



Microfluidic rheology: A new approach to measure viscosity of ceramic suspensions at extremely high shear rates



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ARTICLE INFO

Keywords:

Colloidal processing
Rheology
Zirconia suspensions

ABSTRACT

This paper describes the operation principles of a micro-scale rheometry equipment based on the technology of microchannels on a chip and compares it with a conventional macro-scale rotational rheometer. Both techniques are used for the study of different solutions and suspensions of ceramic particles with different saccharides, which are subjected to a wide variety of shear rates from their preparation to their processing and injection in plasma spraying processes. The results have shown a clear difference between the rheological values obtained between both equipment, clearly influenced by the different measurement method. However, the microfluidic technique has higher accuracy to characterise fluids at high shear rates and low viscosities, and the apparent shear thickening observed in rotational rheometry for low viscosity samples due to wall slippage is not observed. In contrast, the fine microchannels of are easily clogged in concentrated suspensions.

1. Introduction

The knowledge of the rheological properties of fluids (solutions, suspensions, emulsions, among others) is extremely important due to the industrial relevance of understanding the stability and compatibilities of the materials employed, to guarantee a high homogeneity of the sample and to obtain a stable and optimal final product with the required texture and structure for the desired purpose [1].

The behaviour of fluids can be very different from the simplest Newtonian fluids that exhibit a linear relationship between the shear stress and the shear rate i.e., viscosity maintains constant at any shear rate, to non-Newtonian and other complex fluids in which viscosity changes with the applied shear rate. This can occur in a monotonic way (either increasing in the so-called shear thickening behaviour or decreasing in the shear thinning one) or with a mixed behaviour at different shear rate regions [2]. In addition, most concentrated suspensions, pastes and polymer containing samples can exhibit a viscoelastic behaviour, combining a viscous response at small frequencies with an elastic one at high frequencies [3].

In industry, there is a wide variety of fluids that are used on a daily basis and these are subjected to different processing and application stages during the development of an optimal end product. During the manufacture of a product, the fluid sample is subjected to a wide range of

shear rates that can directly affect the quality of the process or the product properties. Therefore, it is essential to understand and control the rheological and colloidal properties of fluids during their complete life cycle, from its preparation to final shaping or application, to avoid problems of agglomeration, clogging, lack of fluidity, homogenisation and productivity, among others.

Although it is customary to report the rheological behaviour of ceramic suspensions emphasising the values measured at the shear rate operating during shaping, the rheology determines the efficiency of any other processing stages, including milling and mixing, storage, pumping, and so on. Fig. 1 summarises the typical shear rates of a variety of common operations and processes used in ceramic manufacturing, from very low shear occurring during capillary filtration or sedimentation at rest to very high shear rates operating on brushing, high pressure injection or spraying processes [2–7]. Some examples illustrating the importance of the rheological properties of a suspension over a wide range of shear rates are the production of coatings by suspension plasma spraying and the injection of ceramic inks for printing on tiles. In both techniques, the ceramic suspension is subjected to large shear changes along its lifetime, due to the use of intermediate shear values during its preparation (milling and mixing), immediately followed by low shear at rest during storage, and moderate shear for its transport from containers to the injector (pipeline flow), where finally very high shear rate of 10^5 s^{-1}

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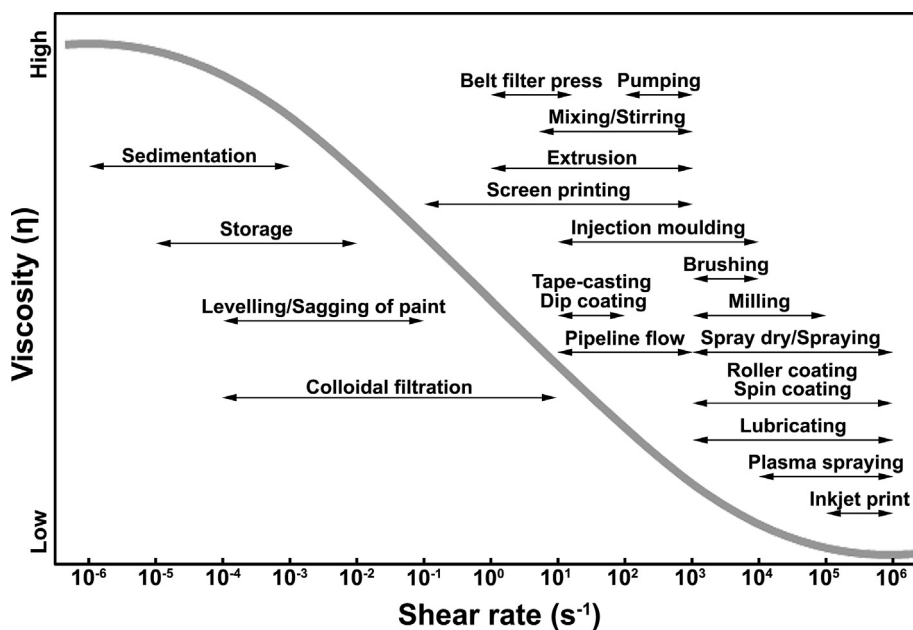


Fig. 1. Typical ranges of shear rates for common industrial processes. Adapted from Ref. [2,4–7] and expanded by the authors.

or even higher are reached when injected through very small diameter holes ($<200 \mu\text{m}$). The adaptability of the fluid to the different operational shear ranges is crucial to maintain the suspension in optimal operating conditions for the different stages of the process and to avoid common problems such as sedimentation or pipe clogging.

The great variety of fluids behaviours and shearing conditions has led to the development of new experimental devices and quantitative methods for the research of rheological properties, which can be grouped depending on the length and time scale into macro and microscale rheometers [8]. Traditionally, macroscale rheometry has been the most widely employed due to its simplification of flow models into a standard set of flows (shear and extensional flows). There is a wide variety of equipment in the market for the study of rheological properties [9], with rotational rheometers/viscosimeters as the most common due to their greater versatility. However, the study of rheological behaviour of some complex fluids through macro rheometry can be a complex and difficult task due to the limitations of the techniques themselves, which considerably reduce the precision of the results [8]. The limitations are associated with the difficulty of miniaturising the mechanical components of the rheometric instrumentation, the appearance of inertia produced by the measuring element, and the mechanical response between the measuring element and sensor, which sometimes does not have enough resolution to detect the phenomena occurring at very small stress or extreme shear rates. Other disadvantages of macro rheometry are the use of large volumes and the possible evaporation of liquid during the measurements [8,10,11].

These drawbacks become larger when complex fluids with very low viscosity or with a high rate of evaporation are studied, so new methodologies and technologies have been developed to study the rheological behaviour of very small amounts of sample in geometries with characteristic length scales in the micrometer range, also known as microscale rheometry [12]. The use of capillaries of a few microns allows the use of microfluidics, which results in flow curves for very low and well-controlled shear rates, as well as the generation of flows with high deformation rates without modifying the Reynolds number, which favours the appearance of strong viscoelastic effects [13]. This effect is very interesting in the study of complex fluids with low viscosity (inks, organic fluids, emulsions, foams ...) since in macroscopic studies complex fluids can present a behaviour opposite to that shown on a microscopic scale, very possibly due to a greater occurrence and influence of inertia during

measurement [14]. Besides, the reduction of the fluid lines and devices used in the micro rheometry allows to overcome some of the limitations of the macro rheometry, such as the use of small sample quantities, the practically null evaporation of the fluid due to the absence of a liquid - air interface, the possibility of reducing the devices turning them into portable sizes or the possibility of displaying the dynamics of the flow in real-time, among others ... [8,11], which results in a significant experimental benefit.

Within micro rheometry, there are different approaches but this paper will focus on the rheometry based on chip microfluidics. The reader interested in the different variants of microfluidics can find precise information in several books and scientific articles [8,10,11,15]. On-chip rheometry aims to characterise the rheological properties of fluids by force-feeding them through a micrometric channel and to subject the microfluid to a much broader range of shear rates. The study of viscoelastic behaviour in chip-type rheometers is not so well developed and requires further knowledge and development of the technique to obtain extensional deformations in fluids, a fact that influences the smaller number of commercial equipment for this purpose [3,10]. Therefore, the technique is mainly used to study the rheological behaviour of complex low viscosity fluids at different shear rates with very interesting results [11,13,16]. Moreover, chip type technology can be used in combination with microscopic monitoring systems or optical techniques to visualize the behaviour and structure of the fluid in real-time [17]. Nevertheless, the chip type rheometers have also some technical drawbacks to overcome, such as the reproducibility of the chips with low volumes, the limitation of optical techniques to measure the flow rate and the chip degradation or possible obstruction of the channels, as well as their possible effects on the flow [11,13]. This is of particular importance in ceramics, since particles tend to accumulate and obstruct the capillary impeding an accurate measurement.

The use of microfluidic rheometers in ceramic processing is still very limited but it can provide very interesting features in applications in which the applied shear rate is very high, well above the measuring range of rotational rheometers. This is the case for applications that are subjected to high shear mixing and pumping or the high pressure injection through a nozzle, such as in injection moulding, pressure casting or in the injection of a slurry for the production of thick coatings in thermal spray processes. Furthermore, one interesting application is the study of the time stability of sol-gel solutions, since the on-chip apparatus can

measure in a single test the viscosity at a broad shear rate range at different temperatures.

The objective of this work was to evaluate the performance of microfluidics in the characterisation of ceramic suspensions subjected to extreme shear rates, such as that needed for the direct injection of a liquid feedstock in suspension plasma spraying (SPS). Since the technology and the commercially available equipment are not sufficiently known in the field of ceramics, the paper will present, firstly, the measurement principle of the microfluidic chip technology and the characteristics of the instrument and secondly, the viscosity results measured for different sugar solutions and zirconia based suspensions at ultra-high shear rates of up to 10^5 s^{-1} . The choice of zirconia is due to its great importance in the field of thermal barriers coatings [18–20], produced by thermal spraying techniques using fluid feedstocks that are forced to pass through a small hole of a few micrometres and injected at high pressure and rate [21,22]. The interest of saccharides solutions is due to their capability to promote the development of columnar microstructures and to their porogenic effect [23–26].

2. Microfluidic chip technology

In this work a new commercial rheometer with micrometric capillaries on a chip Fluidicam^{Rheo} (Formulation Toulouse, France) [27] has been used. The Fluidicam^{Rheo} is based on a visual laminar co-flow of a sample and a standard fluid (with a known viscosity value) in a microfluidic chip with a Y-shape. Thanks to the detection system, image acquisition of the interface formed by the co-flow of the sample and the reference fluid are saved to calculate the viscosity values as a function of shear rate in real time. The interaction of the two fluids forms a visible interface, which together with a high-resolution optical image acquisition system allows the behaviour of the two fluids to be compared in real-time and thus to determine their rheological properties (viscosity) as well as the existence of possible turbulence, formation and destruction of bubbles, counterflow effects, etc.

The configuration of the equipment is composed of four parts (Fig. 2): feeding system, microfluidic chip, image processing and disposal system. The feeding system (1) has a two-platform system, which injects simultaneously the sample and the reference liquid contained in two syringes (2), the pressure produces a uniform flow, which is directed through transparent tubes (3) to the microfluidic chip (4). The microfluidic chip is formed by Y-shaped micrometric channels, with a width of 50 or 150 μm (depending on the chip) and a distance of 13 mm for each micrometric channel (reference fluid, sample fluid and the junction of both fluids) inside the chip. These channels are located inside a square glass block. The detection system consists of a microscope with electronic focus (5) located on the microfluidic chip that allows to analyse the interaction and behaviour at the interface between both fluids. Moreover, the equipment has a fast heating system (6) that allows tests to be carried out between 4 and 80 $^{\circ}\text{C}$. Subsequently, the mixture of interacting fluids is discharged into a waste hopper, through a duct (7). The detection system has a software with an integrated microprocessor (8) that manages the acquisition of images, data calculation, data storage, as well as the control of the interface of the fluids, the applied pressure and the temperature.

Fig. 3 illustrates schematically the measuring principle of the instrument. The laminar flow registered by optical imaging allows determining the actual position of the interface, which depends on the viscosity of both the sample and the reference (η_S and η_R , respectively) and the flow rate ratio between them (Q_S/Q_R). The sample viscosity is calculated from the well-known viscosity of the reference liquid and the shear rate is obtained dividing the flow rate by the channel gap [16,17, 27,28]. The shear rate range depends on the fluid viscosity and the channel diameter. It is possible to combine measurements performed with cells with different channel diameter, thus covering a total shear rate range of more than 10^5 s^{-1} .

The general context of this work is to evaluate the capabilities of the

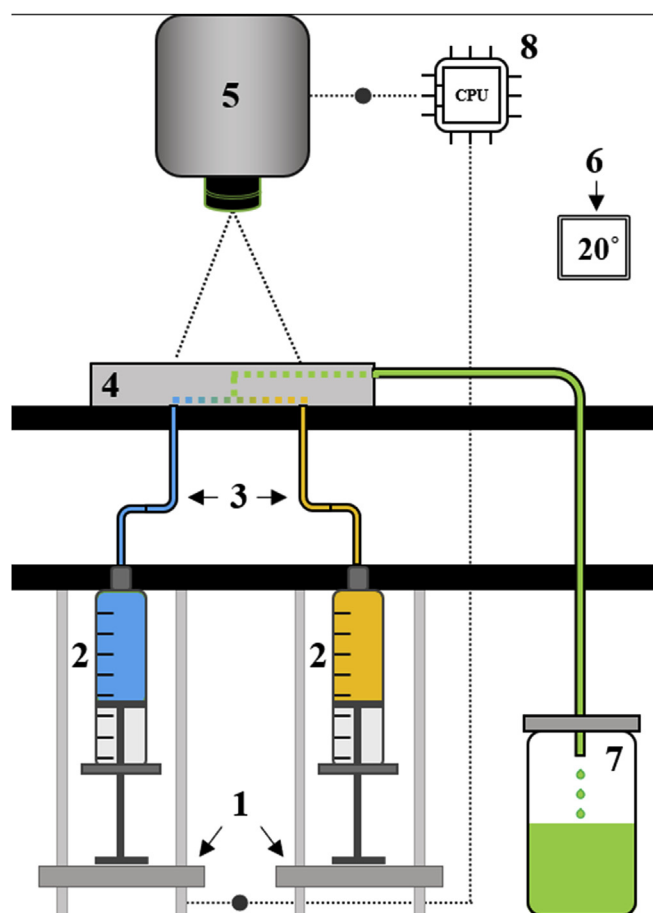


Fig. 2. Diagram and components of the microfluidic chip rheometer “Fluidicam^{Rheo}”.

on-chip technology for the characterisation of concentrated ceramic suspensions and to compare them with the conventional rotational rheometer.

3. Experimental procedure

In this work, different types of fluids such as water (dispersing medium), saccharide solutions (additives for microstructure texturation) and zirconia suspensions (ceramic component to produce SPS coatings) have been used to obtain a wide range of behaviours and to allow the

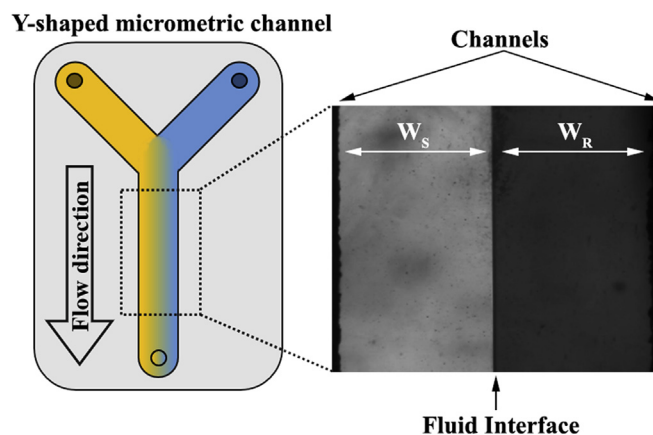


Fig. 3. Detail of the measuring principle of the microfluidic chip in Fluidicam^{Rheo}.

comparison between them. Firstly, deionised water was used for the preparation of all solutions and suspensions, as well as for their characterisation. Secondly, different monosaccharides were used i.e., D-fructose (AppliChem GmbH, Germany), D-ribose (Merck KGaA, Germany) and glucosamine (VWR International, USA), for the preparation of both solutions and suspensions. In addition, ascorbic acid (AppliChem GmbH, Germany) was used for the preparation of solutions and suspensions under the same conditions as the monosaccharides. Finally, suspensions were prepared with 3 mol% yttria-doped zirconia particles (TZ-3YS, Tosoh Co., Japan) at 10 and 20 vol% in solids with 20 wt% saccharides with respect to the powder. The zirconia powder (TZ3YS, with 3 mol% Y_2O_3 , Tosoh, Japan) has an average particle size of $0.4 \mu m$ (D_{50}) with a density and specific surface area of 6050 kg/m^3 and $6.8 \text{ m}^2/\text{g}$, respectively. Moreover, the morphology of the particles is rounded without angular edges, i.e. similar to spheres. More precise information on particle size distribution and particle morphology is detailed in previous work [29]. To facilitate the stabilisation of zirconia suspensions, 0.2 wt% polyacrylic-acid based polyelectrolyte (PAA) was added to water prior to the incorporation of the zirconia particles and 1 min of sonication (UP 400S, Dr. Hielscher GmbH, Germany) was used to disperse them as reported elsewhere [29].

The rheological characterisation of the fluids was performed using two instruments: a microfluidic chip type rheometer (Fluidicam^{Rheo}, Formulacion Toulouse, France) described above, and a rotational rheometer (Haake Mars 60, Thermo, Germany) with a double cone-plate geometry (40 mm diameter and 2° cone angle) with a cap to prevent fluid evaporation.

For the rheological study of all the fluids, two microchips with Y-shaped channels with 50 and 150 μm in diameter were used to study the behaviour of the samples in a wide range of shear rates from (10^2 to $>10^5 \text{ s}^{-1}$). The same "Batch 5" reference fluid from the company Formulacion [27] was also used for all the fluids, whose viscosity under standard conditions is 5 mPa s. In the rotational rheometer, a standard program of controlled shear rate from 0 s^{-1} to 1000 s^{-1} was used with ramps of increasing and decreasing shear rate in 3 min and 1 min dwell. In addition, all experiments were carried out at room temperature 20°C and at 40 , 60 and 80°C to observe the influence of temperature and were repeated successively to obtain consistent values, for both methods.

4. Results and discussion

4.1. Solutions characterisation

Most diluted suspensions and solutions have very low values of viscosity, sometimes in the limits of the measuring range of the rotational rheometers. Therefore, the evaluation and comparison of viscosity results measured with rotational rheometer and microfluidic rheometer is a key

point. In a first step the viscosity of water is necessary as a reference for the solutions of the saccharides. Fig. 4a shows the evolution of viscosity versus temperature of deionised water at a constant shear rate of 1000 s^{-1} measured with the on-chip and the rotational rheometer. For comparison purposes, the values of viscosity reported in literature for water are also included [30]. The clear difference of viscosity between both experimental curves demonstrates the strong influence of the measuring principle. On one hand, the former uses a microfluidic chip, and it is a capillary viscometer and hence it has a high sensitivity and accuracy for Newtonian liquids due to the small flow rate analysed allowing the observation of flow alterations. On the other hand, the rotational rheometer has lower accuracy in the analysis of low-viscosity fluids. However, although a constant decrease in the viscosity of water with temperature can be observed for both curves, the values obtained with microfluidic chip are much closer to the tabulated values than those measured with rotational rheometry.

Fig. 4b shows the variation of water viscosity versus shear rate at room temperature. In this case, the behaviour of deionised water is very different depending on the rheometer. In the curve generated by microfluidic technology the viscosity remains stable with shear rate, that is, it has a perfectly Newtonian behaviour, whereas in the curve obtained with the rotational rheometer there is a slight but constant increase of the viscosity from 200 s^{-1} onwards. This deviation from linearity is likely to occur due to the appearance of slippage effect during the measurement leading to an apparent shear thickening effect. This is only apparent and becomes increasingly important as the viscosity of the sample reduces, as in this case where it is well below the sensitivity range of the apparatus torque. This is an important drawback of the rheometer, and it has been reported elsewhere [2].

Fig. 5 compares the viscosity of different saccharide solutions in water up to a shear rate of 1000 s^{-1} measured in the rotational rheometer. It can be seen that the curves do not present a perfectly Newtonian behaviour, but an apparent shear thickening trend associated to slippage of extremely low viscosity samples as commented before. The curves of the saccharides solutions have the same trend as the water alone curve (W), but the viscosity slightly increases.

Fig. 6 shows the evolution of viscosity of the different solutions for very high shear rates and different temperatures using the microfluidic chip apparatus. Water shows a well-defined Newtonian behaviour over the whole shear interval with a distribution of values that perfectly resembles a straight line that decreases with temperature.

The saccharides solutions (F, R, G and AA) have exactly the same behaviour as water, i.e., a well-defined Newtonian behaviour over the entire shear and temperature range, although the viscosities obtained are higher than that of water. All solutions show a Newtonian trend when using microfluidic chip and an apparent shear thickening for rotational rheometer. This demonstrates the accuracy of the former and the

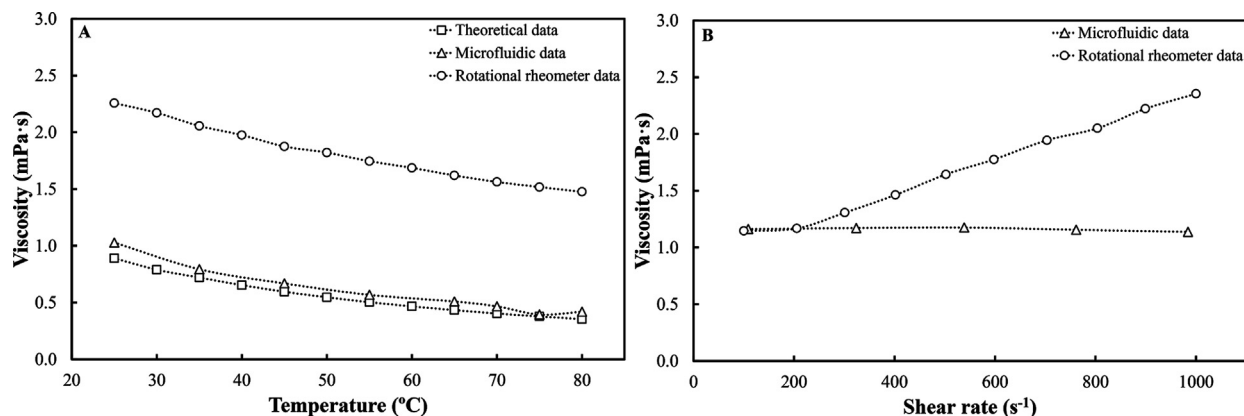


Fig. 4. Variation of viscosity of water with temperature (a) and shear rate (b) measured with rotational rheometer and microfluidic chip technology, compared with tabulated values. The squares, triangles and circles indicate the measurement method employed, theoretical data, microfluidic and rotational rheometer, respectively.

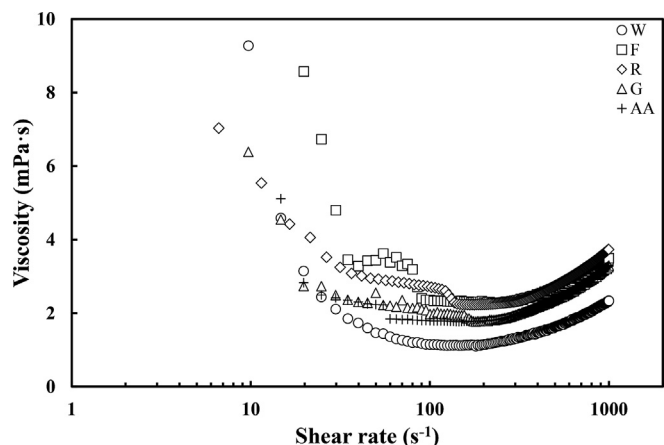


Fig. 5. Comparison of the viscosity curves of different saccharide solutions obtained with a rotational rheometer at room temperature. The letters W, F, R, G and AA indicate the type of solution, only water and aqueous with 20 wt% solutions of fructose, ribose, glucosamine, and ascorbic acid, respectively (represented by circles, squares, diamonds, triangles and sums, respectively).

limitation of the last for very low viscosity samples. It was also observed visually that at temperatures above 60 °C, some small bubbles were detected in the microfluidic chip. However, these were easily eliminated at moderate shear and did not affect the value acquisition. The only exception to linearity is observed in the curve of AA at 20 °C, which shows a shear thinning behaviour with a decrease of viscosity up to 2000 s⁻¹ that maintains constant for higher shear rates. This demonstrates that this solution has some structure at room temperature that breaks on shearing. However, no structure is observed at increasing temperatures, due to its higher solubility [31].

It is worth noting that combining the two Y-shaped cells with diameters of 50 and 150 μm, a maximum shear rate as high as 175 000 s⁻¹ can be reached, which is two orders of magnitude higher than the maximum shear rate attainable by conventional rheometry. This offers interesting engineering solutions for high injection or high shear processes.

4.2. Zirconia-based suspensions

As mentioned in the experimental section, all the suspensions (diluted and concentrated) were prepared using 0.2 wt% PAA and 1 min of ultrasounds to ensure the dispersion of the zirconia particles. Two sets of

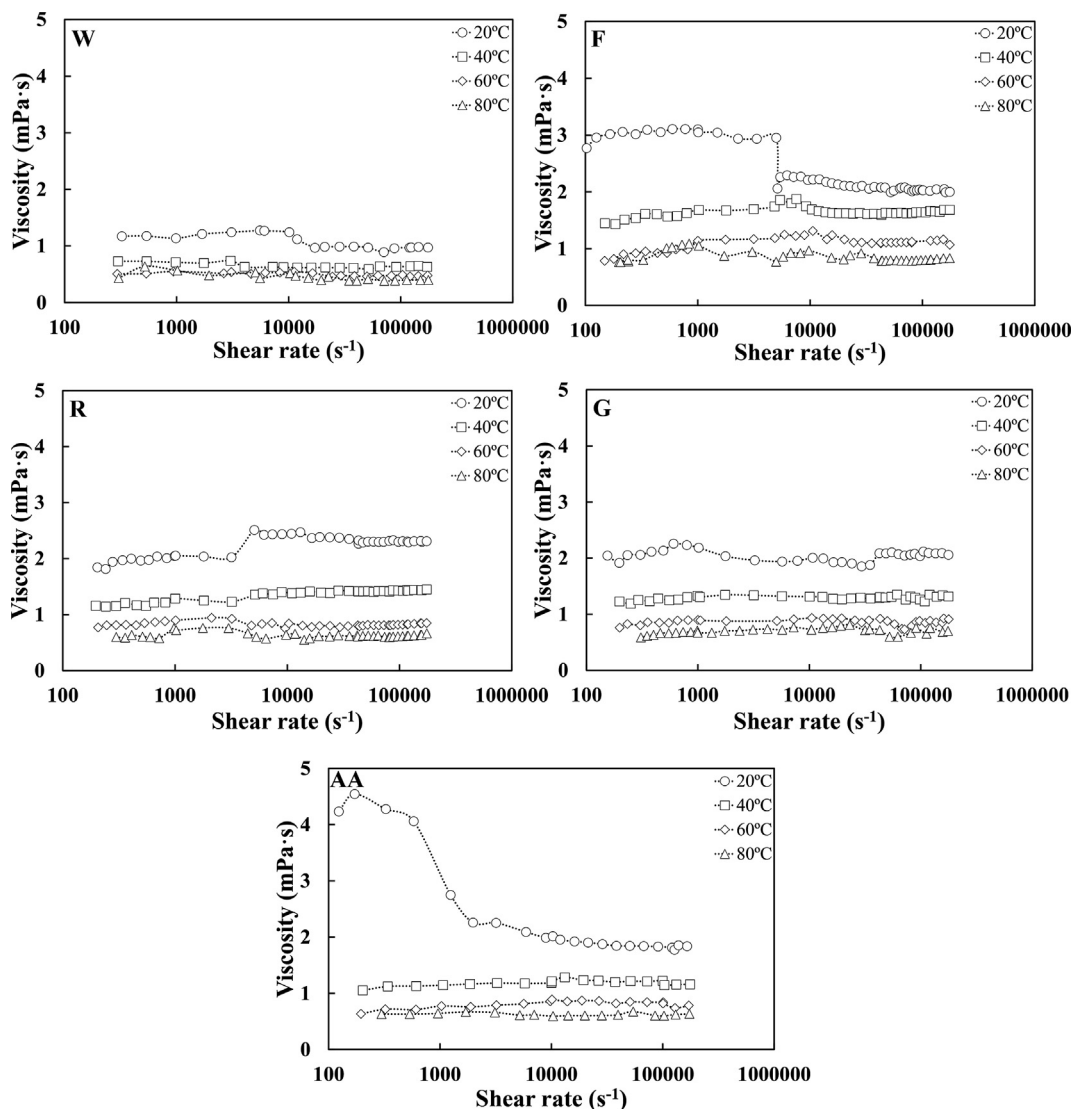


Fig. 6. Viscosity curves of the different solutions of saccharides (20 wt% respect to water) obtained with the microfluidic rheometer for different temperatures. The letters W, F, R, G and AA indicate water and the solutions of fructose, ribose, glucosamine and ascorbic acid, respectively.

suspensions were prepared to solids loadings of 10 vol% (diluted) and 20 vol% (concentrated). As reported elsewhere [25,32], the addition of saccharides produces slight changes in the viscosity of the ceramic suspensions when characterised with a rotational rheometer. The same behaviour is observed for ascorbic acid, which was not reported before.

Fig. 7 shows the evolution of viscosity measured with a rotational rheometer up to a shear rate of 1000 s^{-1} . Suspensions Z, F and R have a similar behaviour to that observed in Fig. 5, i.e. an apparent shear thickening associated to the extremely low viscosity, mainly at high shear rates. Furthermore, this apparent shear thickening is influenced by a wall slippage effect between the rotational rheometer and the suspension [29]. However, the G and AA suspensions have a very different rheological behaviour to that of the Z, F and R suspensions, which is not due to the addition of zirconia particles since viscosity of F and R is the same as for Z, but to a lower affinity of these saccharides that form some structure, which could explain the variation of the behaviour towards shear thinning, as well as a significant increase of the suspensions viscosity. It can also be seen how the addition of saccharides increases the viscosity of the suspension in all cases.

The rheological behaviour of the same suspensions measured with microfluidic chip is presented in Fig. 8, where it can be seen that suspensions with fructose and ribose have a very similar Newtonian behaviour, being the R suspension the one with the lowest viscosity. Meanwhile, G and AA suspensions have a clear shear thinning behaviour and higher viscosity values, very possibly due to a lower affinity in the zirconia surface and to the presence of amine and hydrochloride groups [32]. This is in good agreement with the measurements performed with the rotational rheometer.

Furthermore, it is important to mention that in the G and AA diluted suspensions it was not possible to obtain stable viscosity values at shears higher than $30\,000 \text{ s}^{-1}$ due to the obstruction of the micrometric channels of the chip, however, it seems that at higher shear a plateau of stable viscosity values would be obtained. The microfluidic chip plugging in the G and AA suspensions could indicate a higher presence of agglomerated particles, i.e. these saccharides have a lower affinity and dispersion power of the particles, which would cause an increase of viscosity, as shown in Fig. 8. In the F and R suspensions no plugging was produced during the test, which could indicate a better dispersion of the zirconia particles and would correlate with a lower viscosity.

In Figs. 7 and 8, it can be seen that regardless of the measuring equipment used, the effect of saccharides on zirconia is the same, with fructose and ribose not producing any appreciable change. Furthermore, fructose and ribose produce better dispersions than the other saccharides, which increase the viscosity. However, although the trend of the curves is similar, there is an important change in the magnitude of viscosity values obtained with the two different equipment, mainly for the suspensions with glucosamine and ascorbic acid. The different magnitude has to be influenced by the measuring element used, i.e. in the rheometer the characterisation of the fluid is done macroscopically by the resistance of the fluid on the measuring element and with a quantity of fluid of a few millilitres, which can favour a greater thickening of the fluid, while in the microfluidic chip the characterisation of the flow is done at a microscale range, which results in a smaller quantity of fluid and a greater detail of the behaviour of the fluid due to the small scale. Furthermore, in comparison with the rotational rheometer, where the sample is in a steady state phase until the test starts, in the chip instrument the suspension starts to flow through the ducts and microchannels of the chip before data acquisition. This preshearing can break the possible structure at rest resulting in a lower viscosity.

In order to confirm previous statements and to evaluate the range of application of the microfluidic technology, concentrated suspensions prepared to 20 vol% solids were also analysed. Fig. 9 shows the viscosity curves of concentrated suspensions with and without the different additives. The figure shows a very similar trend to that observed with the diluted suspensions (Fig. 7), with a slight increase of viscosity as a consequence of the higher solids content. As can be seen, F and R

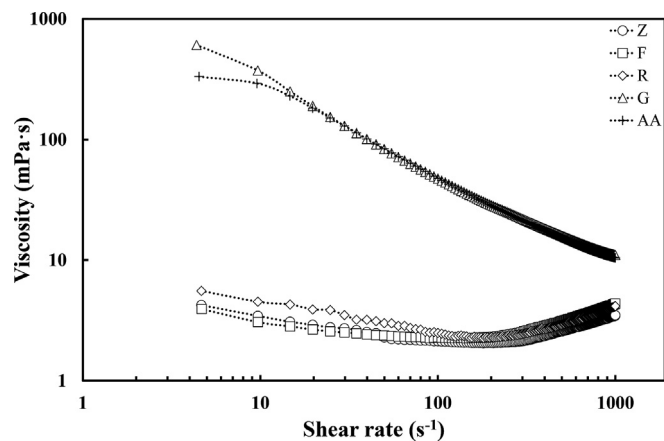


Fig. 7. Viscosity curves of diluted zirconia suspensions prepared at 10 vol% of solids (40 wt%) and 20 wt% of saccharides (respect to powder) measured with rotational rheometer. The zirconia suspension without additives is referred as Z (\circ), while that the letters F, R, G and AA indicate the type of saccharide used: fructose (\square), ribose (\diamond), glucosamine (Δ) and ascorbic acid ($+$), respectively.

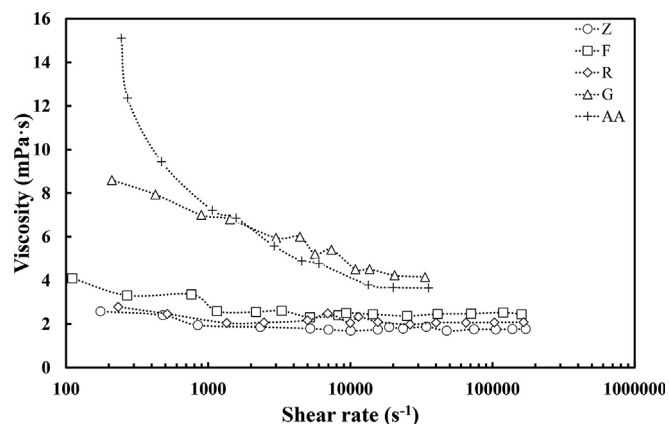


Fig. 8. Viscosity curves of diluted zirconia suspensions prepared at 10 vol% of solids (40 wt%) and 20 wt% of saccharides (respect to powder) and measured with microfluidic chip. The zirconia suspension without additives is referred as Z (\circ), while that the letters F, R, G and AA indicate the type of saccharide used: fructose (\square), ribose (\diamond), glucosamine (Δ) and ascorbic acid ($+$), respectively.

suspensions have a similar trend to zirconia suspension (Z) but with an increase of viscosity, while the addition of glucosamine (G) and ascorbic acid (AA) has produced a notable change in the rheological behaviour of the suspensions that become clearly shear thinning. As usual, at high shear rate the curves Z, F and R seem to have an apparent shear thickening in spite of the expected Newtonian linear trend.

The viscosity curves of the concentrated suspensions determined by microfluidic technology are displayed in Fig. 10. The behaviour of the concentrated suspensions differed quite a bit from that observed with the rheometer (Fig. 9), but in good agreement with the trend observed for the diluted suspensions. In Fig. 10, it can be seen how the addition of saccharides slightly increases the viscosity of the suspensions, as in all previous cases. The curves of the Z, F and R suspensions exhibit a shear thinning behaviour at the lowest shear rate region, and they behave as a Newtonian fluid at high shear rates, above those attainable with the rotational rheometer. The suspensions with glucosamine and ascorbic acid could not be characterised with the chip method because the microchips were rapidly plugged. Chip plugging by G and AA suspensions suggests a lower dispersion of zirconia particles and the appearance of agglomerates that increase the viscosity, as observed in Fig. 9. The clogging of the chip entrance shows the real risk encountered in case of

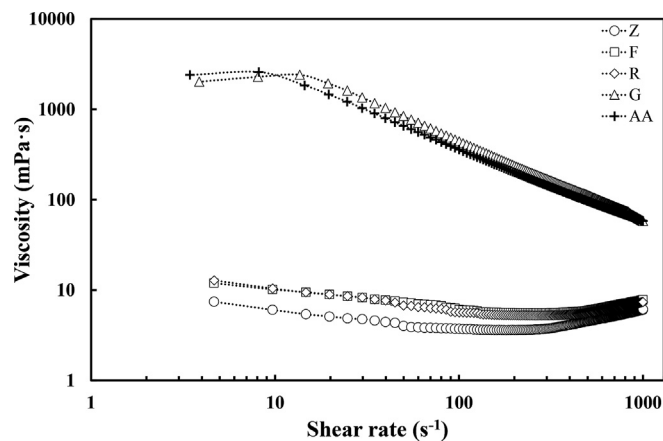


Fig. 9. Viscosity curves of concentrated zirconia suspensions prepared at 20 vol% of solids (60 wt%) and 20 wt% of saccharides (respect to powder) measured with rotational rheometer. The zirconia suspension without additives is referred as Z (\circ), while that the letters F, R, G and AA indicate the type of saccharide used: fructose (\square), ribose (\diamond), glucosamine (Δ) and ascorbic acid ($+$), respectively.

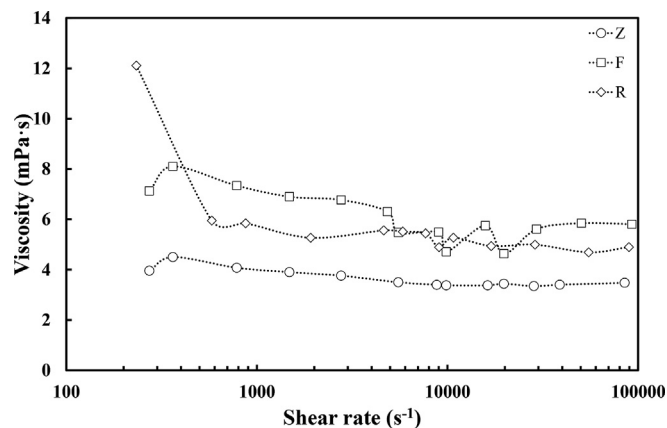


Fig. 10. Viscosity curves of concentrated zirconia suspensions prepared at 20 vol% of solids (60 wt%) and 20 wt% of saccharides (respect to powder) measured with microfluidic chip. The zirconia suspension without additives is referred as Z (\circ), while that the letters F and R indicate the type of saccharide used: fructose (\square) and ribose (\diamond).

using nozzle diameters similar to the chip gap to jet highly concentrated formulations in particles.

Fig. 11 shows the comparison of random samples between both techniques used in the rheological characterisation of suspensions. The concentrated suspensions show a rheological behaviour very similar to that of the diluted suspensions, but with higher viscosities, so it can be said that the increase in solids has mainly influenced viscosity, as expected, but not enough to change the behaviour type. The rheometer allows a fast and accurate characterisation of concentrated suspensions, due to a greater spacing between the rotor and the outer walls of the plate and a more favourable system with very viscous fluids or with the presence of large particles or agglomerates. However, for the microfluidic equipment an increase of viscosity or a greater presence of agglomerates difficult measurements due to the clogging of the micrometric channels of the chip. Conversely, for low viscosities, the rotational rheometer is out of range so that the measurements are often the result of a mathematical algorithm whereas the chip technology gives precise and accurate results. Moreover, this system can offer greater information on the behaviour at high and extremely high shear rate, although it seems that under those shearing conditions there is no place for sedimentation

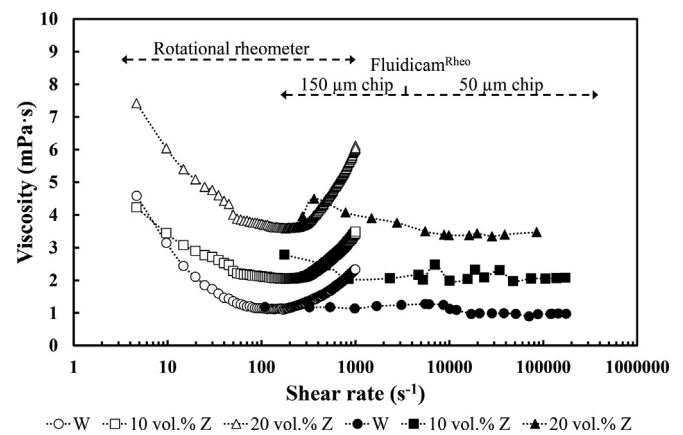


Fig. 11. Comparison of the two rheological measuring systems (rotational rheometer and fluidicam) for three randomly selected samples, such as water, 10 vol% zirconia suspension and 20 vol% zirconia suspension, and which have been referenced as W, 10 vol% Z and 20 vol% Z respectively. The empty symbols indicate the results obtained with the rotational rheometer and the full symbols indicate the results obtained with the microfluidic apparatus.

and structure formation and samples tend to behave as Newtonian fluids. Also, it can be it as a way to verify the adaptability on the formulation to the injection tool. As known the nozzle diameters of the injection are close to the gap of the microfluidic chips, when clogging occurs to the chip, the same issue will be faced during the ink injection. It is worth noting that suspensions with higher solids loadings (30 vol%) were also prepared but they could not be measured in the on-chip rheometer, due to the clogging of the microchannels. In contrast, suspensions with solids loadings as high as 60 vol% can be readily measured in the rotational rheometer.

5. Conclusions

Rheological characterisation of ceramic suspensions is mainly carried out with rotational rheometers, which offer a great variety of analysis for a broad variety of materials in a large spectrum of viscosity ranges. However, they have serious limitations in the measurement at high shear rates and also in the accurate measurement of low viscosity samples, such as solutions (e.g., sol-gel systems) or low solids content suspensions, such as those used in suspension plasma spraying and other ceramic processes. In this work the capabilities and operating principles of a novel type of rheometers, the so-called microfluidic technology, scarcely used in ceramics, is presented. Measurements performed on very low viscosity systems, such as water and saccharides solutions, clearly show the accuracy of this technique for a large shear rate scale in contrast with the lack of reproducibility of rotational rheometers, where slippage has a key role giving curves with an apparent shear thickening that result in large errors in the measured viscosity values. The comparison of viscosities measured with on-chip rheometer and rotational rheometer on zirconia aqueous suspensions with moderate solids loadings (up to 20 vol% solids) reveals that microfluidics is a powerful tool for the characterisation of the flow behaviour at extremely high shear rates, of more than 10^5 s^{-1} . The flow curves obtained with rotational rheometry exhibit in some cases a shear thinning behaviour at low shear rates but always the tendency is to converge to nearly Newtonian flow or an apparent shear thickening at the maximum shear rate affordable with this instrument (about 1000 s^{-1}). In contrast, the on-chip technology has a serious limitation in the measurement of suspensions with higher viscosities and/or solids contents. In practice, zirconia suspensions with 30 vol% solids, which can be accurately measured with the rotational rheometer cannot be measured with the on-chip rheometer due to the clogging of particles in the microchannels curvatures at the entrance of the Y-shaped chip. Although this is a serious limitation in comparison with the robustness of

rotational rheometers, the microfluidic chip rheometers can be adequately used in the characterisation of low-moderate solids contents at extremely high shear rates and at different temperatures in a single test. This is of particular interest for the evaluation of the stability of sol-gel solutions before gel formation as well as suspensions with moderate solids loadings such as those used in suspension plasma spraying.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been supported by Ministerio de Ciencia, Innovación y Universidades (Spain) through the projects RTI2018-099033-B-C31/C33 (MCIU/AEI/FEDER, UE). V. Carnicer thanks the Research Promotion Plan of the University Jaume I for the predoctoral fellowship (ref. PRE-DOC/2017/51). Authors would like to thank Ms. Thanina Amiar (Formulation, France) and IESMAT (Spain) for helpful discussions regarding microfluidic technology.

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