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An investigation on utilization of poly-electrolytes as dispersant for kaolin slurry and its slip casting properties

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Abstract

The ratio of kaolins in the sanitaryware recipes are considered with their certain slip casting properties such as casting concentration (mass% solid), casting rate and unfired strength. Hence, the first condition is to obtain the stability of their high solid contained slurries which are generally regulated with dispersants such as sodium silicate (Na_2SiO_3) and sodium carbonate (Na_2CO_3). In this study, poly-electrolytes were used as a dispersant for kaolin slurry and their effect on certain slip casting properties of kaolin were investigated. Obtained results were compared to tests with sodium silicate. Results indicated that poly-electrolytes were more effective than sodium silicate to decrease the viscosity of kaolin slurries. Casting concentration of the kaolin slurries and strength of unfired kaolin bodies increased noteworthy amount when using poly-electrolytes instead of sodium silicate. However, casting rate of the slurries decreased with using poly-electrolytes instead of sodium silicate.

Keywords: Kaolin; Poly-electrolyte; Sodium silicate; Casting properties; Sanitaryware

1. Introduction

Sanitaryware recipes are ideally based on a formula of 50% plastic clay–kaolin mixtures (clay around 30–35%, kaolin around 15–20%), 25% feldspar and 25% quartz (Fig. 1) [1–3]. The exact proportions of clay and kaolin in the mixture are determined by their certain slip casting properties such as casting concentration (mass% solid), casting rate and unfired strength [2–5]. In general, obtaining of a white and high-quality sanitaryware is in direct proportion to the amount of kaolin in the mixture [4,5]. Its physical properties such as purity, fire-whiteness, particle shape and size distribution, as well as mineralogical and chemical composition meet the desired criteria of producing sanitaryware. However, it has limited uses in the manufacture of this ceramics since they do not fully meet the slip casting requirements due to low plasticity and insufficient unfired strength [3,5]. For these reasons, it is mixed with other clays which may contain impurities such as Fe_2O_3 and TiO_2 that reduce the quality of the ceramic product, but offer higher plasticity and unfired strength. These non-kaolinitic clays also absorb the water into their layer and lead to increase the forming time of ceramic bodies in the moulds. Hence, whiteness, quality and forming time of ceramic bodies directly depend on the amount of kaolin in slips.

As sanitarywares are shaped by slip casting, viscosity of their high solid contained slips must be low enough to be poured into mould easily. If a slip is poured into the mould, water is sucked out by the capillarity leaving a layer of cake on the slip–mould interface [6]. When the cast has attained the necessary thickness, excess slip is poured off and the cast is left to dry until it has shrunk sufficiently to enable removal from the mould. The moulds are made from gypsum for repeated use; therefore water content of slip must be as low as possible in order to minimize their sucking of water to retard their decaying time.

Thus, the economy and success of the casting process depends on rheological behavior of slip and its solid content [7]. While the slips are prepared, solid particles are dispersed in limited amount of water by helping electrolytes to attain required fluidity (generally between 5 and 10 P) and stability. Viscosity of a slip is influenced by every component of the water–solids-dispersant (electrolyte) system. Mineralogical and chemical content of raw materials, their proportion in the recipe, particle shape and size distribution, amount and

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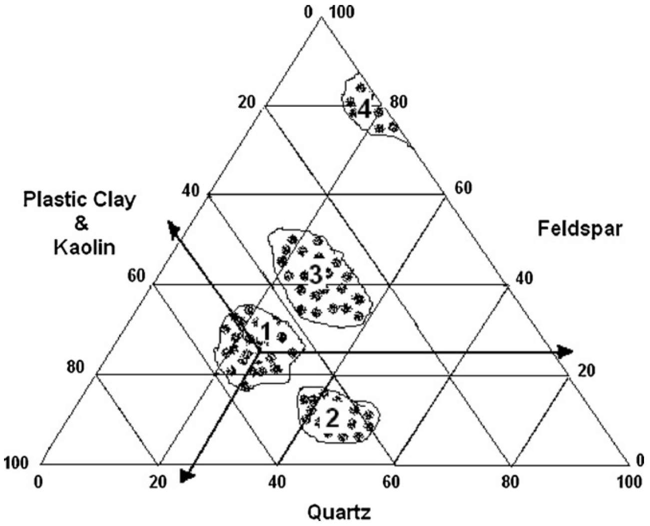

Fig. 1. Triangular diagram created by Hinz: (1) region of sanitaryware and hard porcelain, (2) region of white tile, (3) region of soft porcelain and (4) region of dental ceramics.

quality of water, pH and type of electrolyte determine the final density of a slip and its casting behavior [8,9].

The most common electrolyte used in the sanitaryware slips is sodium silicate (Na_2SiO_3). Some of 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 alkaline–carbonate is achieved by dispersing the particles forming electrostatic repulsive forces that make the suspensions well dispersed, while the poly-electrolytes create additional steric stabilization. Dispersion with sodium silicate occurs through the combination of the silicate ions (${SiO_3}^{2-}$) with the divalent flocking cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) in the system, forming insoluble calcium or magnesium silicates. Sodium ions (Na^+) then replace the divalent cations in the newly opened structure of high-solid content system, creating the electrostatic repulsive forces that cause dispersion [10–11]. However, when poly-valent exchangeable cations are present in the slip, dispersion is not considered complete unless these cations are displaced and retired as insoluble exchange reaction salts. On the other hand, poly-electrolytes provide more homogenous dispersion of the solid particles in the slip than that of sodium silicate [12]. They adsorb on particle surfaces with their anionic or cationic groups, thus particles come closer and move together due to polymeric bridges. Therefore, the adsorbed groups of poly-electrolyte provide a steric barrier between the particles which keep them well dispersed [4,13–15].

In this study, difference of dispersing ability between sodium silicate and poly-electrolytes on kaolin slurry and its certain slip casting properties such as casting concentration, casting rate and unfired strength were investigated. For this reason, three different commercially available anionic poly-electrolytes were used. All studies were conducted by using two different region kaolins.

2. Experimental work

2.1. Materials

Two kaolin samples, Ukrainian kaolin ESK-410 (Eczacıbaşı Esan, TR) and English Kaolin-31 (WBB Minerals Ltd., UK) were used in the experimentally works. The samples were supplied by assistance of Eczacıbaşı Esan Endüstriyel Hammaddeler A.Ş, TR and they were used as received condition. Specific surface area, characteristics sizes, chemical and mineralogical content of the kaolin samples are given in Tables 1–3, respectively.

Three commercially available anionic poly-electrolytes (Aquatreat AR-602-N, Dolapix® G-6, Dolapix® SPC-7) were used as dispersant in order to study their effects on the certain slip casting properties of kaolin samples. Sodium silicate (38 Bé) was also used to compare the results. Aquatreat® AR-602-N (Alco Chem, USA, supplied from Abacı Kimya, TR) is a low-molecular weight sodium poly-acrylate, Dolapix® G-6 and Dolapix® SPC-7 (Zschimmer & Schwarz, supplied from Orteks A.Ş, TR) are poly-carbonic acid's sodium salt and poly-carbonate & silicate compounds, respectively. Molecular weights of Aquatreat AR-602-N and Dolapix® G-6 are 5000 and Dolapix® SPC-7 is 7000 by gel permeation chromatography.

2.2. Methods

The experimental studies were conducted in two-stages. In the first stage, highly concentrated kaolin slurries were prepared with using each of poly-electrolyte and sodium silicate to obtain desired viscosity, 5 P. For this reason, various kaolin slurries in the range of 65–72 mass% solid content were prepared using 0.2 ml of 25% poly-electrolyte stock solutions or 38 Bé sodium silicate additions. In these studies; casting concentration (mass% solid) and optimum poly-electrolyte or sodium silicate requirements of each kaolin sample were

Table 1
Specific surface areas of the kaolin samples and their sizes

Sample code	Source	Specific surface area[a] (m^2/g)	Characteristic sizes (μm)			Oversize (%)	Undersize (%)
			d_{10}	d_{50}	d_{90}	63 μm	2.7 μm
ESK-410	Ukraine	11.29	0.47	1.27	16.51	<1	66.90
Kaolin-31	England	12.29	0.50	1.64	12.42	<1	58.00

[a] By nitrogen adsorption (BET).

Table 2
Chemical analysis of kaolin samples

%	ESK-410	Kaolin-31
SiO_2	47.80	47.90
Al_2O_3	36.30	35.90
TiO_2	0.72	0.08
Fe_2O_3	0.51	0.73
CaO	0.32	0.23
MgO	0.16	0.32
Na_2O	0.20	0.27
K_2O	1.20	2.79
LOI	12.64	11.60

LOI: lost of ignition.

determined to obtain 5 P viscosity. The procedures followed to determine the casting concentration and optimum electrolyte requirement of kaolin slurries are illustrated as a flow chart in Fig. 2. Tap water was used throughout the experiments and the apparent viscosity of the slurries were determined with the Brookfield RTV (Recorder No: FF-RV) dial-reading viscosimeter using spindle No. 3 at 20 rpm.

At the second stage of the studies, certain casting tests were performed depending on the electrolyte type at the casting concentration of kaolin slurries. First of all, density of these slurries was measured with a stainless steel pycnometer. Then, difference of casting rate of the slurries and strength of unfired kaolin bodies were observed. When determining the casting rate of the slurries, cup-shaped (Ø 60 mm × 55 mm) gypsum moulds were used. The slurries were poured quickly into four moulds set in a line and left to rest for 5, 10, 15 and 30 min to take up a thickness. After each period, excess slurries were removed quickly from the moulds. The cup-shaped semi-moist cakes in the moulds were removed after 15 h and dried at 105 °C in a kiln for 12 h in order to measure their thickness. The thickness of the dried samples was measured with a digital calliper at various points and their average was calculated. The thickness values gathered in line with the time were noted as mm^2 on the graph and the slope of this graph ($\tan \alpha$) helped determine the casting rate of the slurries as $mm^2\ min^{-1}$.

On the other hand, the strength data of unfired kaolin bodies were investigated depending on the electrolyte type and amount. Kaolin slurries prepared for this test were poured into the gypsum moulds. The shaped bodies, dimensioned as 200 mm × 20 mm × 15 mm, were removed from moulds after 15 h in a semi-moist state. Afterwards, these bodies were laid to rest in a fan kiln at 60 °C for overnight. The temperature of the kiln was increased to 105 °C for 2 h before breaking the samples. Breaking processes were applied while the samples were not hot enough to hold. The effect of electrolyte type on strength of unfired kaolin bodies was determined for each condition. Minimum three test specimens were prepared for one condition and their average strength values were calculated. The following formula was used when determining the strength of unfired bodies.

$$\text{Unfired strength}\,(\text{kg/cm}^2) = \frac{3f \times l}{2bh^2 \times 10}$$

where f is the breaking load in kg, l the distance from the abutments in cm and b and h are the width and thickness of sample in cm, respectively.

Table 3
Mineralogical content of kaolin samples (rational analysis)

%	ESK-410	Kaolin-31
Kaolin	87.70	83.10
K–Feldspar	7.10	14.20
Na–Feldspar	1.69	2.28
Quartz	1.26	0.09
Others	2.26	0.34

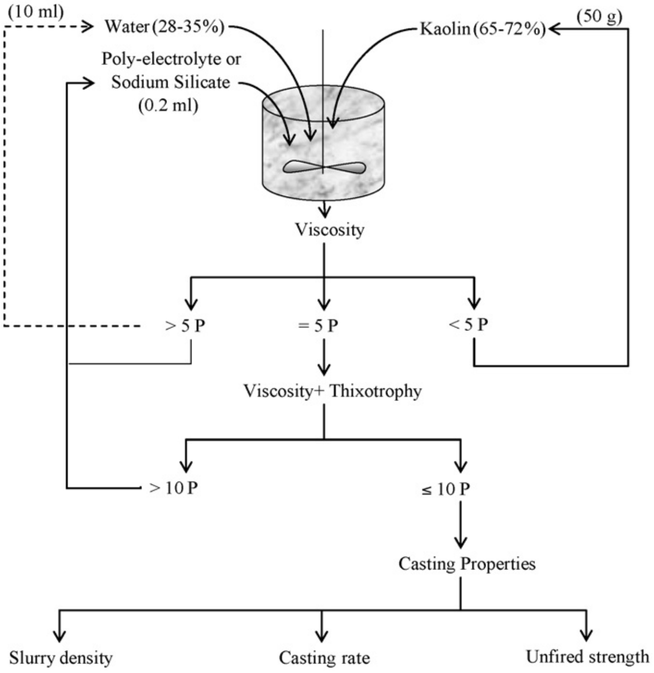

Fig. 2. Schematic diagram for determining the casting concentration and optimum electrolyte requirement of kaolin slurries.

3. Results and discussion

3.1. The effect of the electrolyte type on casting concentration and slurry density of kaolin

The casting concentration (mass solids % at 5 P) of ESK-410 kaolin and Kaolin-31 slurries and their density data obtained from the studies are shown in Figs. 3 and 4 depending on the type of electrolyte. Also, the variations in viscosity recorded at the casting concentrations of both kaolin slurries with each electrolyte are illustrated in Figs. 5 and 6 in line with the amounts of electrolytes used.

As can be seen from Figs. 3 and 4, the higher casting concentration and slip density values were obtained with usage of poly-electrolytes compared to sodium silicate for both kaolin samples. These results explain that poly-electrolytes keep the kaolin particles well dispersed than sodium silicate. As known, clay particles in water generally declivitous to come closer and forming to card house like structure due to van der waals

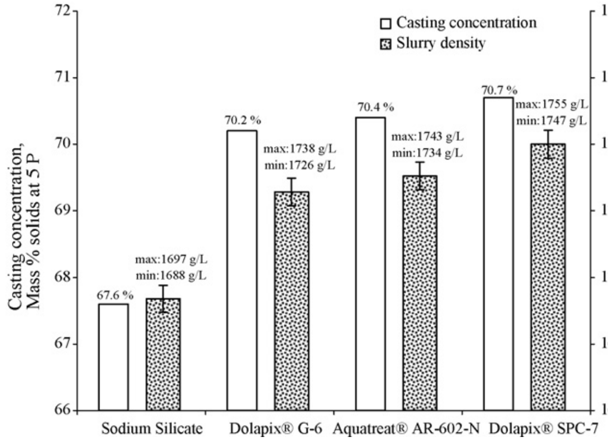

Fig. 3. The casting concentration and density values at 5 P of ESK-410 kaolin slurries depending on the type of electrolyte (max.: maximum and min.: minimum).

attractive forces in the system. Therefore, markedly amount of water is arrested into these structures and rheology of slip is influenced negatively. However, inorganic electrolytes such as sodium silicate and sodium carbonates are employed to obstruct forming of this kind structure and disperse the particles by decreasing the effect of van der waals attractive forces while occurring the electrostatic repulsive forces. But, on the other hand, dispersion with poly-electrolytes occur not only electrostatic repulsive forces but also forming a steric hindrance between the particles due to their polymeric structure. Therefore, kaolin particles are adsorbed by the active anionic groups in chain of poly-electrolytes and this kind of dispersion mechanism provides to loading extra solid into slip without loading extra water due to liberation the water from broken down the card-house like structured particles.

As illustrated in Fig. 5, desired viscosity value (5 P) was reached by addition in the concentration ranges of 0.19–0.25% w/w for both Dolapix® G-6 and Aquatreat AR-602-N, 0.18–0.20% w/w Dolapix® SPC-7 and 0.20–0.27% w/w sodium silicate for ESK-410 kaolin slurries. Similarly, for Kaolin-31 slurries, 5 P viscosity values was reached by addition in the concentration ranges of 0.09–0.11% w/w Dolapix® SPC-7, 0.14–0.20% w/w Dolapix® G-6, 0.12–0.18% w/w Aquatreat AR-602-N and 0.13–0.19% w/w sodium silicate (Fig. 6). It can be clearly understood from this results that slurry of kaolin samples required different amount of electrolyte to reach 5 P viscosity. Also, electrolyte concentration limits to preserve this condition are different.

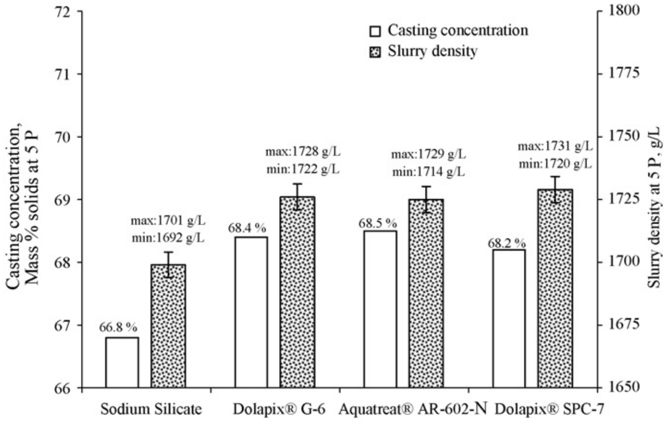

Fig. 4. The casting concentration and density values at 5 P of Kaolin-31 slurries depending on the type of electrolyte (max.: maximum and min.: minimum).

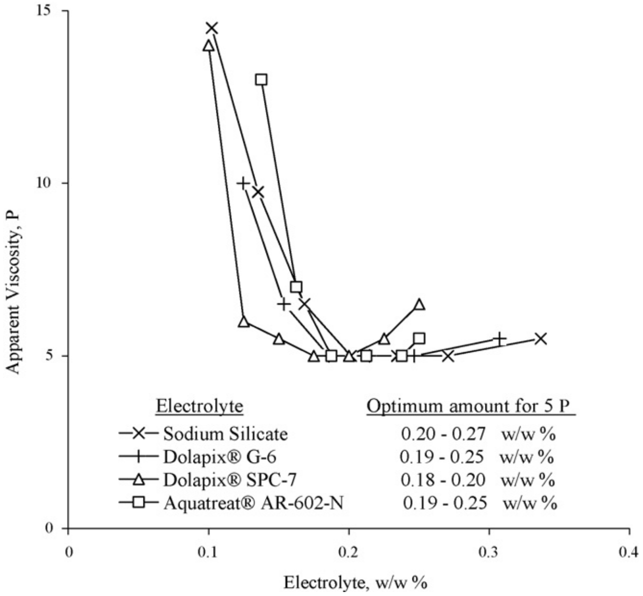

Fig. 5. The apparent viscosity variation results of ESK-410 kaolin slurries at casting concentrations in line with the addition of electrolyte.

3.2. The effect of electrolyte type on the casting rate of kaolin slurries and strength of unfired kaolin bodies

The casting rate results obtained from this study are illustrated in Figs. 7 and 8. As can be seen clearly from those figures, the maximum casting rates for both kaolins are reached

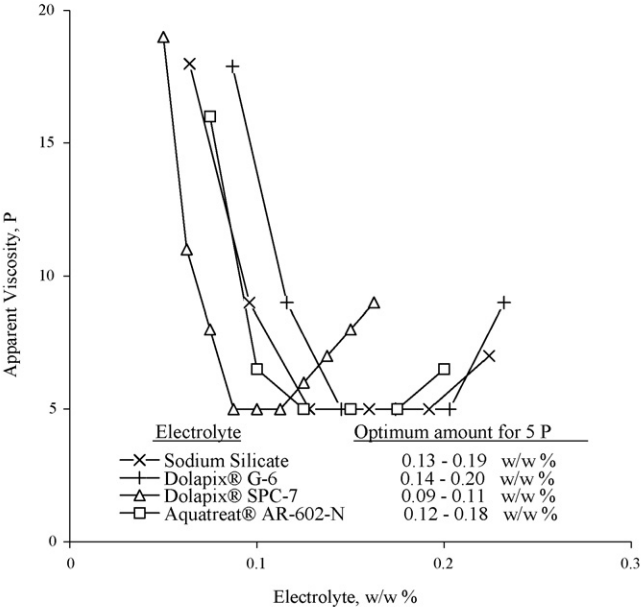

Fig. 6. The apparent viscosity variation results of Kaolin-31 kaolin slurries at casting concentrations in line with the addition of electrolyte.

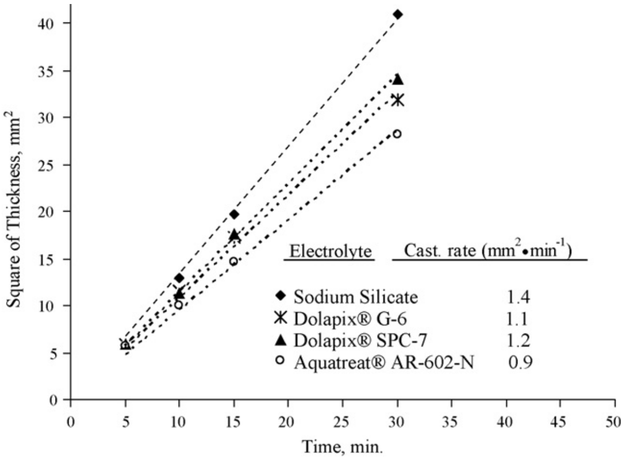

Fig. 7. Square of thickness acquisition values and casting rates of ESK-410 kaolin slurries at casting concentrations in line with time depending on the electrolyte type (apparent viscosity: 5 P).

with the addition of sodium silicate (1.4 mm^2 min^{-1} for ESK-410 kaolin and 1.2 mm^2 min^{-1} for Kaolin-31) while the addition of Aquatreat AR-602-N allow the minimum casting rates (0.9 mm^2 min^{-1} for ESK-410 kaolin and 0.6 mm^2 min^{-1} for Kaolin-31). On the other hand, casting rate of slurries prepared by Dolapix® G-6 and Dolapix® SPC-7 were obtained 1.1–1.2 mm^2 min^{-1} for ESK-410 kaolin and 0.7–0.8 mm^2 min^{-1} for Kaolin-31, respectively.

In order to make the casting process commercially acceptable the rate of casting should be as high as possible. The higher casting rates define that the water in slips is sucked by the moulds in short term periods, which, however, is desired in Sanitaryware industry since this process requires long times. It is generally known that the rate of casting relates to the permeability and porosity of the mould, type of electrolyte used as dispersants and other additions, density of the slip and the mineralogical content of body formulation. Therefore, this study also shows the type of electrolyte/poly-electrolyte effect on the casting rate. The time of getting thickness of the kaolin slurries increases with usage of poly-electrolytes as dispersant.

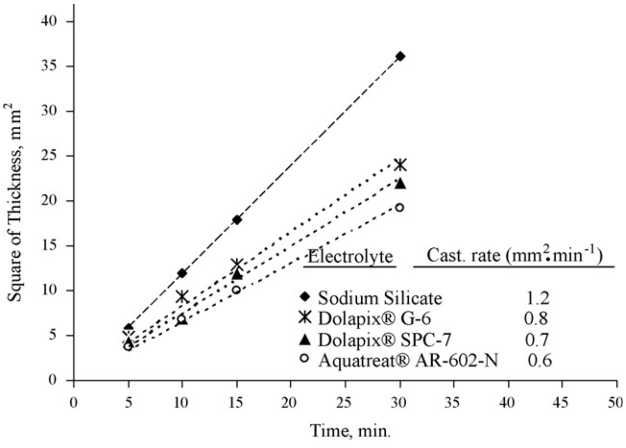

Fig. 8. Square of thickness acquisition values and casting rates of Kaolin-31 slurries at casting concentrations in line with time depending on the electrolyte type (apparent viscosity: 5 P).

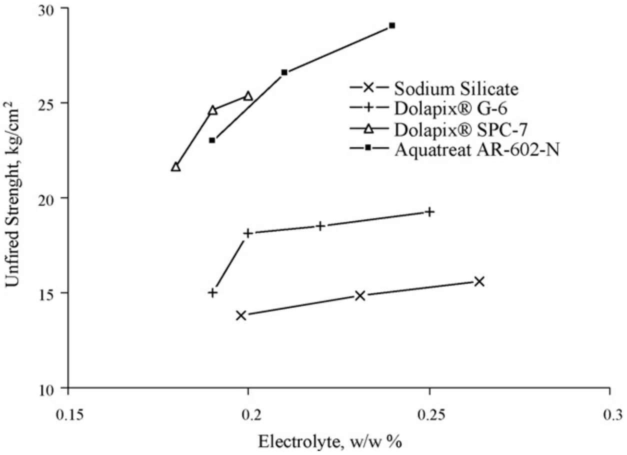

Fig. 9. The strength data obtained on unfired ESK-410 bodies prepared at casting concentrations in line with the addition of electrolyte.

On the other hand, the effect of electrolyte type and concentration on the strength of unfired kaolin bodies are seen in Figs. 9 and 10. As those figures reveal that the strengths of unfired kaolin bodies show differences depending on the utilization of electrolyte and their concentrations. In general, the strength of unfired bodies is promoted increasing the concentration of electrolyte. For both ESK-410 kaolin and Kaolin-31, an increase of sodium silicate concentration from 0.20 to 0.27 w/w and 0.13 to 0.19 w/w results in the enhancement on the unfired strengths from the range of 13 to16 and 22 to 25 kg/cm^2, respectively. Similarly, an increasing the poly-electrolyte concentrations, for example, Aquatreat AR-602-N concentration from 0.19 to 0.24 w/w in ESK-410 kaolin slurry, and 0.12 to 0.18 w/w in Kaolin-31 slurry result in the enhancement on the strength of unfired kaolin bodies from 23 to 29 and 27 to 35 kg/cm^2, respectively. In addition to the effect of concentration on the strength of unfired kaolin bodies, the lowest values are obtained when sodium silicate is used as dispersant which makes clear that poly-electrolytes show superiority to electrolyte of sodium silicate on unfired strengths.

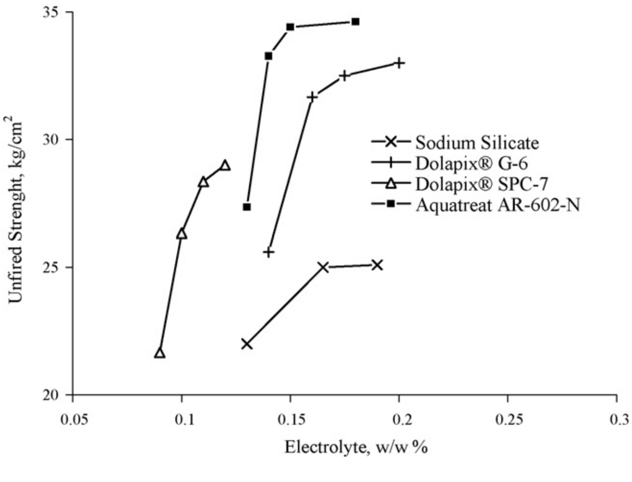

Fig. 10. The strength data obtained on unfired Kaolin-31 bodies prepared at casting concentrations in line with the addition of electrolyte.

Extracting from the catalogues including the wide clay patterns it can be said that in general, casting rate of ceramic clays are two times lower and thus the unfired strengths are quite higher when compared to kaolins. This study also clearly introduces the relationship between casting rates and unfired strengths of kaolin. In another word, in this study, the maximum casting rates accompanying to minimum unfired strengths are reached for the kaolin slips prepared with sodium silicate while Aquatreat AR-602-N poly-electrolyte gives the minimum casting rates accompanying to maximum unfired strengths. Those results also illustrate a clear difference depending on the dispersant structure; the dispersants in polymeric structure give the lower casting rates accompanying to higher unfired strengths.

Therefore, different applications have been addressed and well studied in the past to accelerate the consolidation of the slips [16–18]. In contrast, the higher casting rates results in uneven shrinkage and much deterioration of homogeneous packing of the particles in kaolin slip structure (uniformity of the particles) that causes to reach the further weaker unfired strengths [18].

4. Conclusions

This study introduces the following summarized results:

- The poly-electrolytes are strongly control the rheology and promote the casting concentration of highly kaolin contained slips, since this study shows that poly-electrolytes are superior to sodium silicate. Therefore, the suitable poly-electrolyte and its optimum concentration should be tested depending on the slip mineralogy and type and amount of clays in the recipe prior to determining the casting concentration of the slips.
- In addition, the unfired strengths of the kaolin samples are increased with enhancement on casting concentration by employing poly-electrolytes. This result means that the poly-electrolytes act as a binder and probably dispersing the particles in the formed body. On the other hand, the type and the concentrations of poly-electrolyte have significant effect on the unfired strengths of the slips.
- It was observed that there is a clear relationship between the unfired strengths and the casting rates of the kaolin slips. The kaolin slips with higher casting rates exhibit the lower unfired strengths compared to kaolin slips with lower casting rates. The fast removal of the water in slip structure-this also shows the high porosity of the body-causes the uneven package of the particles which will further result in lower unfired strengths.

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