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Full Length Research Paper

Investigation of the effects of different deflocculants on the viscosity of slips

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Various parameters like the solid concentration of the slip, chemical and mineralogical composition, particle size and distribution and shape, density of slip, type and content of electrolyte, temperature and pH, affect the rheological parameters of slip. In this study, the effect of various electrolytes on Söğüt and Konya clays have been assessed. Slips were prepared by adding various amounts of the electrolytes sodium carbonate, sodium silicate and sodium triployphosphate and their viscosity were measured. The slip used in this study had solid concentration about 65%. The results of the experiments have shown that the lowest viscosity is attained in clay and slip prepared with sodium triployphosphate.

Key words: Viscosity, slip, rheology, deffuloculant, clay.

INTRODUCTION

Slip casting method has been used in classic or modern ceramic industry for two hundred years. In this method, determining the rheologic features of slips is vital for controlling the process (Özel et al., 2002). Slip casting is known to be a suitable and inexpensive compaction process to produce material with high green densities and micro structural homogeneity, even for complex geometries (Xu et al., 2003). The slip casting process is widely used to consolidate ceramic particles from aqueous suspensions. In this process a porous mould is filled with a slip, consisting of a ceramic powder mixed with water. The capillary action due to the pores in the mould withdraws the liquid medium from the slip. Excellent fluidity, low water content, high stability, and high water permeability are essential properties in ceramic slip casting. The main factor for successful wet processing of slips that contain clay is the interactions between the particles. Chemical additions strongly affect the surface chemistry of the ceramic powder by increasing or decreasing the interaction forces between the particles (Deliormanli and Yayla, 2004).

Many scientists have studied the effects of different chemical materials such as sodium tripolyphosphate, sodium hexameta phosphate, sodium polymethacrylates, ammonium phosphate, sodium citrate, polysulfonate on the dispersion behaviour of clay particles in aqueous systems (Papo et al., 2002; Guler and Balcı, 1998; Corradi et al., 1994). Sodium carbonate and sodium silicate are well known deflocculants used for sanitary ware ceramic slips. Mixtures of these two chemical agents are usually the most satisfactory. Sodium hydroxide is also as active as sodium carbonate and sodium silicate, but it is not used to a great extent because of its corrosiveness (Deliormanli and Yayla, 2004). Rheology is the branch of science concerning the fluidity and deformation properties of materials. Therefore it is indicated as the deformation of body under tension. Especially wet mixing, grinding, slip casting, glazing and decorative processes are related to rheology intensely. Moreover, rheologic behaviours of colloidal suspensions depend on the key factors distinctly mentioned as follows:

1. Viscosity of dispersing media
2. Particle concentration
3. Size and shape of particle
4. Interaction of particle-particle and particle-dispersing media (Özel et al., 2002).

The most common electrolyte used in the sanitary ware slips is sodium silicate (Na_2SiO_3). Some alkaline silicates and carbonates such as calcium silicate ($CaSiO_3$), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3) are also used as electrolytes to provide the fluidity. Anionic poly-electrolytes such as poly-acrylates and poly-phospates are used in some case to regulate slip viscosity. Lowering the viscosity with alkaline–silicate and

Table 1. Chemical composition of Konya and Sogut clays.

	Konya clay	Sogut clay
SiO_2	63.00	60.89
Al_2O_3	17.15	18.74
Na_2O	0.98	1.12
K_2O	1.27	1.33
CaO	5.16	5.10
MgO	0.36	0.36
Fe_2O_3	0.96	0.94
TiO_2	0.85	0.85
LOI	10.27	10.67

alkaline–carbonate is achieved by dispersing the particles forming electrostatic repulsive forces that make the suspensions well dispersed, while the polyelectrolytes create additional steric stabilization (Eygi and Ateşok, 2007).

The physical and chemical properties of raw materials used in ceramic industry might differ due to discrete enrichment processing of these materials. Thus, a complexity about rheologic properties of slips appear. Speed and thickness of casting are controlled by the viscosity of the slurry. Hence, the viscosity of casting slip is kept constant in ceramic production plants (Özel et al., 2002). Elgun (2001) reported that viscosity of casting slip depends on the type of raw materials used, particle size distribution, pH value and temperature of the media, mixing type and speed as well as distillation of water. Dinger (2002) mentioned that a typical ceramic suspension is the fluid mixture of very fine powder with inorganic or organic additive in minor amount. The additives are used to adjust the behaviours of ceramic suspensions (Dinger, 2002). For traditional ceramics, the deflocculants (sodium carbonate, sodium silicate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium polyacrilate, sodium citrate etc.) bonding additives such as microcrystalline cellulose, ammonium alginate, metil cellulose, PVA, PMMA, PEG, parafine, wax etc. and additives for plasticity such as ethylene glycol, PEG, glycerol etc. are all used in order to improve the properties of suspension during the process.

Bondioli et al. (2002) reported that deflocculants increase the fluidity of aqueous ceramic suspensions. Sodium tripolyphosphate (STPP-$Na_5P_3O_{10}$) is used widely due to its efficiency and low price. The type and amount of deflocculant used in clay-water suspensions are important factors for fluidity. Elgun (2001) emphasized that high density is required for less wetting of moulds and high speed depth determining, whereas low density is required for spreading slip homogeneously inside the mould. Also, right tixotrophy has benefits for discharging slip from mould easily. Tixotrophy means that an inactive mass has viscosity value, depending on the time under mechanical forces and when the forces are pulled back viscosity begins to rise up again. So, determinig the rheologic properties of raw materials before casting process is really important (Guler and Balci, 1998).

Clay minerals consist of cations (Si^{2+} , Al^{3+} , Mg^{2+} etc.) and anions (O^{-2} ve OH^-). Also, broken bonds are formed at corners, on edges and surfaces. Surface areas and number of broken bonds increase both during grinding (Elgün, 2001). Some ions in clay structure exchange with the ions in suspension. Furthermore, this action may take place in non-aqueus media. Exchangeable cations of clay minerals are Ca^{2+} , Mg^{2+} , H^+ , K^+ , NH_4^+ and Na^+ though exchangeable anions of clay minerals are SO_4^{2-} , Cl^- and PO_4^{3-} (Çağatay and Erler, 1984). The ions Na^+ ve K^+ are absorbed on the middle slab surfaces formed by the aggregates which are composed of clay particles joining mutual. If clay aggregates disperse in water, alcalies become free and enter the water. Thus, base surfaces of clay particles are negatively charged whereas the sides are negatively or positively charged depending on pH value (Ergün, 2000).

All studies about clay-water suspensions disseminate that OH^- ions in water are adsorbed by free zone of clay particles and particles are negatively charged. Hence, this shows a tendency to pull the cations towards in suspension. So, the number of positively charged ions increases around the particle and in water media. Thus, the balance takes place between charges, neutralization and flocculation come out eventually (Ergün, 2000). Sodium silicate is hydrolyzed to give out free alcali and silisic acid, under the effect of inorganically based deflocculants in clay bodies. Silisic acid is determined as protective colloide and it decreases the flocculation tendency of clays down. Insoluble calcium and magnesium silicates occur (Ergün, 2000; Özel et al., 1999).

EXPERIMENTAL

Raw materials

The scope of this study was to investigate the effect of different electrolytes on fluidity property of the slips, prepared by Sogut and Konya region clays in Turkey, widely utilized in ceramic industry. Ilhisar Yakacik clay and Konya Doganhisar clay were provided by Kutahya Guven Cini and Asanlar Company respectively. As electrolytes, sodium silicate (Aklar Chemistry, d = 1.41 50%) sodium tripolyphospate (Technique Israel) and sodium carbonate (Soda San. AS Kromsan) were used. In Table 1, the chemical composition of clays are presented. For the slips prepared by 65% solid percentage, different pH values between 4.82 and 6.16 were measured by pH meter (Elektromag M-822). It becomes apparent from above that these clays are acidic and have low isoelectric point.

Preparing slip

Dry clay was pestled and sieved under 100 µm. Water was added and mixed by lab scale fan mixer with a speed of 700 rpm afterwards. Thus, the slips having the right ratio of solid/water

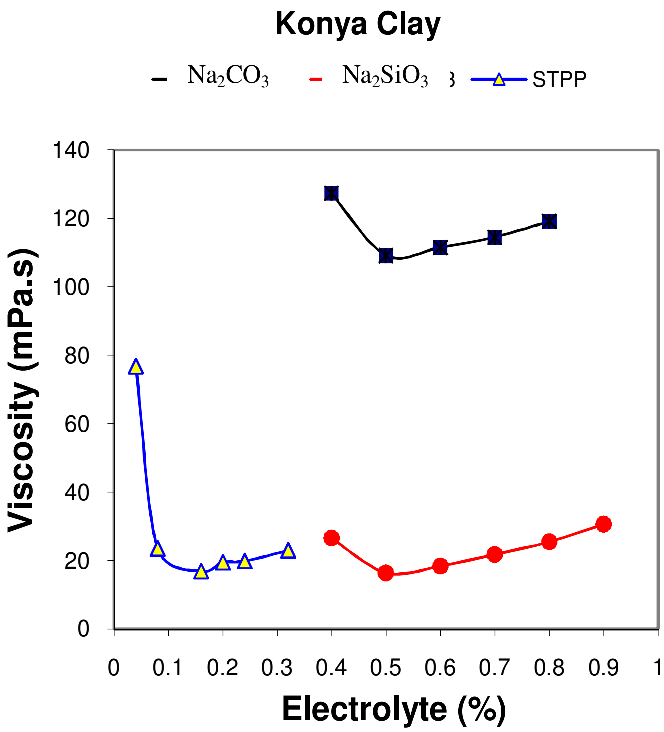

Figure 1. Viscosity values of Konya clay for different electrolytes.

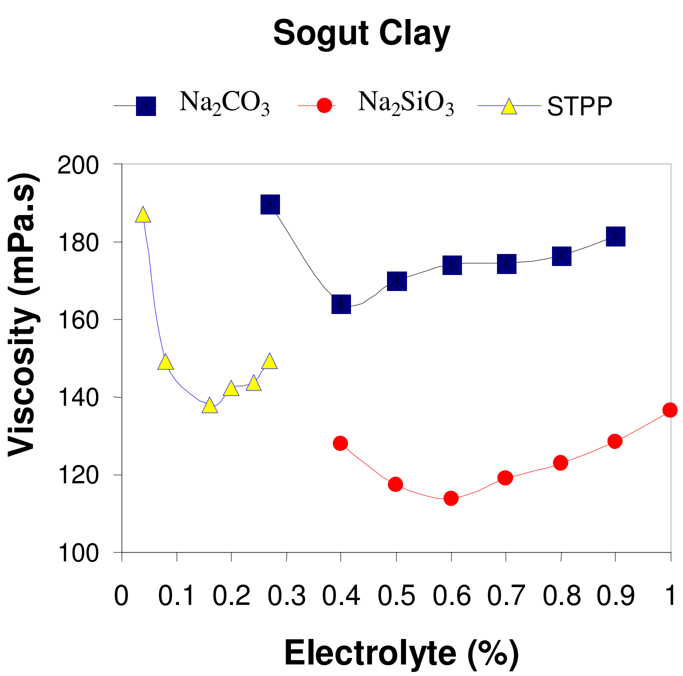

Figure 2. Viscosity values of Sogut clay for different electrolytes.

(65/35) with sufficient fluidity were prepared. After leaving one night, the electrolytes were added in dry form. The viscosity was measured by viscosimeter (Brookfield DV II). On the other hand, liter weight results were determined for Konya and Sogut clays as

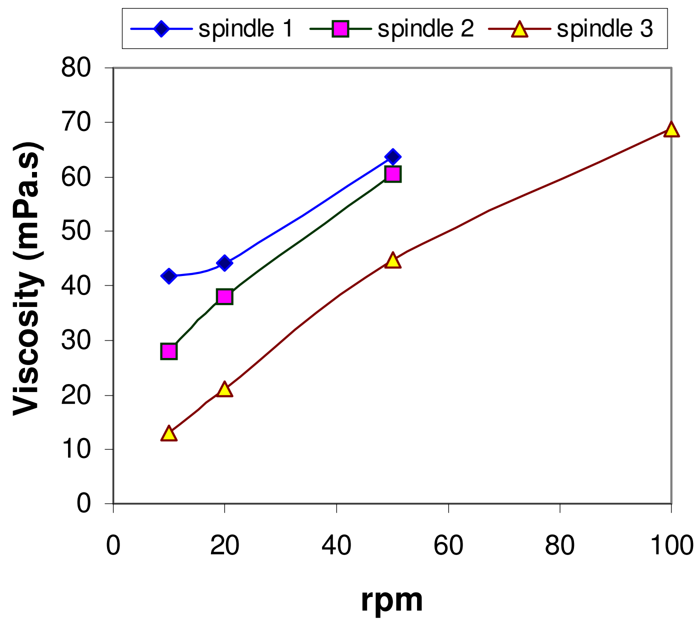

Figure 3. The effect of spindle type and velocity on viscosity.

1727 g/L and 1716 g/L respectively.

RESULTS

The viscosity values of slips were achieved by 2nd type of spindle under 50 rpm depending on the amounts of Na_2SiO_3, Na_2CO_3 and STPP. The results were indicated in Figures 1 and 2. About Konya clay, optimum amounts of electrolytes for Na_2CO_3 , Na_2SiO_3 and STPP were determined as 0.5, 0.5 and 0.16% by weight respectively. About Sogut clay, optimum amounts of electrolytes for Na_2CO_3, Na_2SiO_3 and STPP were determined as 0.4, 0.6 and 0.16% by weight respectively. In his studies about Istanbul and Sogut region clays, Yavuz Ergun emphasized that organic deflocculants (Na-polyacrilate, Na-polycarboxylate) in high solid concentration are more effective for deflocculation of clays than phosphate, phosphate silicate inorganic deflocculants. If sodium silicate and STPP are compared, STPP causes a major decrease in viscosity (Ergün, 2000). Viscosity of Sogut clay including optimum amount of Na_2SiO_3, was measured by using different spindles at different velocities. The results being presented in Figure 3 disseminate the effect of spindle and rotating velocity. Figure 3 indicates that viscosity values increase with increasing velocity and spindle number.

DISCUSSION

Viscosity of slips prepared by clays used in ceramic industry is highly influenced by the amount and type of electrolytes. Nonetheless electrolytes enable preparing slips in high solid ratio but having low viscosity. The optimum amounts of electrolytes for Konya clay were identified as 0.5% for Na_2CO_3, 0.5% for Na_2SiO_3 and 0.16% for STPP whereas the optimum amounts of electrolytes for Sogut clay was identified as 0.4% for Na_2CO_3 , 0.6% for Na_2SiO_3 and 0.16% for STPP. Figures 1 and 2 depicts that as the amount of electrolyte goes up, viscosity values decrease and then start to increase. This is attributed to the excess amount of Na^+ cations in media after minimum viscosity value; because excess amount of Na^+ cations reduces thickness of diffusion layer by slumping on this. Hence, zeta potential value decreases and induces slip flocculation.

When the viscosity of slips prepared by sodium carbonate, sodium silicate and sodium tripolyphosphate are compared, STPP and Na_2SiO_3 are indicated to cause the lowest viscosity, though STPP is in less amount for Konya clay. On the other hand, the lowest viscosity value and least amount are the results of Na_2SiO_3 for Sogut clay. Organic electrolytes are more effective than inorganic ones for deflocculation of clays. Therefore, these electrolytes are preferred for use in minor amounts, also they reveal the possibility to prepare the slips in high solid concentrations. Furthermore, by combination of inorganic and organic electrolytes, optimum amount of electrolyte in maximum solid ratios can be identified. As the solid ratios rise up, less water will evaporate in spray dryers and energy saving will come out consequently.

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