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Influence of shear intensity during slip preparation on rheological characteristics of calcium carbonate suspensions

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Abstract

The shear forces developed during the preparation of ground calcium carbonate (GCC) suspensions by ball milling were varied by using different solids loading in the starting slurries. An ammonium polycarbonate was used as dispersant and two different molecular weight carboxyl methyl celluloses (CMC) were added as binder/thickening agents. The influence of shear intensity on the steady shear viscosity was studied by comparing the measurements made on the starting suspensions, at given solids loading, (non-diluted systems) with those performed on suspensions containing the same solids volume fractions but derived from more concentrated ones (60 vol.%) by adding the required amounts of water (diluted systems). Slip casting experiments were also performed in order to correlate the flow characteristics of the suspensions with their ability towards packing. The results demonstrated that, at a given solids loading, diluted systems are less viscous and pack better than non-diluted ones indicating that high intensity shearing during slip preparation enhances dispersion and deagglomeration of suspended powders, and that the rheological characteristics and packing behaviour can be further controlled by the processing aids.

Keywords: A. Milling; A. Suspensions; A. Slip casting; Calcium carbonate

1. Introduction

Ground calcium carbonate (GCC) is widely used in many different industrial applications such as Portland cement [1], soda-lime glassware, smelting of iron ore in foundries. In a near colloidal size, GCC is widely employed as filler and extender in a variety of applications such as rubbers, plastics, paints, papers, adhesives and other useful products [2–4]. In the domain of ceramic science, GCC has been considered as a flux in earthenware and pottery production [5]. Recent applications as a bioceramic material for implantation purposes have been proposed, due to its biocompatibility and bioresorbability properties [6–9].

Western Europe has an abundant supply of high-purity limestones, which can be processed into high-purity and high-brightness ground calcium carbonate fillers. The principal advantage of using calcium carbonate is its high purity, excellent whiteness and brightness as a pigment, low hardness and reactive properties.

In all the above technological applications, the control of rheology is of paramount importance [9–14], especially when high solids loading suspensions are used [9–11]. The rheological characteristics of aqueous colloidal suspensions depend on several experimental parameters such as particle size and particle size distribution, solids volume fraction, pH of the suspending media, type and amount of added dispersing agents, the number and size of particle agglomerates, and on the energetics of the suspension preparation procedure to destroy the agglomerates [15,16]. It was shown recently that planetary milling was more efficient to promote deagglomeration of silicon nitride-based slurries than ball milling. Stable suspensions containing 60-vol.% solids could be prepared by adding successive incremental amounts of 5-vol.% to a starting suspension containing 45-vol.% [17]. To achieve complete deagglomeration, the time interval mediating two successive increments had to be adequately adjusted, being 6–12 times longer in the case of ball milling. It was also

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observed that the efficiency of the milling process was a complex function of the energetics and solids loading: the efficiency increased with solids loading increasing, reaching maximum values at a given solids volume fraction, which was higher in the case of the higher energy planetary milling, decreasing afterwards due to an excessive increase in viscosity.

On the other hand, a recent experimental intriguing observation revealed that two suspensions containing the same moderate solids volume fraction and prepared under the same conditions exhibited different rheological behaviours depending on the history of the preparation procedure, i.e., if the suspension has been prepared at the required amount of solids, or if it has been diluted from a higher concentrated one. This observation motivated the present study, which aims to evaluate and describe the effects of solids loading and the intensity of the shear forces during milling on rheology and packing ability by slip casting, by using two series of suspensions. In one of these series, suspensions were prepared with the required amounts of solids (GCC), while in the other one, a high concentrated stock suspension was first prepared and then diluted to the same solids volume fractions by adding the required amounts of water. The effects of adding different molecular weight carboxyl methyl cellulose binders on the rheology of the suspensions and particle packing ability on slip casting were also evaluated.

2. Experimental procedure

2.1. Material and slip preparation

A high purity (99-wt.%) natural calcium carbonate grade M1 (Mineraria Sacilese, Italy) was used in the present study. Its fine average particle size ($d_{50} = 1.8$ μm) is suitable for being dispersed in aqueous media and form stable suspensions for colloidal processing [9–11], or other industrial applications such as paper coating [12,13].

The suspensions were prepared by first adding 0.7-wt.% of the dispersing agent, an ammonium polycarbonate (Targon 1128, BK Ladenburg, Germany) to distilled water. It has been shown before that this dispersant is very effective in dispersing calcium carbonate slurries, enabling to obtain very high solids volume [9–11]. Then, while stirring, GCC powder was gradually added in different proportions in order to set the final solid loads at 20, 30, 40, 50 and 60-vol.%. After adding the whole-required amounts of powder, the mixtures were kept under stirring for further 20 min. The suspensions were then transferred to a cylindrical polyethylene container and deagglomeration was performed by ball milling for 24 h using silicon nitride balls as grinding media (diameter = 1.5 cm). Finally, the balls were removed and the suspensions were subjected to a deairing step by rolling them into the milling container, without balls, for 24 h.

From the suspension containing the highest volume fraction of GCC (60-vol.%), portions were taken, accurately weighted, and diluted to 20, 30, 40, and 50-vol.% solids by adding the required amounts of distilled water. These suspensions will be referred to as "diluted" to distinguish them from those that have been prepared from the beginning with the required amounts of GCC. The aim was to study the effect of slip preparation procedure, i.e. the effect of the shear intensity during slip preparation, on the flow properties.

For the diluted and non-diluted suspensions containing 50-vol.% solids, two different molecular weight, M_w, carboxyl methyl cellulose binders (CMC35—$M_w = 35\ 000$ g, CMC250—$M_w = 250\ 000$ g) were added separately, or mixed in a 1:1 ratio in total amounts of 0.1 or 0.2-wt.% relative to the solids to study their effects on rheology of the suspensions and packing ability of the particles on slip casting. These binder/thickening agents were added to the suspensions deagglomerated for 24 h, which were then let to homogenise and deair for another 24 h period, using the same procedure as for the suspensions without CMC.

2.2. Slip characterisation

Rheological measurements were performed at a strictly controlled temperature of 20C, after the slips have been deaired for 24 h, using a rotational stress controlled rheometer (Carri-med 500 CSL, UK). The measuring configuration adopted was a concentric coaxial cylinder and stress sweep and multi-step shear measurements (10 points, max. equilibrium time of 1 min) were performed in the shear rates range from about 0.1 s^{-1} until 550 s^{-1}. Before starting a measurement, preshearing was performed at high shear rate for 1 min followed by a rest of 2 min in order to transmit the same rheological history to the whole suspension being tested.

2.3. Preparation and characterisation of green bodies

The packing ability of the dispersed particles on slip casting is a good index of the dispersion degree achieved in the suspensions, and was evaluated by pouring the required amounts of the slips into 25 mm diameter plastic rings based on an adsorbent plaster plate to obtain cakes with a thickness of about 7 mm. The green bodies were first dried at room temperature for 24 h and then put in an oven at 110 °C for another 24 h period. The density of green bodies was measured according to the Archimedes method by immersion in mercury. The relative density was calculated assuming a theoretical density of calcium carbonate of 2.71 g/cm^3 as measured before [9–11].

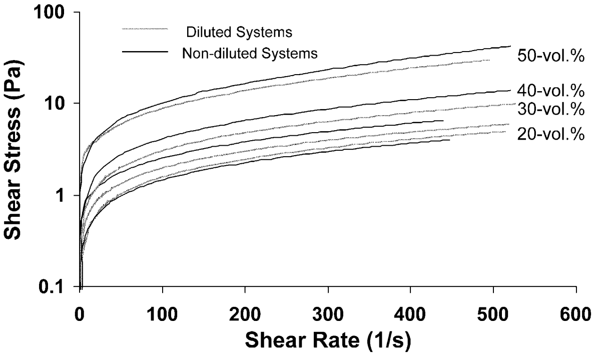

Fig. 1. Effects of solids load and the suspension preparation procedure on the flow curves of $CaCO_3$ suspensions.

3. Results and discussion

3.1. Effects of solid loads and slip preparation procedure on rheology

The flow curves of the diluted and non-diluted suspensions containing different volume fractions of GCC (in the range of 20–50-vol.%) are displayed in Fig. 1. It can be seen that all suspensions exhibit pseudoplastic-type behaviour with shear stress and apparent (or extrapolated) yield stress values increasing as the volume fraction of GCC increases. This is a rather expected evolution. The new and most salient features are, however, the differences between diluted and non-diluted suspensions. In fact, diluted systems always require lower stress values for flowing under shear, compared with the non-diluted ones. In the same way, the steady shear viscosity curves of diluted systems are always below those of the non-diluted ones, as Fig. 2 shows. These results suggest that the best dispersing degree would have been obtained for the suspension containing the highest volume fraction (60-vol.%) of GCC.

It is conceivable that the deagglomeration/milling efficiency would increase with increasing the volume fraction of solids up to an optimal solids load. For lower concentrations than the optimal one, the probability for the agglomerates or even the coarser primary particles to be smashed between two milling elements decreases, while for higher concentrations than the optimal one, the concomitant increase in viscosity will decrease the dispersion efficiency. The optimal level of solids would also depend on other factors such as particle/agglomerate size and particle/agglomerate size distribution, specific surface area of the powder, and on the chemistry of solid/liquid interface [18], dispersion mechanism [19], and so on. It is expected that optimal level of solids would decrease as the average particle size decreases. With the GCC used in the present work having a $d_{50} = 1.8$ μm, it was very hard to incorporate solid loads higher that 60-vol.%. Therefore, this solids volume fraction seems to be the optimal one, which is higher than that previously found (50-vol.%) for silicon nitride-based powder suspensions with $d_{50} \approx 0.4$ μm. This explains why the diluted systems have improved flow properties compared with the non-diluted ones.

3.2. Influence of adding carboxyl methyl cellulose binders on rheology

Rheology modifiers and thickeners are commonly added to calcium carbonate and/or clay suspensions used in the field of paper coating mainly to achieve desirable rheological properties and to improve runnability during the coating process. Carboxyl methyl cellulose (CMC) binders are typical examples of thickeners used in this technological application. However, as reported by Sandås and Salminem [20], most of the works have been carried out using only CMCs of rather low molecular weights. On the other hand, the effects of CMC on aggregation of individual pigment particles are still far from being quite understood [21]. Therefore, this part of the work aims to bring some light about the role played by this type of additives on rheology and particle packing.

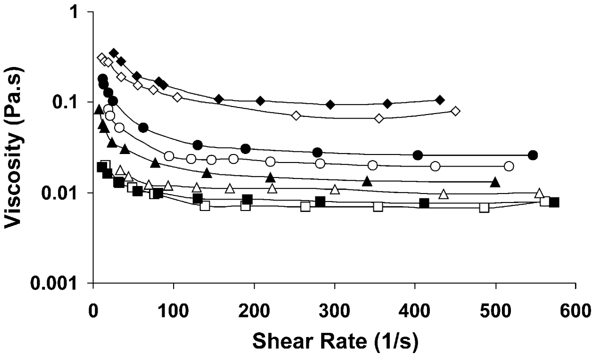

Fig. 2. Effects of solids load and the suspension preparation procedure on the steady shear viscosity curves of $CaCO_3$ suspensions. Full symbols: non-diluted systems; open symbols: diluted systems (■,□ 20% vol.; ▲,△ 30% vol.; ●,○ 40% vol.; ◆,◇ 50% vol.;).

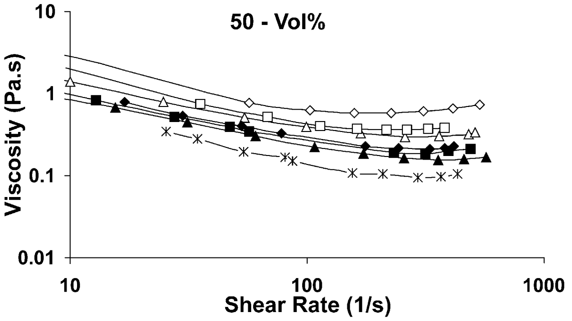

Fig. 3. Influence of the amount and molecular weight of carboxyl methyl celluloses (CMC) on steady shear viscosity curves of non-diluted $CaCO_3$ suspensions containing 50-vol% solids. Full symbols: 0.1 wt.%; open symbols: 0.2 wt.% (⁎ without CMC; ■,□ CMC35; ▲;△ CMC35–250; ◆,◇ CMC250).

Fig. 3 shows the influence of the molecular weight and added amount of CMC on steady shear viscosity curves of non-diluted GCC suspensions containing 50-vol.% solids. It can be seen that all the suspensions present shear thinning along the lower shear rate range, flowed by a slightly thickening trend for higher shear rates. As expected, the suspension without CMC is the most fluid one. Adding increasing amounts of binders causes a gradual thickening effect. However, differences can be distinguished between the effects of the two CMC binders when added individually or mixed in equal weight proportions. The high molecular weight CMC250 has a higher thickening efficiency when compared with the low molecular weight CMC35 or with the mixtures of both. When the mixtures of (CMC35 + CMC250) are used, some synergetic effects on viscosity seemingly occur, depending on the total concentration of binders. At the lower concentration (0.1 wt.%), a stronger dispersing effect is observed, compared with the same amount of CMC35. This might be due to a more favourable polymer configuration at the surface of particles. The low molecular weight CMC35 would be more prone to form an airy-type configuration, that will increase the apparent size of the particles, which, in turn, will enhance the viscosity of a relatively high concentrated suspension (50-vol.% solids), while the CMC250 would tend to form less extended loops and tails to the aqueous solution, but its chains are able to combine more water molecules and produce a stronger thickening effect. Therefore, different effects would be observed when mixtures of both binders are used in different concentrations. At low concentrations, the dispersing effect prevails, while the thickening effect dominates at high concentrations due to either an over deflocculating effect or to an unfavourable polymer configuration of CMC35 combined with the higher capability of CMC250 chains to immobilise water molecules.

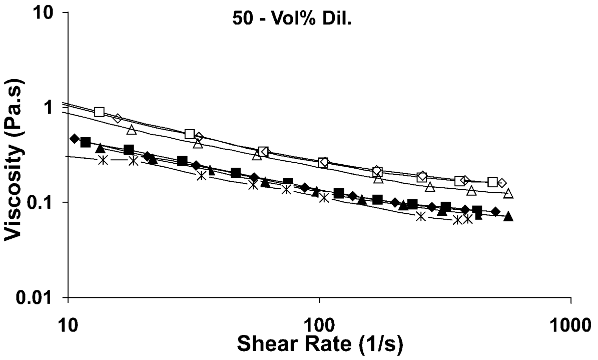

Fig. 4. Influence of the amount and molecular weight of carboxyl methyl celluloses (CMC) on steady shear viscosity curves of diluted $CaCO_3$ suspensions containing 50-vol.% solids. Full symbols: 0.1 wt.%; open symbols: 0.2 wt.% (⁎ without CMC; ■,□ CMC35; ▲,△ CMC35–250; ◆,◇ CMC250;).

Fig. 4 shows the influence of the molecular weight and added amount of CMC on steady shear viscosity curves of diluted GCC suspensions containing 50-vol.% solids. It can be seen that in the presence of the CMC binders, diluted systems are also less viscous compared with the non-diluted ones, in good agreement with the results presented in Figs. 1 and 2. Further, besides the curve of the suspension without binder, the less viscous one, two sets of curves can be clearly distinguished, each one corresponding to each total concentration of CMC, 0.1-wt.% and 0.2-wt.%, respectively. In each set, the curves appear almost superimposed. The above-referred synergetic effects of the mixtures of (CMC35 + CMC250) on dispersing are still apparent, but less pronounced than in non-diluted suspensions. These results show that a better dispersing degree still prevails in diluted systems after the addition of binders, which seem do not promote aggregation of the particles, at least under the concentration range used. This differs from the observations of Engström and Rigdahl [21], for lower solids concentrated (60-wt.%) clay-based systems, in the presence of CMCs of similar molecular weight as CMC35, but with added doses up to 2.5-wt.%. Our results show that when the system is previously well deagglomerated, adding up to 0.2-wt% of CMC binders, does not promote reagglomeration of the primary particles, even if the molecular weight is in the range of a few hundred of thousand grams.

3.3. *Effects of solid loads, slip preparation procedure and adding CMC binders on particle packing*

It is known that the particle packing density of green bodies obtained by slip casting is a good index of the degree of dispersion achieved in the suspension [15–16]. Therefore, slip casting experiments were carried out to evaluate the effects of the intensity of shear during the

Table 1
Effect of solids loading on green density of slip cast bodies of calcium carbonate prepared from non-diluted and diluted suspensions

Systems→	Solids volume (weight) fraction									
	Non-diluted [vol.% (wt.%)]					Diluted [vol.% (wt.%)]				
Green density	20 (40)	30 (54)	40 (64)	50 (73)	60 (80)	20 (40)	30 (54)	40 (64)	50 (73)	60 (80)
ρ (g/cm^3)	1.44	1.50	1.60	1.72	1.85	1.72	1.76	1.79	1.80	1.85
% TD	53%	55%	59%	63%	68%	64%	65%	66%	67%	68%

Table 2
Effect of molecular weight of carboxyl methyl cellulose (CMC) on green density of slip cast bodies of calcium carbonate prepared from non-diluted and diluted suspensions containing 50-vol% solids

Additives→		CMC 35 (wt.%)		CMC 250 (wt.%)		CMC 35 + CMC 250 (wt.%)	
Systems ↓	Green density ↓	0.1	0.2	0.1	0.2	0.1	0.2
Non-diluted	ρ (g/cm^3)	1.77	1.68	1.72	1.69	1.72	1.68
	% TD	65%	62%	63%	62%	63%	62%
Diluted	ρ (g/cm^3)	1.76	1.75	1.75	1.75	1.75	1.74
	% TD	65%	65%	65%	65%	65%	64%

slip preparation on the state of dispersion and deagglomeration of the GCC. Table 1 shows the relative density of the green bodies obtained from the non-diluted and diluted systems, at different solid loads. It can be seen that for both systems, the density of the green bodies increases with solid loads increasing, reaching a maximum value of 68% of the theoretical density at the highest solids volume fraction. At lower solid contents, particles segregation due to either the gravity force (sedimentation) or to the clogging effect of the cake by the finer particles are the main reasons for the observed discrepancies in green density among bodies derived from different solids loaded suspensions [22,23]. However, these differences are much smaller in diluted systems (4% maximum) compared with the non-diluted ones (15% maximum). This clearly illustrates the importance of the shear intensity during the slip preparation on the efficiency of the deagglomeration/milling process. The differences observed in the slip casting results between diluted and non-diluted systems become even more obvious than those observed in the rheological measurements. This proves again that slip casting is a good technique to evaluate the degree of dispersion of suspensions [15,16], even when other technological applications are envisaged.

Table 2 shows the effect of molecular weight of carboxyl methyl celluloses (CMC) on green density of slip cast bodies of calcium carbonate prepared from non-diluted and diluted suspensions containing 50-vol.% solids. It can be seen that the theoretical density of the green bodies derived from non-diluted systems are mostly in the range of 62–63% of the theoretical density, except for 0.1 wt.% CMC35 where a green density of 65% could be achieved, due probably to the prevalence of the dispersing effect exerted by this CMC at the lower concentration. Interestingly, this value is higher than that obtained from the suspension with the same solids volume fraction but without CMC (63%). This difference can be attributed to the thickening effect promoted by the binder, hindering the particle segregation phenomena. In a consistent way, diluted systems also show a better packing ability in the presence of the binders, compared with the non-diluted ones. However, the green density is generally 2% lower compared with that obtained from the diluted suspension with the same volume fraction of solids but without CMC. This can be understood since the apparent volume of particles with adsorbed CMC chains would increase and on deposition, the physical presence of the loops and tails of adsorbed polymeric chains, or even of the non-adsorbed ones, hinders particles from a close mutual approach.

All the above-discussed results show that the intensity of shear during slip preparation has a great influence on the degree of dispersion/deagglomeration, the rheological characteristics of the suspensions and their packing ability on slip casting.

4. Conclusions

The results presented in this work enable us to draw the following conclusions:

1. The intensity of shear during slip preparation, as controlled by the solids volume fraction, has a great influence on the dispersion/deagglomeration efficiency, which in turn, is reflected in the rheological characteristics of the suspensions and their packing ability on slip casting.
2. When a high degree of dispersion is desired to be achieved in low or moderate concentrated suspensions, it is advisable to start from a high concentrated one with an optimised solids load and then add the required amounts of water (or solvent in non-aqueous systems) to set the final concentration.
3. The efficiency of dispersion can be accessed by rheological measurements and complemented by slip casting experiments. The green density seems even more reliable in the evaluation of the dispersing degree.
4. Adding up to 0.2-wt.% of CMC binders with molecular weights up to a few hundred thousand grams did not promote the aggregation of the particles, but hindered the segregation phenomena due to their thickening effects.

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