Rheological properties of re-melted paraffin-wax suspensions used for LPIM

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Abstract

The influence of re-melting of suspensions of ceramic powder and paraffin-wax used for LPIM on the yield stress and the flow behaviour was investigated. As a model system we used alumina powder and paraffin-wax, which has a liquid/solid phase transition at around 58 °C. The only parameter that was changed during this study was the number of particles per unit volume and, consequently, the number of attractive, interparticle interactions in the suspensions per unit volume.

During cooling the particles took up closer interparticle distances than in the prepared suspension due to the huge shrinkage associated with paraffin-wax, which occurs below the liquid–solid phase transition. This resulted in an increased, attractive interparticle interaction (and so an increased yield stress) and an increase in the strength of attractive particle network formed after re-melting, which can be destroyed by homogenization, as was shown during the flow-curve measurements, and the initial flow properties of the paraffin-wax suspensions can be regained.

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1. Introduction

Low-pressure injection moulding (LPIM) is a cost-effective near-net-shape method for producing complex-shaped ceramics.[1–3] In this process, suspensions of a ceramic powder and paraffin-wax are used for the formation of green ceramic parts. These suspensions must have a low viscosity at the moulding temperature (70 °C), at which point they are injection moulded into a cold, metallic model, where the suspension cools below its melting temperature and retains the shape of the model.

The overall success of the low-pressure injection moulding of ceramics relies primarily on the properties of the ceramic-powder, paraffin-wax suspension. It is desirable that the suspension contains a high loading of homogeneously dispersed particles in a liquid carrier to ensure suitable moulding characteristics.[4–6] The appropriate addition of surfactants is, therefore, one of the most important requirements that signifi-

cantly enhances the dispersion of the powder in the binder, which in turn results in an enhanced powder loading at a reasonably low viscosity. Fatty acids are the most widely used surfactants; they are introduced to disperse suspensions of ceramic-powder and paraffin-wax in many industrial procedures.[7] Stearic acid is considered to be one of the most appropriate candidates due to its carboxylic functional-group anchoring at the powder surface and a carbon chain containing 18 carbon atoms dissolving into the binder matrix. The adsorption of the stearic acid is usually via hydrogen bonding, although covalent bonding has also been reported.[8] However, Johnson and Mossison[9] and Liu[10] have indicated that the use of small molecules such as stearic acid (the length of stearic acid is ~2.4 nm) does not provide true stabilization. They indicated that, for example, stearic acid is effective only in reducing the van der Waals attraction and/or the short-range forces, but it is not capable of creating a repulsive potential between the particles, and the resultant interparticle potential is attractive and the suspensions are weakly flocculated. When the overall interaction potential in the suspension is attractive, there is a certain volume fraction of solids whereby a continuous network is formed and a certain shear stress is needed to overcome the interparticle forces in order to induce flow. This

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Table 1
Granulometric analysis and BET surface area of the A16, CT 1200 SG and CT 800 SG powders.

	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Surface area (m²/g)
A16	0.34	0.72	2.01	7.5
CT 1200 SG	0.99	1.69	3.40	3.7
CT 800 SG	1.27	3.28	6.52	1.0

shear stress or yield stress has been shown by many studies to be dependent on the interparticle forces, the volume fraction, the particle size, and the size distribution.[10–12] Furthermore, all these parameters also affect the flow behaviour of these suspensions, after the yield stress of the suspensions is exceeded. The flow behaviour of these suspensions is determined with flow-curve measurements and the type of flow behaviour can usually be described as pseudoplastic flow.[13]

The yield stress, i.e., the strength, of the attractive particle network, plays an important role in the mould-cavity filling step. However, if the organic vehicle is thermally removed from the moulded part, the yield stress as a measure of the strength of particle network is also likely to be an important parameter for the successful thermal debinding. During this processing step the moulded parts are slowly heated up to a temperature that is well above the melting temperature of the paraffin-wax blend (up to 240 °C).

In order to prevent the deformation of specimens, the attractive particle network plays a crucial role and must prevent the introduction of defects into the moulded parts. The introduction of defects can arise because of the migration of particles caused by the extraction of the molten paraffin-wax into the surrounding powder bed or because of sample deformation due to its mass.

In this study the influence of re-melting ceramic-powder, paraffin-wax suspensions used for LPIM on the yield stress and the flow behaviour was investigated. As a model system we used three alumina powders with different granulation, and paraffin-wax, which has a liquid/solid phase transition at around 58–62 °C, was used for the preparation of the suspensions, which contained from 50 to 60 vol.% of powder.

2. Experimental work

Three alumina powders were used: a submicron-sized alumina powder A16 SG (Alcoa, USA) and two micron-sized alumina powders CT 1200 SG and CT 800 (Martinswerk, Germany). Granulometric measurements of the particle size for these three powders are given in Table 1.

The powder suspensions were prepared using INA 58/62 paraffin-wax (INA, Croatia) with a melting point in the temperature range 58–62 °C as a liquid medium and stearic acid (Carlo Erba, Italy) as a surface-active agent. In the slurry preparation the alumina powder was dried at 140 °C for 4 h before compounding with a molten mixture of paraffin-wax and stearic acid. After compounding, the suspensions were homogenised at 80 °C using a water-heated three-roller mill (Exact, Germany). Three passes through the gap between the rollers was sufficient for the

preparation of the homogeneous suspensions, as experimentally determined in our laboratory.[14]

For each alumina powder the amount of stearic acid needed for the preparation of the suspensions was calculated per surface area of used alumina powder. A total of 0.5 mg of stearic acid per square meter of the surface of the powder was used for the preparation of the suspensions.[15] The volume fractions of solids in the suspensions were 50, 55 and 60 vol.%, respectively.

After the preparation of the paraffin-wax suspensions the rheological properties were measured. This was done in two ways, which differed only in terms of the conditioning of the prepared suspensions. First, the samples denoted as freshly prepared suspensions were rheologically characterized immediately after their preparation, i.e., the suspensions were not cooled below the liquid/solid phase transition of the liquid medium and, second, the suspensions denoted as re-melted suspensions were cooled below the liquid/solid phase transition of the liquid medium and then re-melted to the temperature at which the rheological characterization was performed. The rheological properties were analysed with a MCR 301 rheometer (Anton Paar, Austria) using a cone-and-plate geometry and a PK-25-1 sensor system. If not stated otherwise in the text, the rheological measurements were performed at 70 °C. In order to determine the flow curves of these suspensions, a shear rate range from 0.1 to 100 s⁻¹ was selected. To determine the yield stress of the paraffin-wax suspensions, controlled shear-stress measurements were performed in the shear-stress range from 1 to 30,000 Pa. In order to have reproducible results and to exclude the effect of the cooling temperature of the suspensions on the yield stress for re-melted suspensions, the cooling of the suspensions were performed directly in the apparatus. The freshly prepared suspension was put in the apparatus, where the flow-curve was measured. After the flow-curve measurements the sample was cooled at a rate of 10 °C/min to 40 °C. The suspension was then held at this temperature for 20 min to obtain equilibrium temperature conditions, and then the sample was re-heated at 10 °C/min to 70 °C (if not stated otherwise). The sample was held at this temperature for an additional 20 min before the yield-stress measurement in order to obtain an equilibrium temperature for the sample. This procedure was repeated for each measurement, and also for the repeated yield-stress measurements.

3. Results and discussion

In Fig. 1 are the flow curves at 70 °C for a re-melted paraffin-wax suspension containing 60 vol.% of A16 alumina powder. Repeated measurements on the re-melted suspensions (see Section 2) show that after 3 cycles the measurements of the flow-curve became constant and are the same as that of the freshly prepared suspension. During the first measurement of the flow-curve the thixotropy of the suspension is observed, which is more pronounced in the low shear-rate region. With an increased number of cycles the thixotropy is decreased and, as is shown in Fig. 1, after 3 cycles no thixotropy can be observed, and after this point there is no further change in the flow-curve. This was observed for all the paraffin-wax suspensions prepared in our laboratory.
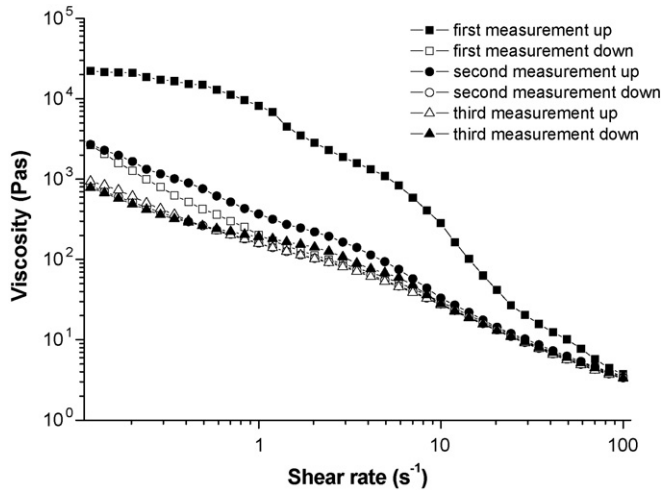
Fig. 1. Flow-curve measurements for 60 vol.% A16 alumina paraffin-wax suspensions after re-melting: first measurement, second measurement and third measurement.

Fig. 3. Flow-curve measurements of 55 vol.% A16 alumina paraffin-wax suspensions after re-melting: first measurement, second measurement and third measurement.

It is important to point out, that when the flow-curve measurement of liquid medium alone was performed no differences between flow curves of liquid medium after the preparation nor after re-melting of liquid medium was detected. This means that liquid medium alone should not have any important effect on the presented behaviour of suspensions.

However, the differences between the flow curves of the re-melted paraffin-wax suspensions prepared with different solids contents and with different particle sizes were determined. The flow curves with different solids contents are presented in Figs. 2 and 3, and the suspensions prepared with different particle sizes are presented in Figs. 4 and 5. With decreased solid contents in the paraffin-wax suspensions, the stationary state is reached more quickly (see Figs. 2 and 3). Furthermore, the prepared suspensions containing the same solids content, but an increased particle size, achieved the stationary state more quickly (see Figs. 4 and 5) in comparison to the suspensions
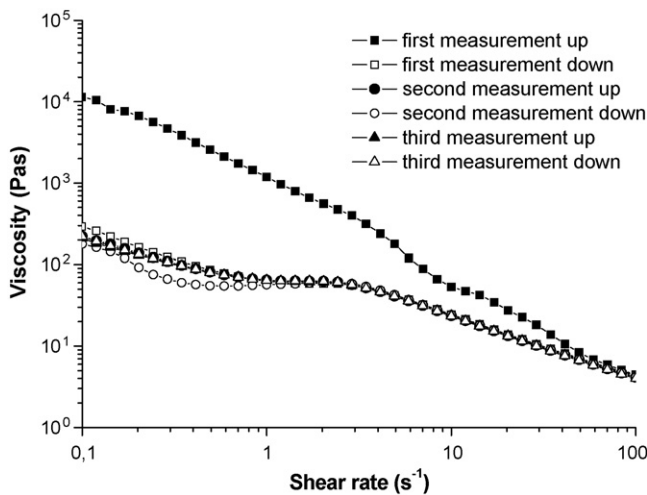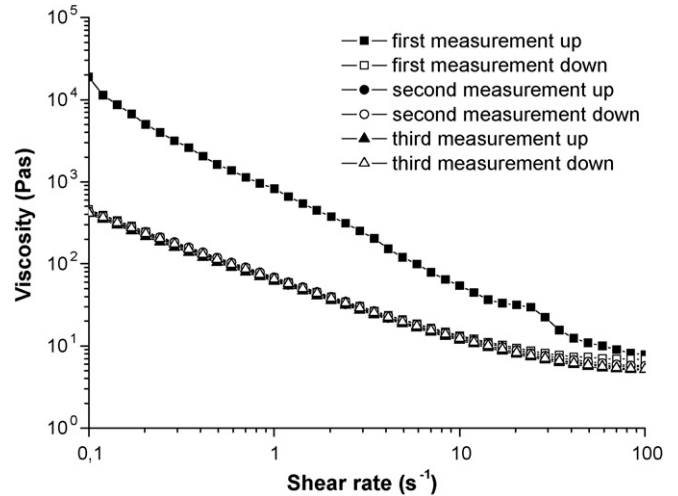
prepared with finer powders. This result leads us to an interesting question: what happens during the cooling of the suspension below the temperature of the liquid–solid phase transition of the liquid medium? From these measurements we can determine that when cooling the suspensions below the liquid–solid phase transition of the liquid medium and after re-melting of the suspension, the flow properties change and the initial flow properties can be obtained after homogenization, which in the presented case was obtained by repeated measurements of the flow-curve on the same sample. This revealed that the processes responsible for the changes in the flow properties of the re-melted suspensions are reversible.

In both presented cases, if the composition of the suspensions is taken into account, the only important parameter, which is connected with both systems, is the change in the number of particles per unit volume. A smaller number of particles is the result of a decreased volume content

Fig. 2. Flow-curve measurements of 50 vol.% A16 alumina paraffin-wax suspensions after re-melting: first measurement, second measurement and third measurement.
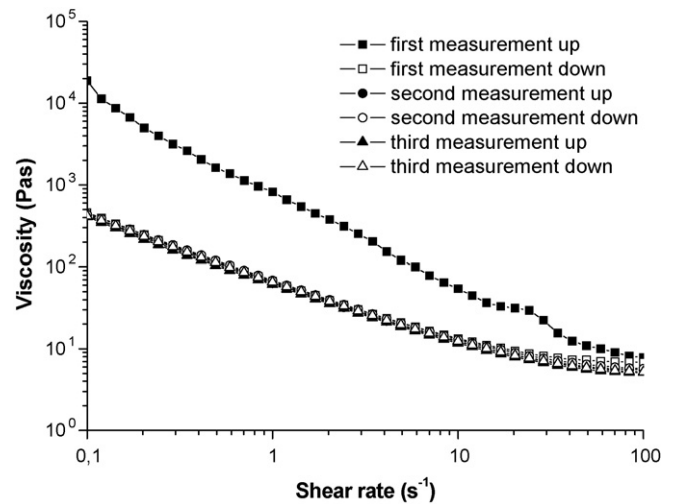

Fig. 4. Flow-curve measurements of 60 vol.% CT 1200 alumina paraffin-wax suspensions after re-melting: first measurement, second measurement and third measurement.
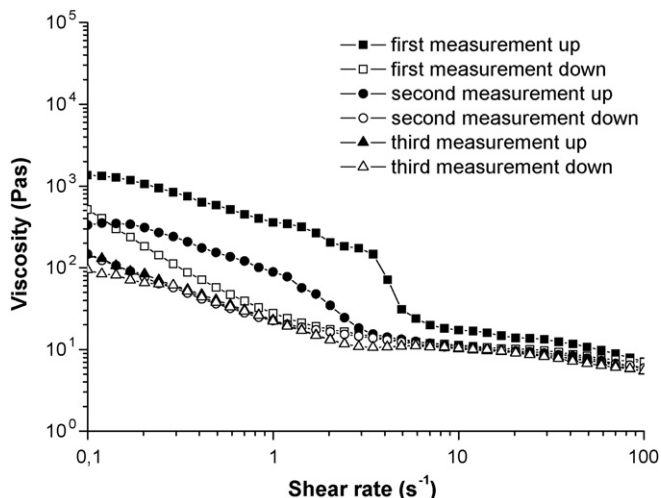
Fig. 5. Flow-curve measurements of 60 vol.% CT 800 alumina paraffin-wax suspensions after re-melting: first measurement, second measurement and third measurement.
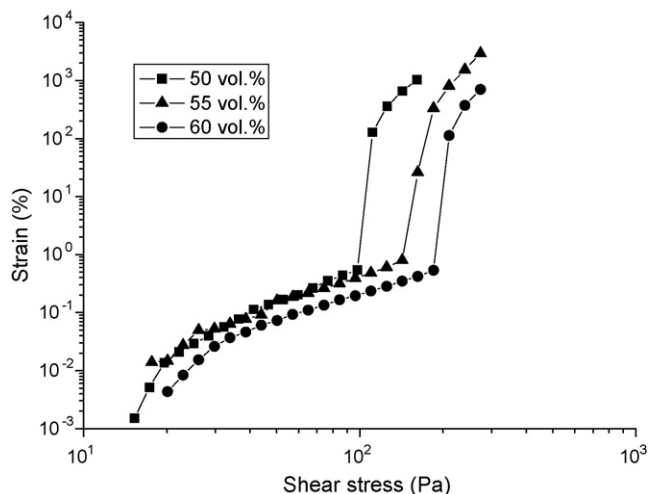

Fig. 6. Dependence of the yield stress on the solids loading of the prepared A16 alumina, paraffin-wax suspensions at 70 °C.
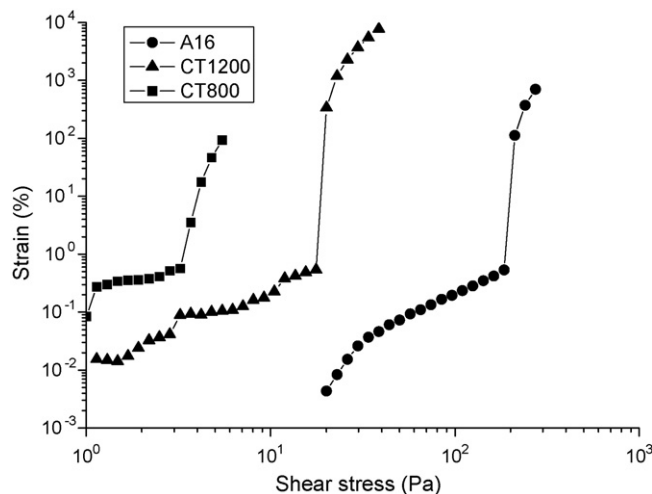

Fig. 7. Dependence of the yield stress on the particle size of the prepared 60 vol.% alumina, paraffin-wax suspensions at 70 °C.
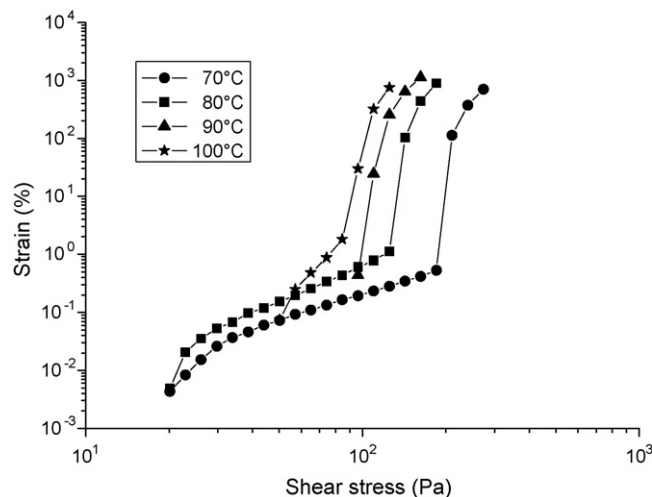

Fig. 8. Temperature dependence of the yield stress for prepared 60 vol.% A16 alumina, paraffin-wax suspensions.

of particles in the suspensions, as well as an increased size of particles for a constant volume content of solids. From the literature it is well known that for such suspensions, which can be described as suspensions with a high solids loading and having in mind that the interactions between the particles in these suspensions are attractive, a continuous network is formed at rest. The rigidity of this continuous network depends almost entirely on the number of interparticle interactions. Nevertheless, even if in the presented system we used the same liquid medium and aluminas, which differ only in terms of the particle size, the differences in the particle size for the used aluminas have an effect on the van der Waals forces. However, this effect was neglected in our study (the differences in d_{50} are in the range from 0.7 to 3.2 μm).

If a continuous, attractive network is formed in the suspension, this must result in a certain shear stress (yield stress), which is needed to overcome the interparticle forces and to induce flow in the suspension.

First, the existence of the yield stress and the dependence of the yield stress (the rigidity of the network of particles that is formed) on the solids loading and the particle size of the prepared alumina, paraffin-wax suspensions were determined. The dependence of the yield stress for the prepared A16 alumina suspension is shown in Fig. 6, and as expected with an increased solids loading the yield stress was increased. The measured yield stresses were in the range from 100 Pa for the suspension with 50 vol.% solids to 200 Pa for the suspensions with 60 vol.%.

An increased yield stress of the prepared suspensions was also observed for suspensions with a smaller particle size of the powders used for the preparation of the suspensions, as shown in Fig. 7. As the particle size decreased from d_{50} 2.2 to 0.7 μm the yield stress increased from 3 to 180 Pa for the prepared suspensions containing 60 vol.% of alumina. Also, the yield stress of the prepared suspensions decreased with the increased temperature, as presented in Fig. 8. These results are in agreement with the results presented in several other studies.[11,12,16]
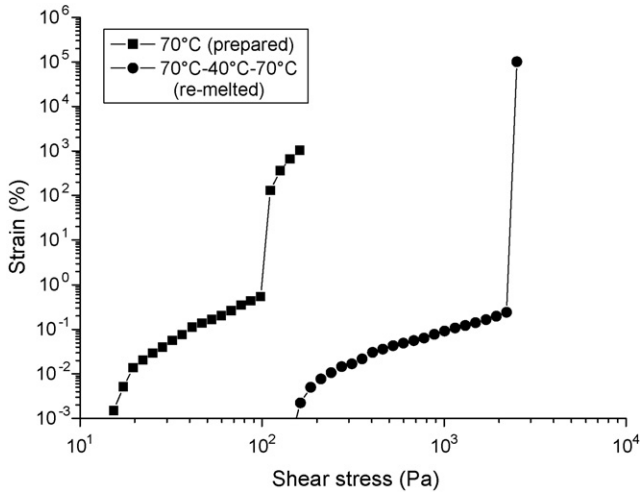
Fig. 9. Yield stress of the freshly prepared and re-melted 50 vol.% A16 alumina, paraffin-wax suspension measured at 70 °C.

Fig. 11. Dependence of the yield stress on the particle size for re-melted 60 vol.% alumina, paraffin-wax suspensions measured at 70 °C.

As the formation of the continuous, attractive particle network in the freshly prepared paraffin-wax suspensions was confirmed by determining the yield stress, the effect of cooling the suspension below the liquid–solid phase transition and re-melting on the yield stress was also determined. In Fig. 9 is the yield stress for the prepared and re-melted 50 vol.% A16 alumina suspension. The yield stress changed from more than one order of magnitude for the re-melted suspension in comparison to the prepared suspension. Furthermore, the yield stress of the re-melted suspensions also increases with an increased solids loading and a decreased particle size, like with the prepared suspensions, which is shown in Figs. 10 and 11, respectively. On the basis of a similar dependence of the yield stress for the prepared and re-melted suspensions, the formed structure in the suspensions must play a crucial role. An increased yield stress can only be the result of an increased rigidity of the formed network, which is a consequence of increased, attractive interparticle forces in the suspension. As can be seen from Figs. 10 and 11, the stronger the starting suspension's structure
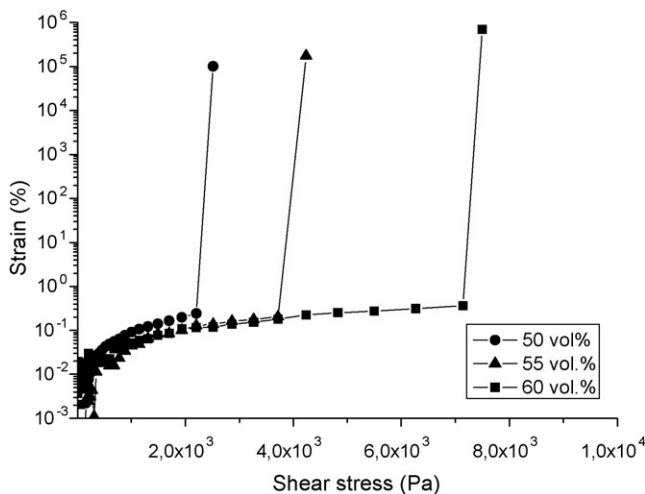

Fig. 10. Dependence of the yield stress of the solids loading for re-melted A16 alumina, paraffin-wax suspensions measured at 70 °C.
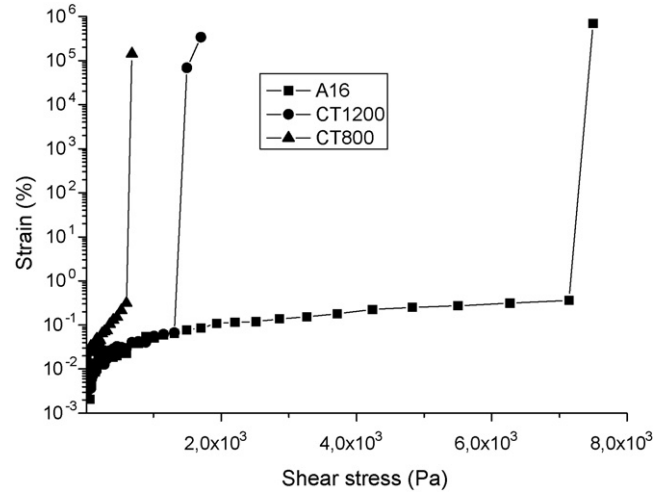
the more pronounced is the change in the yield stress, which confirmed that this change is affected by the number of particle "contacts" between the particles per volume unit.

Although the measurements of the yield stress of the prepared and re-melted suspensions were conducted at the same temperature, important changes occurred during the cooling below the liquid–solid phase transition of the liquid phase. Since, in the used system the temperature change affects only the dispersing medium, there is no effect on the ceramic powder, and the reason for the formation of a stronger network must be the change of the liquid medium. During the phase transition of the liquid medium, in this case paraffin-wax (a mixture of n-paraffins), the shrinkage is around 20 vol.%. This large shrinkage of the paraffin-wax during the liquid/solid phase transition must result in a reduced distance between the particles. According to the measured, higher yield stress after the re-melting of the suspension (Fig. 9), we can suppose that the "nearest-neighbour" distances between the particles in the network are the same as in the frozen state, while the parts (or branches) of the network can accommodate the paraffin-wax extension.

It is well known that van der Waals forces increase rapidly with a decreasing distance between the particles. So, a shorter distance between the particles results in larger attractive forces and an increased strength for the network of particles. This increased strength of the network of particles in the suspension appeared then as the increased yield stress of the re-melted suspension in comparison to the prepared suspension. An important observation from these measurements, which indicates and also supports the previously stated assumption, is that the change in the yield stress between a freshly prepared and a re-melted suspension is more pronounced for the suspensions with larger numbers of particles per unit volume and, consequently, with more interactions between particles.

Furthermore, the observed thixotropy of the suspensions during measurements of the flow curves is also the result of smaller distances between the particles in the re-melted suspension, which occurred during the cooling below the liquid/solid phase transition of the liquid medium. However, with a gradual

homogenization of the suspensions as a result of flow-curve measurements (in our case) the formed structure is slowly destroyed, which means that the particles occupied the equilibrium interparticle distances as they did in freshly prepared suspensions. As can be seen from Fig. 1, to obtain the initial flow properties of the paraffin-wax suspension, a different degree of homogenization is needed (in the presented case the number of measurements), which can also be used as empirical criteria for the estimation of the strength of the formed network of attractive particles after the re-melting of the suspension.

4. Conclusions

In this paper the effect of the re-melting of suspensions of alumina and paraffin-wax after cooling below the temperature of the liquid–solid phase transition, on the flow properties and yield stress is presented.

The flow-curve measurements of the re-melted suspensions reveal the presence of the thixotropy. With homogenization of the re-melted suspension the thixotropy vanished. However, the required degree of suspension homogenization to obtain the flow-curve of a freshly prepared suspension is increased with a decrease in the particle size and an increased solids volume content of the particles used for the preparation of the paraffin-wax suspensions.

The yield stress of the freshly prepared paraffin-wax suspensions was measured. The origin of this yield stress is the "small" attractive interaction between the particles and the formation of the attractive particle network in the suspension at rest. The yield stress of the prepared suspensions increased with a decrease in the particle size and an increased solid content used for the preparation of the paraffin-wax suspensions. After the cooling of the prepared suspensions below the liquid–solid phase-transition temperature of the dispersing medium and re-melting, the measured yield stress increased. A more pronounced increase in the yield stress was measured for suspensions prepared with smaller particles and/or a higher solids volume used for the preparation of the suspensions.

The only parameter that was changed during this study was the number of particles per volume unit and, consequently, the number of interparticle attractive interactions in the suspensions per unit volume. During cooling the particles took up even closer interparticle distances due to the huge shrinkage associated with paraffin-wax below the liquid–solid phase transition. This resulted in an increased, attractive, interparticle interaction (an increased yield stress) and an increased strength of the formed, attractive particle network, which can be destroyed by homogenization as was shown during the flow-curve measurements and the initial flow properties of the paraffin-wax suspensions can be obtained.

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