EVALUATION OF PERFORMANCE OF MODIFIED SODIUM LIGNOSULFONATE ADDITIVES AS REINFORCING AGENTS IN PORCELAIN STONEWARE TILES

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ABSTRACT

A sodium salt of a modified lignosulfonate at different percentages was added to a porcelain stoneware suspension and the effects on the rheological properties of slips and on the mechanical properties of prepared samples were investigated. As the presence of sulfonates groups can change the stability of dispersion, a rheological characterisation was necessary to find the critical concentration to obtain well dispersed suspensions and high MOR values. The suspensions stability was tested by oscillatory measurements and the increase of the elastic modulus in the suspension corresponded to a MOR and to Young's modulus increase as well. Finally, to explain the results obtained by the mechanical characterisation of the prepared samples, a model drawing on the composite materials experience, is suggested.

1. INTRODUCTION

In the manufacturing process of ceramic tiles, the mechanical properties of the unfired bodies, i.e. flexural strength MOR and Young's modulus, *E*, are of considerable importance to limit the scrap percentages in green and dried conditions, actually estimated in about 3%. The scrap percentage after firing, as consequence also of damage induced during the stages of the process before firing, amounts to 2%. In UE, the problem causes a consistent default of production and solid wastes, the recycling of which, represents a source of further costs. The reducing of the scrap may enhance the production/costs ratio, with a decrease both of energy consumption and environmental impact. In order to restrict this problem, in addition to the additives, organic binders, usually are added to the slurry [1]. These products do not allow to modify always the mechanical behaviour of the green bodies, even if they favour, during pressing, the powders compaction. As well known, the percentages have to be limited in the range 0.1-0.3, to avoid in fired products, the black core phenomenon. So, considering also the rheological characteristics of the slurries and the aspects related to their spray drying, the mechanical behaviour of the green products can be only partially enhanced [2].

Some critical steps of the production process in which the probability to introduce damages is high, were identified and some analyses attributed the high percentage of scrap to the low values of flexural strength of the green bodies, considering fundamental this parameter. However, materials characterised by high values of mechanical resistance, sometime evidence a considerable tendency to damage. The knowledge of flexural strength can not to be considered enough to define the mechanical performances of these semi-manufactured products. Another parameter, such as Young's modulus, influences the behaviour of green ceramic bodies. In particular, the stiffness of the material or, in other words, the strain tolerance should be considered as a fundamental parameter to assure the integrity of a green body. Starting from these observations and taking note that, contrary to the advanced ceramics, in the field of traditional ceramics, very few investigation were performed on this topic [3], the work analyses some aspects directly attributable to the role played by the organic binders, in the body mixes [4]. As known, to enhance the mechanical behaviour of green bodies, organic binders of different nature are added to the slurry. These additives favour during pressing, the mutual adhesion of the powder granules and consequently their compaction and confer to green ceramic bodies a higher mechanical resistance in terms of tolerance to the stresses and corresponding strains as consequence of the industrial operations before sintering. Then, the survival probability of green ceramic bodies during all the stages of the process, drying, possible glazing, conveying, storage and firing, depends on their mechanical properties, in particular the tendency to relax the mechanical and thermo-mechanical stresses and arrange the corresponding strains. Regarding to this aspect, it seems to be necessary a suitable arrangement between strength and Young's modulus that, without giving up the mechanical

strength in terms of flexural resistance, allows to reduce the stiffness, enhancing the tolerance to the deformation induced in the material.

2. EXPERIMENTAL

Two different kinds of samples to test were prepared. The standard samples with the industrial formulation were prepared with two different chemical class of dispersant. In order to control the behaviour of additive and dispersant, a modified sodium lignosulfonate (LS) supplied by Borregaard Industries Ltd. is added at different amount in the two standard formulations.

The standards slurries were prepared by using an industrial formulation of porcelain stoneware. The formulations are reported in table 1. In a porcelain jar, 500g of powder were added to 260g of water (34.2wt% on the slurry) in which, previously, 4g of dispersing agent (0.5wt%) were solved. In the case of standard 2 the dispersant was a silico-acrylate, while in the case of standard 3, the dispersant was an acrylate. The raw materials were milled with 500g of porcelain balls for 45min in a rotational mill. The additivated samples are prepared with the same procedure and the reinforcing agent is added with the dispersant.

Sample	Formulation (wt%)						
	Dispersant Silico-acrylate	Dispersant Acrylate	Clay	Waste	Sodium Feldspar	Potassium Feldspar	Kaolin
STD 2	0.5	--	26.6	1.8	19.3	11.6	6.5
STD 3	--	0.5					

Table 1. Formulation of standard preparations.

After milling, a part of slurry was sieved at 63μm, in order to evaluate the milling residual, then density and pH were measured. Rheological characterisation was performed immediately. The density and the sieve residual are measured in order to obtain the same values which are found in industrial process.

3. RHEOLOGICAL MEASUREMENTS

The rheological steady state and oscillatory measurements were carried out at 25°C, using a rheometer, equipped with cone plate as a sensor. Before each measurement, a boost of $20s^{-1}$ for 60s and a steady at $0s^{-1}$ for 60min was performed, to uniform all the samples.

A controlled rate flow curve within the range up to 0-$50s^{-1}$ and from 50 to $0s^{-1}$

was employed to study the shear behaviour and to evaluate the viscosity which depends on the shear conditions. The yield stress, which is a typical parameter of ceramic slip, was measured by employing a controlled stress flow curve in the range up to 10Pa. The yield stress is the region corresponding to the slope change in a plot in which the viscosity is reported in function of the stress. This plot is constructed with the shear rate and the shear stress data in order to show the complete behaviour of the material at low and at high shear rate conditions.

Oscillatory measurements were performed in order to evaluate the LS effects on the stability of suspensions and the time dependency. Before the oscillatory tests, it is important to determine the viscoelastic region in which the moduli are independent of strain at any given frequency. This region was found by performing an oscillatory measurement as a function of the strain amplitude at a fixed frequency, (1Hz).

Measurements were then carried out as a function of frequency (0.1-10Hz) at the fixed amplitude of strain, corresponding to the linear viscoelastic region and the elastic and viscous moduli were evaluated. Oscillatory measurements were performed in the function of time too.

The moduli are defined in equation 1:

$$G' = G^*\cos\delta \quad G'' = G^*\sin\delta \quad y \quad G^* = \tau_0/\gamma_0 = G'+iG''$$

Equation 1.

where G' is the elastic modulus and G'' is the viscous modulus.

The viscoelastic behaviour of suspensions is usually evaluated by the oscillatory tests. These tests consist of applying a small amplitude sinusoidal oscillation to the material and the resulting stress is compared with the strain. From this kind of measurements, it is possible to obtain information about the suspension stability. It is not a destructive test, as the applied strain is very low in order to operate in the viscoelastic region. The elastic and viscous moduli depend on the interactions among the particles. In general, diluted or well dispersed suspensions exhibit a behaviour like the Maxwell model, where loss modulus G'' exceeds the elastic response G'. Ceramic suspensions typically show a behaviour like the Kelvin model or "solid-like", where G' exceeds G'', but the moduli are not constant for well dispersed "solid-like" suspensions in the range of frequency studied.

4. MECHANICAL CHARACTERISATION

The data of elastic modulus, *E*, and modulus of rupture (MOR), *σ*, and the corresponding standard deviations determined in the present investigation,

represent the average of at least 20 valid results obtained, subjecting to 3-point bending test, bars having a rectangular cross section with dimensions approximately 70x10x5mm.

After the rheological characterization, the slurries were dried and then granulated. The powder obtained, were firstly humidified at 5÷6% and then, pressed at ~450MPa, in form of the bars, having the specified dimensions. The bars dried for 12h in oven at 110°C, were cooled till room temperature in a dryer. Finally, they were taken out of the dryer from time to time, and subjected to 3-point bending test. For these tests, the following experimental parameters were chosen:

Span length: L = 60mm and crosshead speed: 0.5mm/min.

The modulus of rupture (MOR), σ, was calculated by the expression 2:

$$\sigma = \frac{3}{2} \cdot \frac{PL}{bh^2}$$

Equation 2.

where P is the breaking load, L is the span length and b and h are the width and thickness of the bar, respectively. The elastic modulus *E* was calculated, measuring, during the bending tests by means an extensometer fixed at the test fixture, the deformation f of the bar, in correspondence of the middle of the surface subjected to maximum tensile stress and applying the following expression [5]:

$$f = \frac{PL^3}{48EJ} \qquad \text{and} \qquad J = \frac{bh^3}{12}$$

Equation 3.

where P and L, are the parameters previously specified, and J is the inertial moment of the bar. Since, only *E* is unknown, the expressions 3 allow to calculate it.

To explain the results of the bending strength and the elastic modulus and better correlate them with the rheological behaviour of the corresponding slurries, the data were separately considered, taking the dispersant used, as reference.

5. RESULTS AND DISCUSSION

The first dispersant considered is the silico-acrylate of sodium (D1). It was employed in the industrial standard slurry selected to test the additives. In table 2, formulation and mechanical properties are reported. In this case we found that the best concentration of LS is 0.5wt% with the 0.5wt% of D1. The slurry exhibited the same shear behaviour of the standard, as reported in figure 1.

Sample	Formulation			Mechanical properties			
	LS (wt%)	Dispersant D1 (wt%)	pH	*E* (GPa)	Stand. dev.	σ (MPa)	Stand. dev.
STD2	-	0.5	8.91	3.31	0.67	3.22	0.83
MIX01D1	0.1	0.5	9.27	3.85	0.64	3.72	0.81
MIX05D1	0.5	0.5	9.16	4.82	0.76	4.84	1.00
MIX1.0D1	1.0	0.5	9.15	6.29	1.15	7.49	1.54

Table 2. Formulation, physical and mechanical properties of samples with D1 dispersant.

In figure 1, the increase in viscosity is evidenced. In these plots the behaviour at very low shear rate can be observed. This curve summarizes the data from the flow curve at shear rate control (high value of shear rate) and at shear stress control (at low shear stress corresponds very low shear rate). So that it is possible to study the material in a steady state conditions (at very low shear rate values). The yield stress region is also shown. We can observe that the most important rheological properties change, happens when LS was added. In particular, with the 1.0wt%, the yield stress begins to appear (about 3Pa, not dramatically), while at lower concentrations, there is no yield stress.

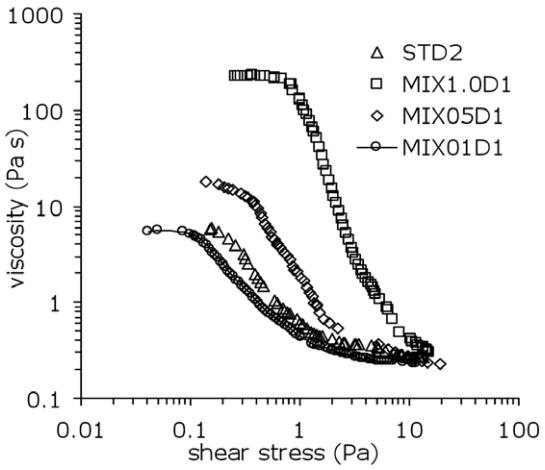

Figure 1. Flow curves of the investigated slips. The behaviour at low shear rate and shear stress is reported (<1Pa). In the case of MIX1.0D1 the region of yield stress can be observed (about 4-5Pa). The MIX1.0D1 curve represents a typical plastic behaviour. At about 120Pas the η_0 is found. This value is the initial viscosity of the slurry before the yield stress. This viscosity is constant as before the yield stress the slurry doesn't flow.

The oscillatory tests confirmed the data found. In figure 2, it is evident as MIX1.0D1 is the less stabilised suspension. The moduli are constant and very high and the solid character of the suspension was increased. G' is higher than G'' and the difference between the two moduli, is higher in comparison with the other samples. The other sample moduli are not constant and very similar to the standard too. A higher percentage of additive increases the solid behaviour of the slurry. The phenomena evidenced by oscillatory measurements can be explained as the network which is created by the additive is increasing as the percentage of

additive becomes higher. The storage modulus increases by increasing the additive concentration.

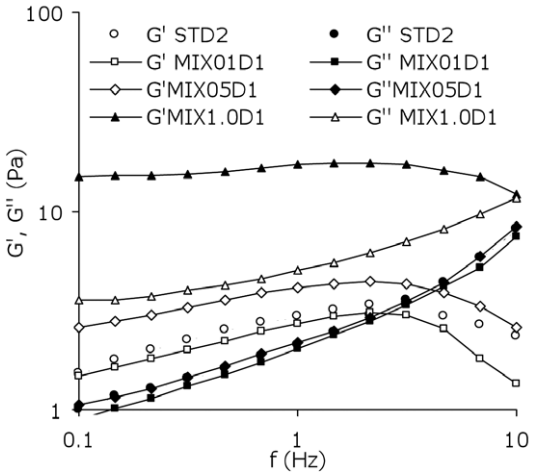

Figure 2. The oscillatory tests for the sample prepared with the dispersant 1 and increasing LS amounts. The solid modulus is particularly influenced by the additive amount as the additive creates a network which is stronger when its concentration increases. At high values of LS a destabilisation of the slurry occurs, as the behaviour becomes gel-like.

Concerning the mechanical properties, sample STD2 presented values of MOR and E and the corresponding standard deviations, usually obtained for dried sample of a porcelain stoneware mix. The differences introduced by the additive at dispersant different content are more interesting. As reported, the presence of the additive caused an increase both of MOR and the elastic modulus in respect to the results of the STD2 sample. In particular the maximum values were reached in correspondence of the same percentage 1.0 of the additives. These values, particularly high, σ = 7.49±1.54MPa and E = 6.29±1.15GPa for the additive LS were confirmed by the rheological results. In general, it seems that 0.5% represents the critical concentration of the additive. Even if the stiffness of the dried samples is considerably high, nevertheless the results of MOR could be very interesting for the industrial point of view, in order to reduce the scrapes during the process. On the other hand, the corresponding slurries demonstrated a remarkable stiffness aspect very important for a correct spray-drying. Since, in these cases, it is fundamental to come to an arrangement, the attention was focused on samples able to offer a good compromise between rheological behaviour and mechanical performance.

The standard STD3 was prepared by replacing dispersant D1 with D2, a sodium polyacrylate. In general, this dispersant is less active than the D1 one and the suspensions are less stable. This can be due to the pH which decreases or to the nature of polymer. In the presence of additive, the mechanical properties increased more than in the case of D1. In this case too, the best concentration to achieve good dispersion conditions was 0.5wt%, but the best mechanical properties were found with 1.0wt%, see table 3.

Sample	Formulation			Mechanical properties			
	LS (wt%)	Dispersant D2 (wt%)	pH	*E* (GPa)	Stand. dev.	*σ* (MPa)	Stand. dev.
STD3	--	0.5	8.10	5.09	0.64	4.75	0.83
MIX01D2	0.1	0.5	8.12	5.26	0.88	5.28	1.28
MIX05D2	0.5	0.5	8.26	6.04	0.81	6.53	1.25
MIX1.0D2	1.0	0.5	8.39	7.43	1.12	8.19	1.32

Table 3. Formulation, physical and mechanical properties of samples with D2 dispersant.

In figure 3, the flow curves at shear rate controlled conditions are reported. The minimum viscosity is reached by MIX01D2, (figure 3). But in despite of the good rheological parameters, the mechanical properties are not so high in comparison with other samples with HS, as the concentration of LS is too low in order to have a significant increase of *E* and *σ*.

More interesting appears the MIX05D2, even though the viscosity increased. As in the previous samples, the 1.0wt% increased the viscosity (figure 3). A yield stress appears at the concentration of 1.0wt% of LS and, as shown in figure 3, the MIX05D2 exhibits a low yield stress also.

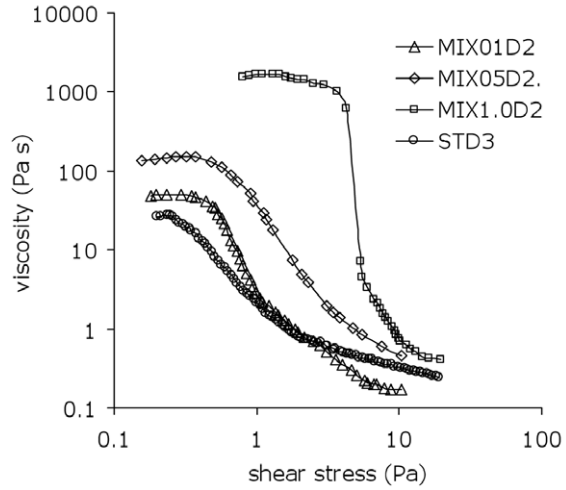

Figure 3. Flow curves of the investigated slips. The deflocculant D2 is less active than D1, so that samples viscosities are higher than in the case of dispersant D1. In the presence of the additive another network is also created and the initial viscosity of MIX1.0D2 (η_0) is higher (about 1000Pas) than in the case of the same sample with the dispersant D1 (about 100Pas).

Figure 4 displays the moduli as a function of the frequency. The highest concentration of LS exhibited a gel-like behaviour. The moduli are constant and higher than the standard ones.

In this case also, the additive tends to build a network between the particles but this network is summed to the structure of the slurry due to the presence of dispersant D2 which is less active than D1 to stabilize the suspension as reported in figure 5.

In this figure the different behaviour of dispersants D1 e D2 at the same additive concentration, is evidenced. It is probably that the presence of acrylate group in dispersant D2 can react with the additive more than the dispersant D1. The particles are more aggregated and the elastic modulus increases even if the concentration of the additive is not changed.

The rheological behaviour is confirmed by the mechanical results.

It has to be noted that, the sample STD3, presented, in dried conditions, high average values of MOR and $_{E}$. In the field of dried ceramic bodies, these results are rather unusual, confirming a good effect induced by the dispersant used. Analysing the data reported, it is also possible to underline the synergic effect due to the presence of the additive. The results are close if not higher than those related to the reference sample STD3. For any sample, MOR and *E* are very high, revealing on the one hand an improved flexural resistance and on the other hand, as in the previous analysis, a trend to increase the stiffness of the dried body. As well known, ceramic materials highlight a poor propensity to the deformation and an increase of MOR usually coincides with an increase of the elastic modulus *E*. This trend is rather clear by the analysis of the results.

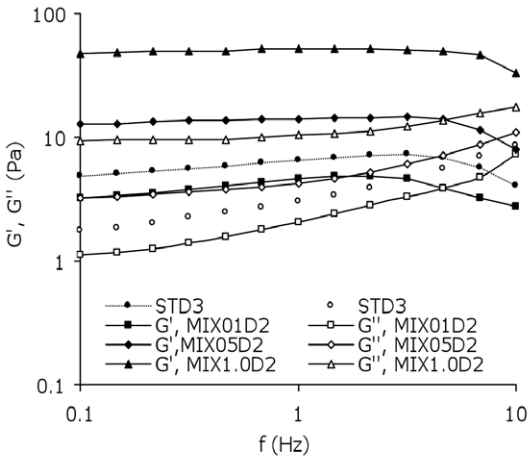

Figure 4. Behaviour of the G' and G'' moduli, as a function of frequency. As in the previous case (MIX1.0D1) the additive increases the elastic modulus. As the dispersion is not well dispersed, the moduli are also constant at 0.5% binder.

In order to explain the mechanism of binder reinforcement, a model is proposed.

The model was considered the basis to investigate the behaviour of a slurry containing an organic binder, since, it is seems reasonable to assume that the binder, during the slurry preparation, is not able to involve all the powder granules.

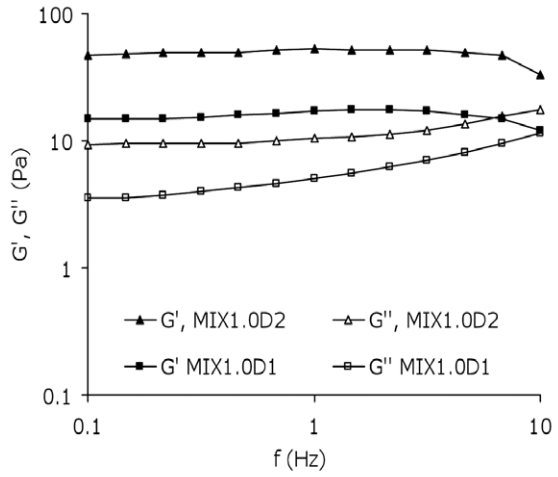

Figure 5. Behaviour of the G′ and G″ moduli, as a function of frequency. The increase in elastic moduli in presence of an acrylate dispersant is more important than in the case of a silicate dispersant.

A schematic of the model is reported in figure 6, where the material is represented as a complex net constituted by the power granules (the spheres), the binder represented with the springs among the particles and the dispersant polymer represented by loops between the particles. In the same figure 6, it is also schematised the bridging effect between the adjacent surfaces. Clearly, as shown in figure 6, the binder chains adhere to the adjacent powder granules and they form a complex structure (net-like).

In figure 6 is also reported the final step of the process i.e. sintering, in which the development of the liquid phase prevails, even if the technological memory in terms of density, remains.

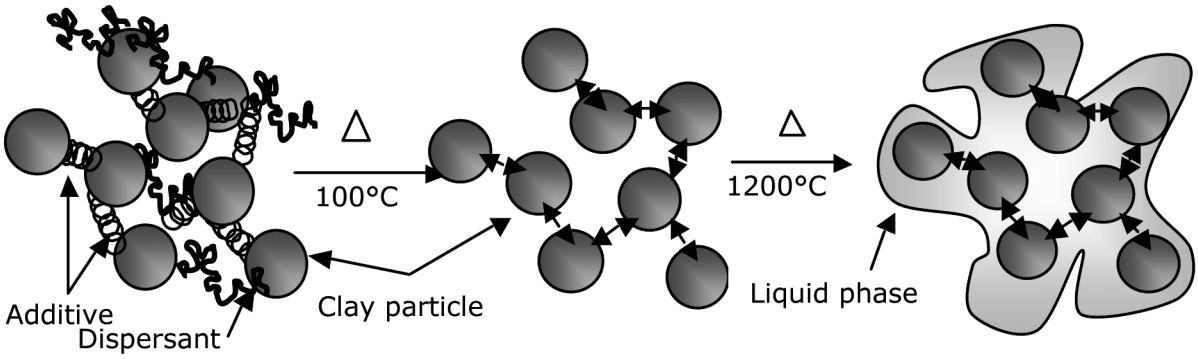

Figure 6. Model of the reinforcement mechanism. We expect the network between the particles to remain even when the organic binder is burned out, so that the sintering process should be easier in the presence of binder and we expect a reduction in shrinkage.

On the basis of these hypotheses, the reinforcing mechanism can be attributed both to the binder (springs) and to the interaction between the binder and the dispersant. So, the reinforcement can be considered the result of a rather complex phenomenon attributable to two different and concomitant mechanisms. We can

assume that the polymer tends to bring the particles nearer to each other and, therefore, that the action of the binder can be increased. It could be reasonable to give a hypothesis of a chemical interaction between the acrylate groups and the -H or -OH group of lignosulfonate, but further investigations are necessary. It is possible that the D2 is more active in the reinforcing agent with the same binder as the acrylate group is freer than in the case of D1, where the presence of silicate group can obstacle the reaction.

We expect that the particles maintain a memory of the network during the drying process and the sintering too, but further investigations are necessary to confirm this hypothesis.

6. CONCLUSIONS

The effects due to the addition to a porcelain stoneware slip of different percentages of a sodium salt of modified lignosulfonate, a silico-acrilate of sodium and a sodium polyacrilate, were investigated. Since, the presence of sulfonates groups can change the stability of dispersion, to find the critical concentration or in other words, well dispersed suspensions and high MOR values, the rheological characteristics of the slips and the mechanical behaviour of the prepared samples, were determined and compared. The suspensions stability was also tested by oscillatory measurements and it was confirmed an agreement between the increase of the elastic modulus in the suspension and MOR and Young's modulus in the samples. In order to explain this behaviour, a model was proposed, considering the dried material, as a composite.

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