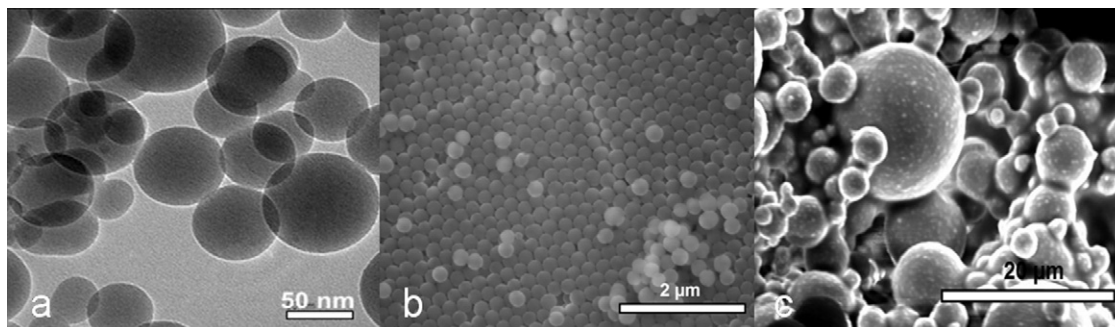
Fig. 1. Electron microscope micrographs of the silica powders used in this study. (a) TEM of "nano" (b) SEM of "submicron" and (c) SEM picture of "micron".

fixed temperatures in the range of 13–55 °C for "nano", "submicron" and "micron" dispersions to elucidate the effect of temperature on the rheological properties. Mixtures of "nano" and "micron" were measured in the temperature range from 23 to 55 °C. All runs were preceded with 30 min temperature equilibration. Two kinds of concentric cylinder systems were used in the experiment procedure in order to work in a torque range of 0.5–50 m Nm providing sufficient accuracy. The volume of cylinders was 3 cm^3 and 17 cm^3 with a gap of 0.59 mm between two cylinders, respectively. All viscosity measurements were made with 60 points linearly spaced in the 20–1000 s^{-1} range. The existence of a critical shear rate, defined as the shear rate where the viscosity begins to rise[9] was explored up to a shear rate of 1000 s^{-1}. Measurements of shear thickening dispersions at low temperatures were often out of range when the measured torque exceeded the measurable range of the rheometer.

3. Results and discussion

This paper has been divided into chapters corresponding to different particle sizes of silica used in study. It starts from the dispersions of the smallest "nano" through "submicron", up to "micron" silica. The last part explores the rheology of mixtures of "nano" and "micron" powders.

3.1. "Nano" dispersions

One should commence this part by considering dispersions of "nano" silica in a monomer mixture of PEG200DA/2-HEA. Fig. 2 presents the dependence of shear viscosity on silica solid

loading in the 13–55 °C temperature range for dispersions having 10–43 vol% particles. The 10 vol% dispersion (Fig. 2a) has Newtonian or slight shear thinning behavior and their viscosity varies between 0.005 Pa s (13 °C) and 0.016 Pa s (55 °C). The decrease of viscosity with temperature is largely due to the monomer mixture. At this temperature range the viscosity of the monomer mixture PEG200DA/2-HEA shows an Arrhenius dependency η (Pa s) = 3×10^{-7} exp(2949/T).[16] The viscosity at 10 °C is 0.01 Pa s and at 40 °C it drops to 0.0037 Pa s.

The 30 vol% dispersion (Fig. 2b) also exhibits Newtonian behavior up to about 100 s^{-1} and slight shear thickening above about 100 s^{-1}. The viscosity at room temperature, however, does not exceed 0.1 Pa s at 1000 s^{-1}. Much more pronounced shear thickening behavior is observed as the solid loading is increased, as seen for 40 and 43 vol% of "nano" silica (Fig. 2c and d). The vertical lines in Fig. 2c and d indicate torque values out of the measurable range (as mentioned in Section 2). Such shear thickening behavior was seen in other nano silica dispersions in polar organic medium.[6,17]

As expected the viscosity increases with the solid loading. Nevertheless, at shear rates below about 100 s^{-1} and 18 °C even the 43 vol% dispersions have viscosity lower than the maximum viscosity used in most rapid prototyping techniques.

Fig. 3 shows the influence of temperature and solid loading on the viscosity of the "nano" dispersions (measured in 100 s^{-1}) in a 3D representation. The viscosities of dispersions for the lowest temperature (13 °C) are at least four times higher with comparison to the highest temperature (55 °C). Such high temperature dependence is visible for all solid loadings. The effect of solid loading on viscosity can also be clearly seen. For 10 vol% of

Table 2
UV curable monomers used in the study.

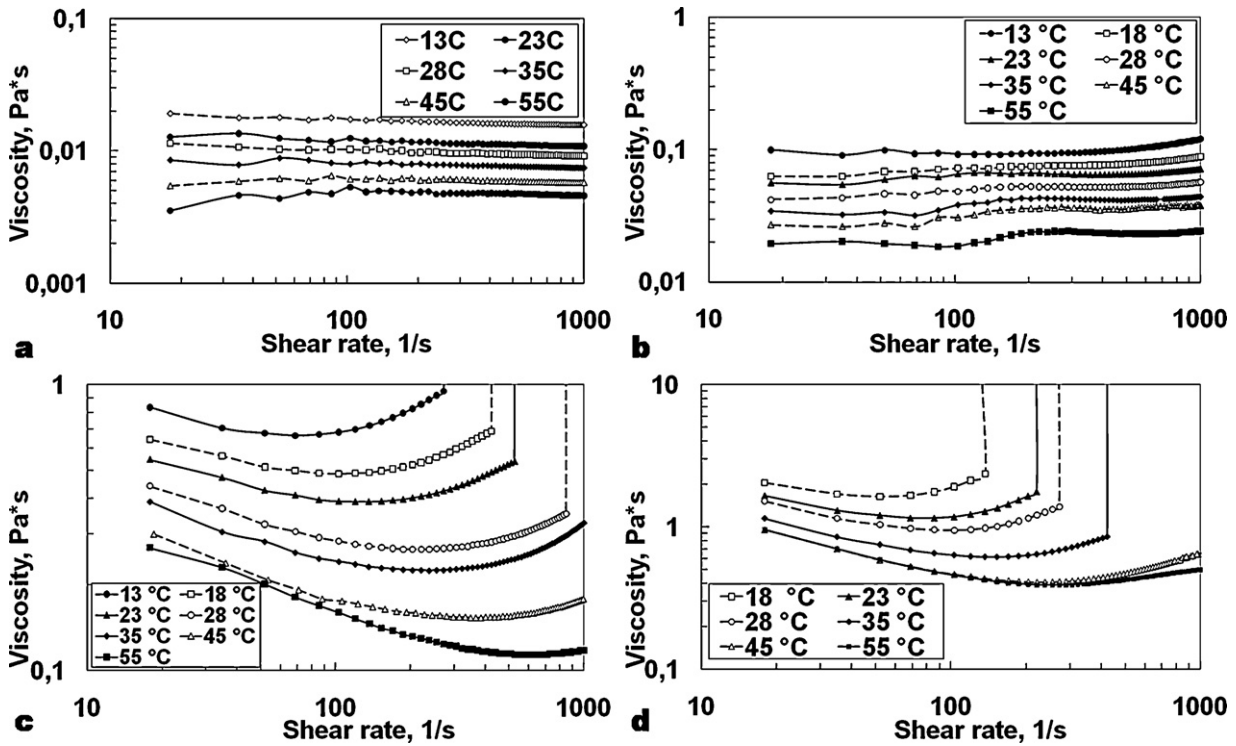| Name, provider	Function	Formula	Refractive index	Density g/cm^3
4-Hydroxybutylacrylate (4-HBA), BASF	Monomer		1.454	1.039
2-Hydroxyethyl acrylate (2-HEA), BASF	Monomer		1.451–1.454	1.106
Polyethyleneglycol 200 diacrylate (PEG200DA), Rahn	Monomer		1.464	1.12

Fig. 2. Viscosity of "nano" SiO_2 dispersions in PEG200DA/2-HEA monomer mixture as a function of shear rate and temperature at different solid loadings. (a) 10 vol%, (b), 30 vol%, (c) 40 vol% and (d) 43 vol%.

silica the viscosity barely surpasses 0.01 Pa s for all temperatures. Viscosity for the 30 vol% comes up to a maximum 0.09 Pa s, but for 43 vol% varies already from 0.4 to 2 Pa s for 13 and 55 °C, respectively.

The critical shear rate is defined as the shear rate at which shear thickening begins to occur.[18] The dependence of critical shear rate on solid loading of "nano" is showed in Fig. 4. The critical shear rate depends on the temperature and solid loading. The critical shear rate decreases with the increase in solid loading.

For example in 18 °C shear rates are 400, 115, 60 s^{-1} for 30, 40 and 43 vol% "nano", respectively. A sharp decrease is between 40 and 43 vol%. This sharp change is not unexpected since the 43 vol% represents the maximum solid loading experimentally attained in the "nano" system which could be processed with the dissolver at room temperature. It can also be observed that the effect of temperature on the critical shear rate is at a fixed solid loading is very significant. For example, the 43 vol% dispersion shows about fivefold increase in the critical shear rate between 18 and 55 °C.

We suggest that high loading/low viscosity dispersions are enabled due to the formation of solvation layers on the silica nanoparticles. The above mentioned solvation phenomenon is caused by the organization of hydrophilic, OH terminated monomers forming H-bonds with silanol (Si–OH) groups
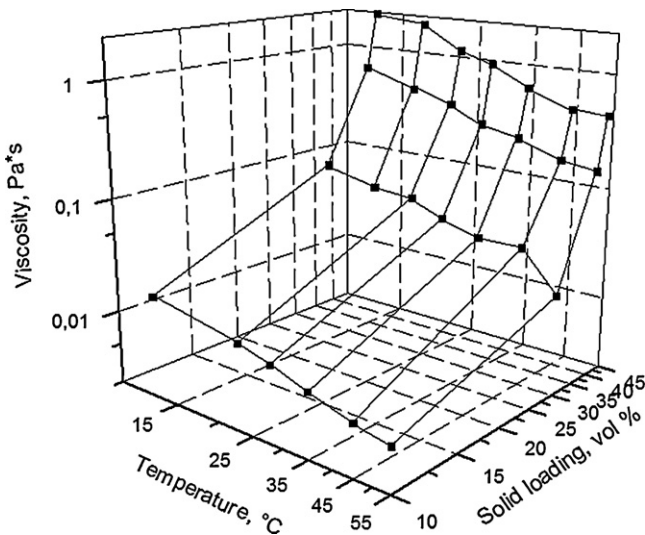

Fig. 3. 3D representation of the influence of temperature and solid loading on the viscosity of "nano" SiO_2 dispersions in PEG200DA/4-HEA monomer mixture (at 100 s^{-1}).
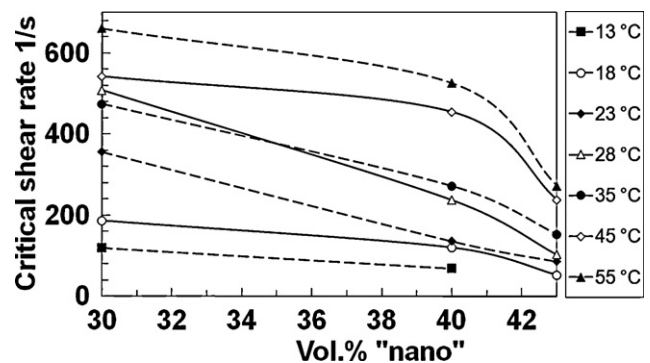

Fig. 4. Critical shear rate as a function of solid loading for "nano" SiO_2 dispersions PEG200DA/4-HEA monomer mixture.
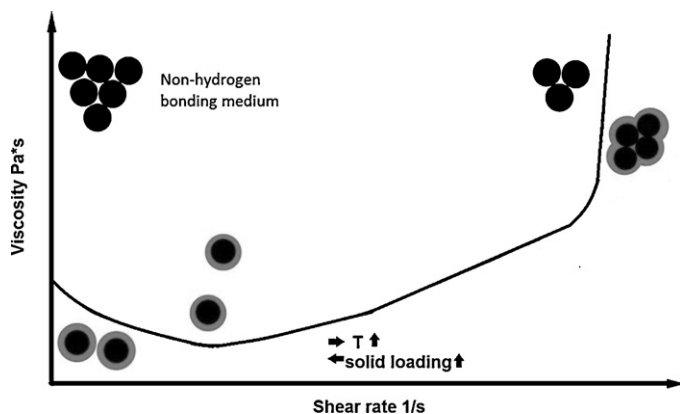
Fig. 5. Schematic illustration of shear thickening behavior of SiO$_2$ in polar media.

present on the silica surface. In the present system the monomers were chosen such that their refractive index match that of silica.[9] Under these conditions, even low molecular weight OH terminated monomers in the solvation layers cause the short-range repulsive forces and in this way prevent silica particles from approaching one another (Fig. 5, black circles surrounded by red solvation layers). For low shear rates solvation layers contribute stable sol behavior of dispersion. This situation lasts until solvation layer's forces are overcome by shearing stress, thus particles coming closer to one another cause shear thickening behavior (Fig. 5). It is frequently shown that after reaching a local viscosity maximum second shear thinning zone proceeds.[18] Unfortunately, probing such phenomenon with the present dispersions was not possible due to rheometer shear rate limitations.

Another argument for solvation layers is the analysis of the exact opposite situation at which dispersion of hydrophilic silica in monomer has no H-bonding capability. Butyl acrylate analyzed in Wozniak et al.,[9] which is a methyl terminated, non-polar analog of 4-HBA and 2-HEA, fails to provide low viscosity dispersions above 10–15 vol%. This indicates a direct comparison of the effect of end group polarity on dispersion properties. In such case, the formation of a solvation layer around each particle is precluded by the low affinity between liquid molecules and the silica surface (Fig. 5, black circles without grey layers). Instead, the silica particles are envisioned to directly interact with each other through H-bonding interactions

between the surface silanol (Si–OH) groups. The preponderance of such interparticle bonds throughout the sample volume will then result in a colloidal gel.[17] These dispersions show only shear thinning behavior, suggesting the dispersions are in effect within their second shear thinning zone.[18]

3.2. "Submicron" silica dispersions

Fig. 6 shows the effect of shear rate and temperature on the viscosity of 50 and 54 vol% "submicron" dispersions in a PEG200DA/2-HEA monomer mixture. The 50 vol% of "submicron" (Fig. 6a) could be continuously measured up to 1000s^{-1}. At temperatures up to 45 °C the dispersions show shear thinning followed by shear thickening. The transition from shear thinning to thickening shifted to higher shear rates with the increase in temperature. This trend is similar to that seen previously with the "nano" dispersions (e.g. Fig. 3c). At 55 °C shear thickening is not seen at shear rates of 1000s^{-1}. However, judging from the tendency seen at lower temperatures, it appears that for higher shear rates this dispersion would start to display shear thickening. The maximum viscosity measured with the 50 vol% "submicron" is 0.9 Pa s for 1000s^{-1} at 13 °C, compared to 0.1 Pa s measured at 55 °C at the same shear rate. For the 54 vol% "submicron" dispersion (Fig. 6b) it was possible to continually measure up to 1000s^{-1} only above 45 °C. At lower temperatures a sharp jump in viscosity at with increased shear rate, similar to that seen with the high concentrated "nano" dispersions (Fig. 2c and d) is noticed.

The critical shear rate of the 50 and 54 vol% "submicron" dispersions in the 13–55 °C temperature range is shown Fig. 7. It can be seen that the critical shear rate occurs for 50 vol% "submicron" already at shear rate values of 200 s^{-1} for the lowest measured temperature of 13 °C, As visible, an increase of temperature leads to the shift of the critical shear rate value. For 55 °C this point is increased beyond fivefold to over 1000s^{-1}, which was the maximum reachable shear rate. For the 54 vol% of "submicron" the tendency is the same. Critical shear rate occurs in lower shear rates, e.g. for 13 °C is in 50 s^{-1} but for 55 °C is already 550 s^{-1}.

Let's compare the highest concentrated "nano" with "submicron" dispersions in respect of critical shear rate occurrence (Figs. 4 and 7). The shear rate values for 43 vol% "nano"
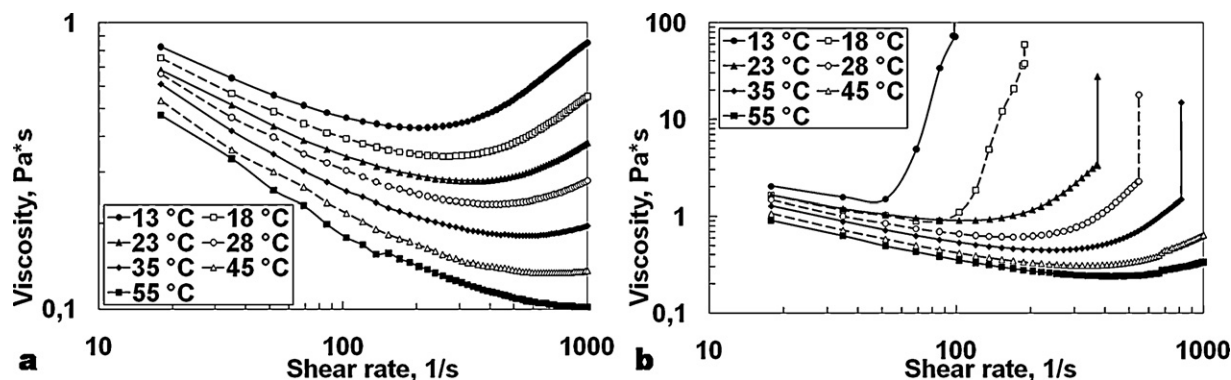

Fig. 6. Viscosity of "submicron" SiO$_2$ dispersions in PEG200DA/2-HEA monomer mixture as a function of shear rate and temperature at different solid loadings. (a) 50 vol% and (b) 54 vol%.
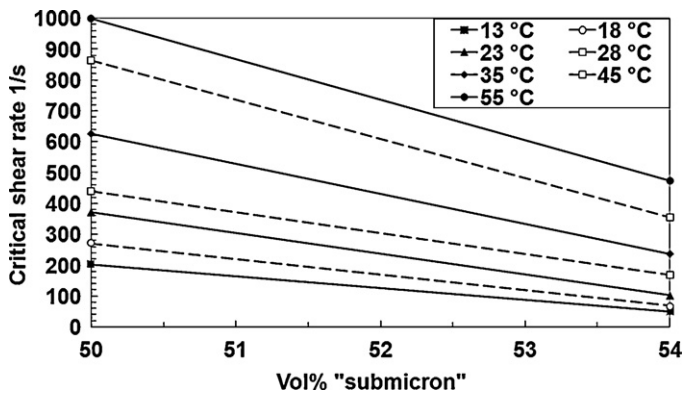
Fig. 7. Critical shear rate as a function of solid loading of "submicron" SiO_2 dispersions PEG200DA/2-HEA monomer mixture.

and 54 vol% "submicron" for the lowest measured temperature (13 °C) are on the same level which do not surpass $100 \, s^{-1}$. The difference occurs for the highest temperature (55 °C). As it visible even much more concentrated "submicron" dispersion has much higher critical shear (close to $500 \, s^{-1}$) in compare to "nano" ($300 \, s^{-1}$). It means, that in some specific cases, the nanosuspensions require the lower shear rate to induce shear thickening effect. It is generally conjugated with stronger interactions among nanoparticles than among any larger ones. Grains of nanosilica, which have a higher surface energy than microsilica ones, are likely to form an expanded and resistant 3D network in a suspension stabilized by an adequate continuous phase.[19] When temperature of the nanosuspensions is increased, the viscosity of the liquid is decreasing, but the silica network is found

to be preserved to some extent. The network can be the cause of the shear thickening behavior which is induced at some lower shear rate than in the case of "submicron" silica dispersions.[20]

3.3. "Micron" silica dispersions

Fig. 8 shows the three "micron" silica dispersions in a PEG200DA/4-HBA monomer mixture for three different solid loadings between 40 and 60 vol%. The 4-HBA monomer has similar OH and acrylate termination as 2-HEA but has two additional CH2 units (Table 2). While the viscosity of 4-HBA is slightly higher than 2-HEA, its interaction with the silica surface and formation of salvation layers is similar. As seen in Fig. 8 the rheological behavior of the "micron" particles is much different in comparison to the "nano" and "submicron" dispersions (Figs. 2 and 6). Instead of shear thinning followed by shear thickening seen with the "nano" and "submicron" dispersions (Figs. 2 and 6), the "micron" dispersions of 40, 50 and 60 vol% (above 35 °C) show only shear thickening behavior (Fig. 8). Shear thickening followed by shear thinning is seen at 60 vol% at or below 28 °C (Fig. 8c). The maximum viscosity is therefore seen at or close to $1000 s^{-1}$ at 13 °C. The maximum valued are 0.15, 0.3 and 2 Pa s for the 40, 50 and 60 vol% dispersions, respectively. These numbers indicate a sharp increase in viscosity from 50 to 60 vol% dispersions. This trend can similarly be inferred from Fig. 9, where the viscosity ($100 s^{-1}$) is compared in the 3D graph. High dependency of the viscosity increase is already seen in the lowest measured shear rate ($18 s^{-1}$). For
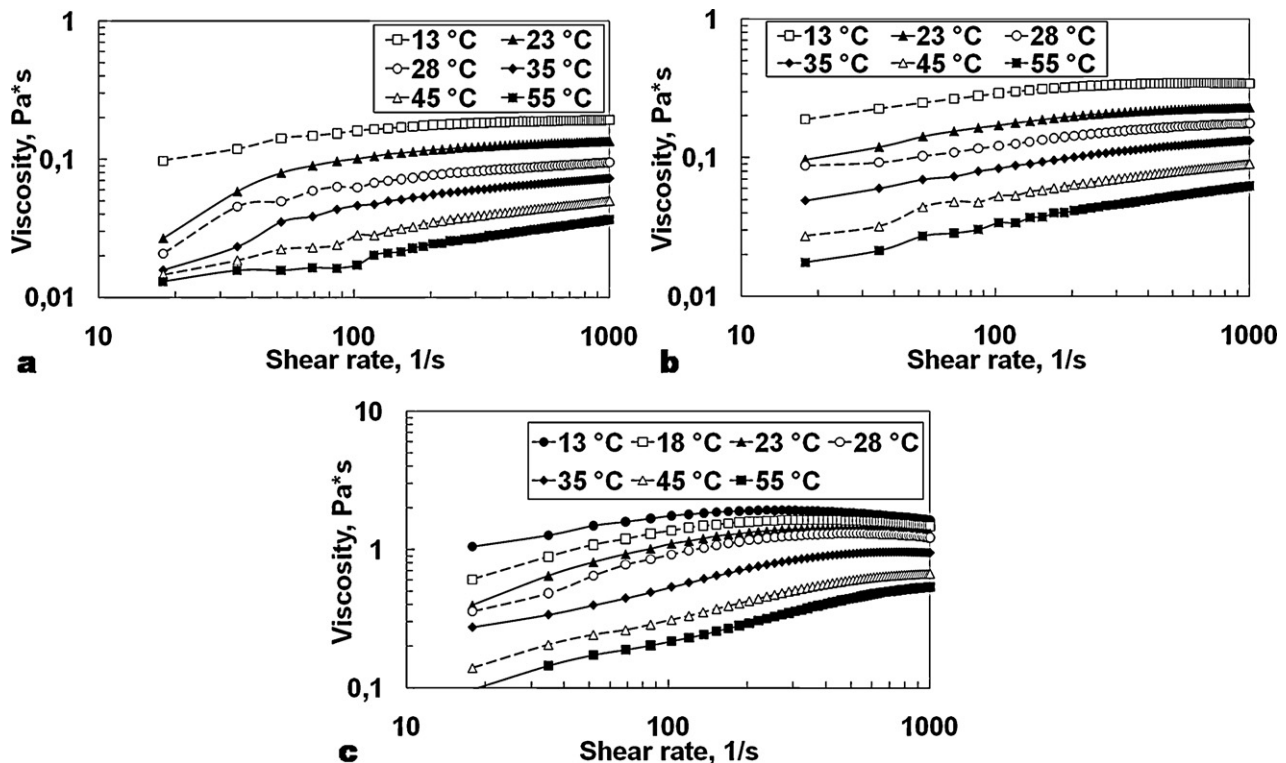

Fig. 8. Viscosity of "micron" SiO_2 dispersions in PEG200DA/4-HBA monomer mixture as a function of shear rate and temperature at different solid loadings. (a) 40 vol%, (b) 50 vol% and (c) 60 vol%.
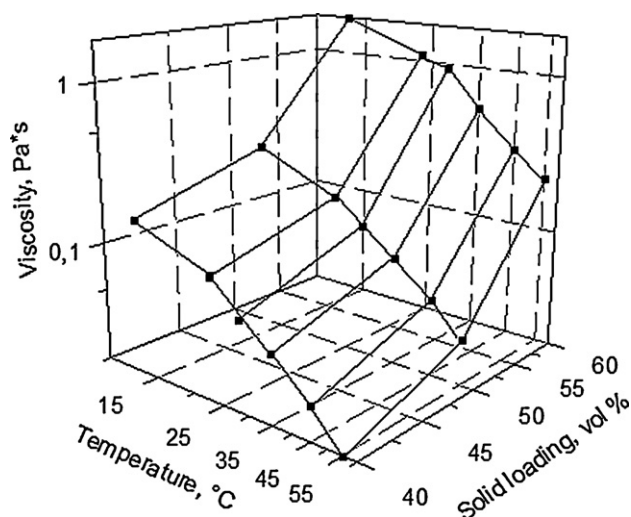
Fig. 9. 3D representation of the influence of temperature and solid loading on the viscosity of "micron" SiO_2 dispersions in PEG200DA/4-HBA monomer mixture (at $100\,s^{-1}$).

50 vol% viscosities for such shear rate are in the range of 0.017 and 0.19 Pa s instead of 0.14 and 1.06 Pa s for 60 vol%.

The microsilica dispersions are required to propose any different mechanism of dilatancy. The shear thickening effect is slowly increasing over the entire range of the increasing shear rate. In this case there is assumed, that no thoroughgoing change of the structure or any type of interactions in the liquid takes place. The increase of the viscosity/shear stress (Fig. 8) is too mild to be induced by any radical mechanism of dilatancy; for example by clustering, *order–disorder* theory or "bridging". The rheological behavior of the microsilica dispersions can be associated with its simplest mechanism; i.e. the increase of the system volume, which means, that the larger particles of the powder, the more feasible is the effect of dilatancy; see Fig. 10 which illustrates the mechanism. The described effect shows some similarities with the data obtained by Olhero and Ferreira[21] for the aqueous dispersion of 2.2 μm silica. The authors of the paper also suggest excluding this behavior by using the above-mentioned mechanism.

3.4. Mixtures of "nano" and "micron" silica

Dispersions which contain mixtures of "nano" and "micron" silica in PEG200DA/2-HEA were prepared to investigate the influence of the bimodal particle size on the dispersion rheology (Fig. 11). The graphs are ordered from the highest to the lowest
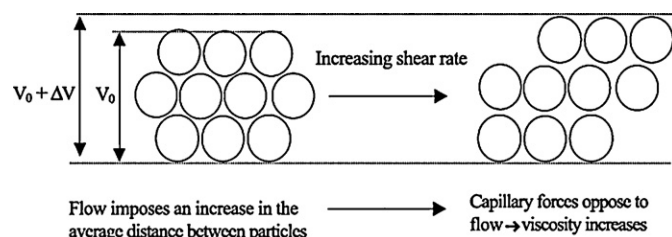

Fig. 10. Schematic illustration of the effect of the shear-thickening behavior.[21]

concentration of "nano" silica (Fig. 11a–f). The solid loading of "micron" silica increases in opposite order. Note that the total solid loading is the sum of both particles which is either 45 (Fig. 11a and f) or 50 vol% (Fig. 11b–e). In general, the rheological behavior follows the behavior of the major component. Shear thinning followed by shear thickening is observable when the "nano" is the major component (Fig. 11a–c) whereas shear thickening is easy to observe when the "micron" is the major component (Fig. 11e–f). As it is presented in Fig. 11a, addition of 5 vol% "micron" silica to the 40 vol% "nano" powder, does not change the rheological behavior of the dispersion, and at 23 °C viscosity is even lower, which is 0.4 Pa s instead of 0.55 at $18\,s^{-1}$ (Figs. 2c and 11a).

Such rheological behavior could be the result of the broadening particle size distribution. As it is known from Farris theory,[22] dispersions containing high range of particle size are of much higher fluidity in comparison to monosized particle suspensions.

This phenomenon can be also caused by different dispersion preparation procedures. Highly concentrated 43 vol% "nano" dispersions were diluted and "micron" was added. Initial higher shear stress for 43 vol% and additional mixing time could have influence on lower dispersion viscosity. For 50 vol% of silica (Fig. 11b, 40 vol% "nano" and 10 vol% "micron" silica) the viscosity at 23 °C at $100\,s^{-1}$ is significantly increased to 0.8 Pa s, which is almost 3 times more than for 40 vol% "nano" plus 5 vol% "micron". The trend of viscosity graph versus shear rate is still close to the highly loaded pure "nano" dispersions. When nanosilica has majority over microsilica in the suspension it determines an increase of viscosity – Farris effect is diminished. "Large" microsilica particles are too rarely dispersed in the suspension to evaluate the effect.

The rheological behavior starts to change when the amount of "micron" silica reaches 20 vol% in 50 vol% dispersion (Fig. 11c).

Viscosity of these suspensions is almost one quarter of those from Fig. 11b. Nanosilica particles which are nominally more than 30 times smaller than microsilica ones is far above critical particle diameter ratio (6.46)[23] what allows small particles to fit into the triangular pores between larger particles. The small spheres are free to flow through the labyrinth created by the larger spheres diminishing viscosity of the dispersion.

It is worth to note that such dispersion does not exhibit high decrease of viscosity at low shear rates after which it starts to be shear thickening. Initially, almost Newtonian flow convert to shear thickening behavior. This flow shows the same rheological behavior as the highly loaded "micron" dispersions (see Fig. 8). Thus it is easily proved that polydispersity can give a lower viscosity at the same volume fraction assuming that small as well as larger particle are of adequate diameter ratio. Researches also proved that broadening of the particle size distribution can increase the volume fraction at which shear thickening occurs what has also agreement with work of, e.g. Wagstaff and Chaffey.[24]

50 vol% silica dispersion obtained by using 25 vol% "nano" and 25 vol% "micron" (Fig. 11d), behaves as an apparent Newtonian fluid up to $1000\,s^{-1}$. This can be regarded due to the
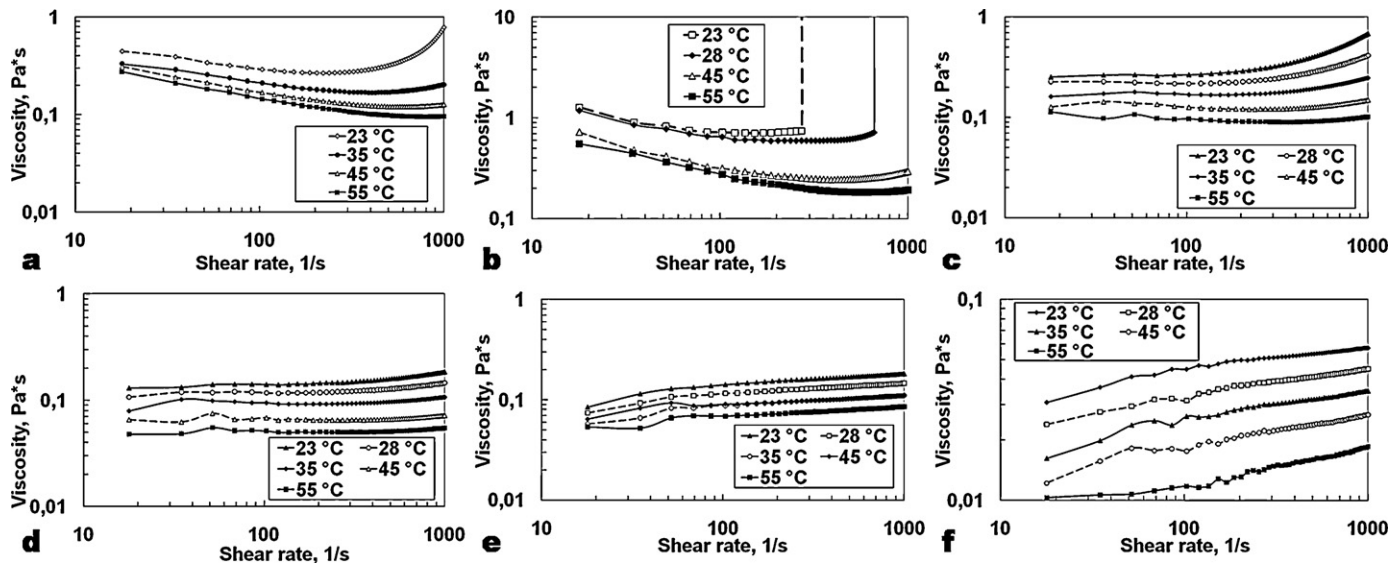
Fig. 11. Viscosity of mixed "nano" + "micron" SiO$_2$ dispersions in PEG200DA/2-HEA monomer mixture as a function of shear rate and temperature at different solid loadings. (a) 40 vol% "nano" + 5 vol% "micron", (b) 40 vol% "nano" + 10 vol% "micron", (c) 30 vol% "nano" + 20 vol% "micron", (d) 25 vol% "nano" + 25 vol% "micron", (e) 15 vol% "nano" + 35 vol% "micron", (f) 10 vol% "nano" + 35 vol% "micron".

combination of two fluids with opposite rheological behavior. The shear thinning "nano" dispersion and the shear thickening "micron" dispersion, if mixed in an appropriate ratio, produce a Newtonian fluid. With 50 vol%, the viscosity of 25 vol% "nano" +25 vol% "micron dispersion is found to lie between 0.05 Pa s (at 55 °C) and about 150 Pa s (at 23 °C).

The presented results stay in accordance with,[25,26] what means that dilatant behavior can be avoided by broadening the particles size distribution.

4. Conclusions

In this work the steady shear properties of concentrated UV curable silica dispersions for rapid prototyping applications have been studied. High solid loading of dispersions (up to 43 vol% of nanosilica and 60 vol% of microsilica) with viscosity less than 2 Pa s in 1000s^{-1} was accomplished by proper selection of monomers having matched refractive index and hydrophilic properties to silica. Comparable refractive indices diminish Van der Waals attraction and made dispersions highly transparent. Thanks to partially hydrophilic OH terminated monomers, hydrogen bonds are created on silica surface. Such hydrogen bonds called solvation layers round each silica particle and contribute short range repulsive forces which prevent approaching particles one another causing steady sol behavior. Nevertheless the main obstacle for using of such dispersions is shear thickening which starts to occur when attractive forces in high shear rate overcome forces of solvation layers. One way to decrease viscosity and delay shear thickening to the higher shear rate is heating the dispersions or reducing solid loading.

Other way of delaying or diminish shear thickening tendency is use of different rheological behavior of dispersions based on nano and micron silica powders. Dispersions based on these powder mixtures can have Newtonian flow even up to 1000s^{-1}.

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