

Deflocculation and Gelation of Porcelain Ceramics

T. Tonthai

Abstract—Deflocculation and gel characterization were investigated for three different composition of porcelain slips at specific gravity 1.8. The suspensions were dispersed with sodium silicate (Na_2SiO_3) in under-deflocculated slips and fully deflocculated slips. The rheology characterization of slips was conducted by the deflocculation curves and the gel curves. The results showed that decreasing the amount of the ball clay composition in the slips consumed less dosages of the dispersants. The under-deflocculated slips tended to have a gelation rate faster than the fully deflocculated slips.

Keywords—Ceramics, Deflocculation, Gelation, Porcelain

I. INTRODUCTION

PORCELAIN is defined as a ceramic product of dense white, translucent character. The body of standard porcelain consists of a mix of kaolin, feldspar and quartz. The particle size of the raw materials for a porcelain body should essentially be smaller than 40 micrometer. Classification of porcelain is often made according to the firing temperatures. Porcelain fired at temperatures between 1380 and 1460 °C is called hard porcelain, whereas soft porcelain is fired at temperature as low as 1200 °C [1].

As particles dispersed in a liquid, a surface charge can acquire. The main processes are preferential adsorption of ions, dissociation of surface groups, isomorphous substitution and adsorption of polyelectrolytes. Preferential adsorption of ions from solution is the most common process for ceramic particles, whereas isomorphous substitution is commonly found in clays. In the crystal lattice, some of the cations are replaced by other cations of lower valence without altering the crystal structure for example Si^{4+} ions are replaced by Al^{3+} or Mg^{2+} ions. This process leads to a deficit of positive charges, which is balanced by other positive ions (e.g. Na^+ , K^+ or Ca^{2+}) adsorbed on the surface of the clay particles.

In case the zeta potential of clay particles in clay-water suspension is high, there is interaction between them so that flow occurs readily, and the viscosity is low. For low zeta potentials, there is maximum interaction between particles, resulting in a high viscosity. The former system is called to deflocculated slips, the latter flocculated. In general deflocculated clay suspensions are required for casting slips. In order to alter the state of a given system, it is necessary to replace the existing counter-ion produces a high zeta potential, clay suspensions are most frequently deflocculated by the addition of sodium salts e.g. sodium silicate.

Tienchai Tonthai is with Department of Chemical Engineering, Faculty of Engineering, Mahidol University, Nakronpathom, 73170 Thailand (email: egttt@mahidol.ac.th).

Rheology is the study of the relationship between the applied stress and the resultant deformation of matter. The stress may be applied in various methods ; tensile, compression, shear, or any combination of the three. Most ceramic systems, especially those with colloidal size particles, exhibit a rheological behavior between a Newtonian viscous fluid and a Hookean elastic solid, and exhibit both viscous and elastic characteristics. These systems are called viscoelastic. The behavior of such systems depends on the viscosity of the liquid, the amount of the solids, the size distribution of the solids, and interactions between the solid particles and between the solid and the liquid [2].

The viscosity of a fluid is a measure of a materials resistance offered to the relative motion of different parts of the liquid. Viscosity is defined as the ratio of the stress to the corresponding strain rate. The stress is measured in Pa (N/m^2) and strain rate is measured in per second. Viscosity can be given in the units Pa-s. The units mPas (millipascal seconds) are most commonly used, which are equivalent to another commonly used term cps (centipoises) [3]. The flow of bodies is termed ideal or Newtonian if the viscosity is constant, independent of the shear rate applied. The majority of materials and systems included in the processing of ceramic components are non-Newtonian.

II. EXPERIMENTAL PROCEDURE

A. Raw Materials and Slip Formation

The important raw materials for the manufacture of porcelain are clay mineral, quartz and feldspar. At the beginning of the formation, the body consists of a 30% by weight ball clay, 20% kaolin, 30% feldspar and 20% silica. The raw material compositions in the slips were varies by the ratio of ball clay and kaolin. At first the slips were prepared by mixing ball clay with distilled deionized water in a high shear mixer. During mixing deflocculant (sodium silicate, Na_2SiO_3 , N brand) and kaolin were added in the slurry. In convenience to adjust viscosity of slips, dispersant was diluted to 50% weight by distilled deionized water. After having slip viscosity build up 50-100 centipoises, the slips were taken to pass screen 80 mesh. Then the appropriate addition of feldspar and silica were added and blended. The specific gravity at the end was controlled to be 1.80 (%solid 72.22), while maintaining the appropriate ratios between the material additions. Mixing time and intensity were maintained at a near constant level by using a constant speed and blade size mixer. Slips were allowed to age for one day before testing because of the stability of the slurry.

B. Rheological Characterization

The rheological characterization consisted of measuring the deflocculation behaviors of the different slips by the Brookfield viscometer (RVTD model). The slips were mixed for three minutes prior to measurement. Viscosities were measured at a 20 rpm with RV type disc spindles. The viscometer readings were taken 20 seconds after the instrument was started. The desired viscosities were selected for a gel curve measurement. The under-deflocculated slips were the viscosities of approximately 530 centipoises. The fully deflocculated slip was of approximately 180 centipoises as shown in Fig. 1. The Brookfield gel curves were obtained at a low angular speed 0.5 rpm. for 20 minutes.

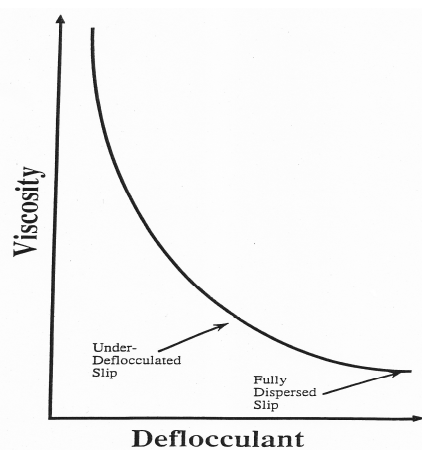


Fig. 1 Schematic representation of dispersion levels tested

III. RESULTS AND DISCUSSIONS

A. Powder Characterization

The particle size distribution of the raw materials was shown in Table I. The ball clay was the finest material used, with the mean particle size of 1.20 micrometer. The kaolin average particle size was 1.80 micrometer. The feldspar and silica were the coarsest materials with mean particle sizes of 10.55 and 16.00 micrometer, respectively.

TABLE I
PARTICLE SIZE DISTRIBUTION OF THE RAW MATERIALS

% PASSING (MICRON)	BALL CLAY	KAOLIN	FELDSPAR	SILICA
10	90	86	42	29
5	82	72	24	16
2	66	51	11	7
1	53	36	5	4
0.5	39	20	2	1

The specific gravity of the materials were 2.55, 2.60, 2.65, and 2.65 for the ball clay, kaolin, feldspar, and silica,

respectively. The chemical composition of the raw materials was shown in Table II.

TABLE II
CHEMICAL COMPOSITION OF THE RAW MATERIALS

%	BALL CLAY	KAOLIN	FELDSPAR	SILICA
SiO ₂	57.1	45.5	68.3	99.6
Al ₂ O ₃	28.3	38.5	18.8	0.1
TiO ₂	1.9	1.7	nil	trace
Fe ₂ O ₃	0.8	0.3	0.1	trace
CaO	0.1	trace	1.5	trace
MgO	0.3	trace	trace	trace
K ₂ O	1.3	0.1	4.1	nil
Na ₂ O	0.2	trace	7.0	nil
C	0.7	nil	nil	nil
LOI	10.0	13.5	0.1	0.2

For clarity, the slips will be classified base on the composition of raw materials (% weight) as shown in Table III.

TABLE III
THE COMPOSITION BY WEIGHT OF THE SLIP

SLIP	A	B	C
Ball Clay	30	25	20
Kaolin	20	25	30
Feldspar	30	30	30
Silica	20	20	20
SO ₄ ²⁻ (ppm)	440	360	320

B. Slip Rheology

The rheological behavior of the three slips were determined the deflocculation curves in Fig. 2. The minimum viscosity was generally associated with the conception of strongly repulsive primary particles in a metastable state. Slip with a lower concentration of dispersant was termed an under-deflocculated slip. The minimum viscosity for slips dispersed with deflocculant was approximately 120 centipoises (cps). The amount of deflocculant required to achieve minimum viscosity of slip A was 8.5×10^{-3} cc./g.clay which more than of slip B (7.5×10^{-3} cc./g.clay) and slip C (6.2×10^{-3} cc./g.clay) as shown in Fig. 2 because slip A had more sulfate ion (SO₄²⁻), calcium ion (Ca²⁺), and magnesium ion (Mg²⁺) from ball clay than in slip B and C. These ions increased the viscosity of the slips. Schelker et al [4] reported that soluble sulfates in the clay influence slip viscosity. Increasing sulfate content augments the amount of deflocculant required for deflocculation. These divalent ion resulted in the compression of the double layer causing reduction of zeta potential.

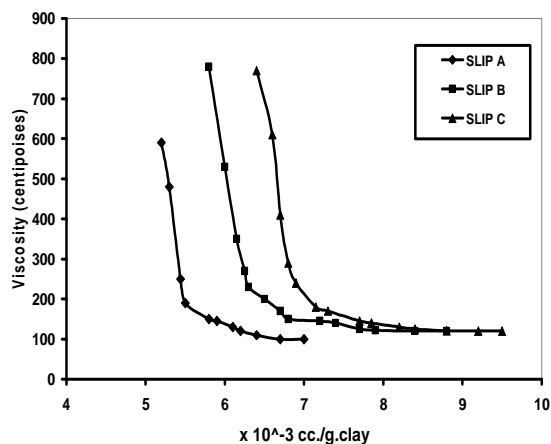


Fig. 2 Deflocculation curves for sodium silicate dispersant

The gel curve of each type of slip was then measured as shown in Fig. 3 and 4. The gel curves showed the time dependent structural characteristics using a Brookfield viscometer. The under-deflocculated and fully deflocculated slips were compared to examine the difference in their structure over time. The under-deflocculated slips had the viscosity of approximately 530 cps. The slips had the viscosity of approximately 120 cps. Assuming the fully deflocculated slips.

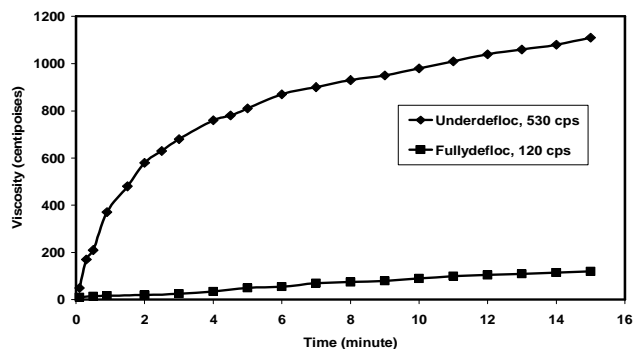


Fig. 3 Gel curves of slip A for sodium silicate dispersant

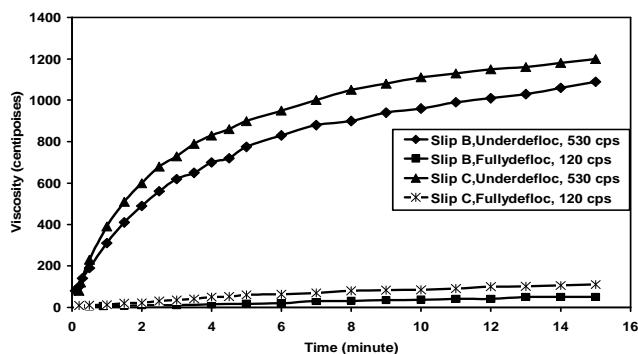


Fig. 4 Gel curves of slip B and C for sodium silicate dispersant

All of different composition slips depicted similar behavior of the gel curves both under-deflocculated and fully deflocculated slips. The gel curves showed that the viscosity for the under-deflocculated slips increased more steeply to a

high viscosity plateau region than of the fully deflocculated slips. The fully deflocculated slips exhibited a slower gelation. The under-deflocculated slips had a faster gelation rate than did the fully deflocculated slips. This behavior was similar to that seen by J.M. Keller [3]. Keller explained this behavior that the under-deflocculated slips had a stronger agglomeration in the form of clusters and chains than did the fully deflocculated slips as shown in Fig. 5. The fully deflocculated slips could form long chain-like network in the absence of shear. Chain structures were thought to be preferred over cluster as a result of a high repulsion potential. The under-deflocculated slips favored the formation of both cluster or particle agglomerates and network structure in the absence of shear. Gelation continued to rise slowly over the time which meant a constant flocbuild up was still occurring in the structure.

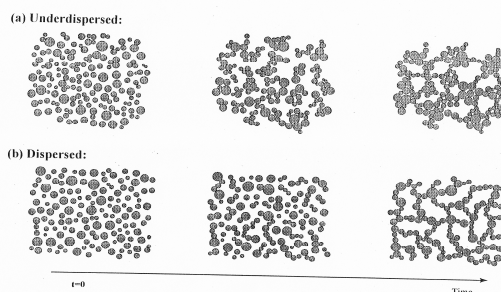


Fig. 5 Postulated structural model of gelation on the colloidal level for (a) underdispersed, and (b) fully dispersed slips [3]

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