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Effect of $BaTiO_3$ Nanopowder Concentration on Rheological Behaviour of Ceramic Inkjet Inks

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Abstract. The relationship between rheological properties of ceramic inkjet inks based on $BaTiO_3$ nanopowder and solid phase concentration has been investigated. In the ink volume takes place the formation periodic colloidal structures (PCS). The determining factor of structure formation is powder-dispersant ratio. Structural constitution of in the system with the low pigment concentration represented as PCS_2, that contains solid particles in deflocculated that stabilized by the presence of adsorption-solvate layers. Dilatant structure formation for such inks explained by constrained conditions of the interaction. Samples with high $BaTiO_3$ concentration have been classified as PKS_1. Dilatant properties of the PKS_1 resulted in particles rearrangement under the influence of the flow. In the region of some values powder-dispersant ratio take place conversation PKS_2 to PKS_1 and ink structure transformation from monodisperse to aggregate state.

1. Introduction

Current trend to decreasing portable devices leads to significant reduce the overall size of capacitors with a simultaneous increase in the specific capacity. It is known that the specific capacitance of a ceramic capacitor can be increased by thinning the dielectric layers and increasing of electrodes number. Thickness dielectric layers can be decreased to 100-200 nm by using of nanosize particles and new techniques of layer manufacturing. Inkjet printing is one of the most promising techniques for this application. The main advantages of inkjet printing, compared to other deposition methods one-step processing, low-cost and compact equipment, and applicability to various substrates [1].

Rheology of the ink is of great importance for its performance during jetting and spreading on the substrate. During the printing process high shear rates are exerted on the ink, so the shear dependent viscosity of an ink may strongly influence the inkjet pumping mechanism. In accordance with [1-3] the rheology of suspensions in general shows a shear dependency that depends on the volume fraction of solids, the particles size and shape, and the interparticle forces.

In accordance with our previous research [4-5], the most significant stabilization of the 5 wt. % pigment was observed for samples formulated n-butyl alcohol doped with 20 wt. % of dispersant. Rheological behavior has been changed on adding different amounts of dispersant. But the most important factor which effects on rheology directly has been solid fraction content. Thus, work is aimed at dependence of rheological behavior of ceramic inkjet inks based on $BaTiO_3$ nanopowder from powder content.

2. Materials and Methods

Inks have been formulated in the medium of n-butanol (Lab-Scan). BaTiO3 nanopowder with a mean particle size of 20 nm has been used as green material for the preparation of ceramic inks by the mechanical mixing method. Saturated aliphatic polyatomic alcohol with a symmetrical arrangement of hydroxyl groups has been used as a dispersant.

The ink for this application has been produced by two steps. At first one, the barium titanate nanopowder has been milled for one hour with liquid dispersant in planetary-type mill to obtain adsorbed layer on the surface of particles and then solution of the rest components has been added and milled for an hour again. Agate balls of 5 mm in diameter were used to pulverizing the soft agglomerated particles into primary particles. Formulated inks have been characterized by rheological viscosity analysis in shear stress range 1 – 1500 Pa at 25°C with using of rotary viscometer Rheotest RN 4.1 (Rheotest Messgerate Medingen GmbH) with cylinder measuring system.

3. Results and Discussion

The flow curves in the Fig. 1 – 4, Table 1 shows that all ceramic inks based on $BaTiO_3$ nanopowder demonstrate dilatant flow with an established rate of dilatant deformation. It means that all systems flow as completely deflocculated dispersions after attaining the established equilibrium level of strain rate [6]. In general, according to the changing of viscosity and rheological characteristics all formulated inks can be groped into newtonian-dilatancy and dilatant-thixotropic systems.

Table 1. Composition and rheological properties of investigated ceramic inks

Ink	Composition, wt. %			Viscosity, mPa·s (22 Pa)	Dilatancy degree, a.u.	Boundary shear stress, Pa	Tixotropy degree, mPa/s	Equilibrium shear rate, s^{-1}
	$BaTiO_3$	dispersant	n-butanol					
Ink 1	0	20.0	80.0	10.95	2.88	16.08	–	3205
Ink 2	0.5	19.9	79.6	9.49	4.74	8.84	–	3210
Ink 3	1	19.8	79.2	9.56	5.10	6.21	–	3235
Ink 4	2	19.6	78.4	9.79	5.68	2.45	–	3240
Ink 5	3	19.4	77.6	10.06	6.89	0.88	-76.93*	3080
Ink 6	4	19.2	76.8	10.72	13.68	1.84	1169.15	3130
Ink 7	5	19.0	76.0	11.52	15.15	3.19	1487.03	3140
Ink 8	10	18.0	72.0	18.22	18.56	4.60	2477.96	3150

*Note: The value modulo corresponds to the rheopexy degree

In general, such rheological behavior can be explained by physicochemical and molecular-kinetic interactions between components of the system. The determining factor of structure formation is powder-dispersant ratio which determines the composition and shape of the structural elements and their interaction conditions. Fig. 5 and Fig. 6 shows that in the absence of the solid phase (Ink_1), the structural elements formation occurs due to the fluctuation dipole interaction through the hydrogen bonds formation between hydroxyl groups of the dispersant and n-butanol. While the shear stress is low, hydrogen bonds have time to regroup, which leads to the longest length of newtonian initial region. At higher shear rates fluctuation contacts are destroyed, resulting in compressed deformation conditions [7].

Adding to system the small amount of powder (Ink_2), accompanied by a reducing amount of the free kinetic dispersant through the formation of adsorbed solvate shells on the highly developed surface of barium titanate nanopowder. In connection with the decreasing of kinetically free hydroxyl groups leveling couple fluctuation and the consequent degeneration of the ability of the structure to the applied shear stress relaxation is take place. This causes a sharp decreasing of the viscosity value of the Ink_1 - Ink_2, and duration initial Newtonian segment.

Further increasing $BaTiO_3$ concentration Ink_2 - Ink_5 resulted in the growth of specific effective volume of the dispersed phase and the expansion of adsorption layers. In turn, vacancy volume reducing results in more confined structure deformation conditions that makes difficult relaxation of the applied stress. This causes displacement of the beginning dilatant area flow curves in the region of smaller shear rates and higher pressures and also the gradual reduction newtonian flow range. In addition, there is a gradual increase in viscosity and degree of dilatancy values. Ink_5 components ratio corresponds to the formation of highly filled system.

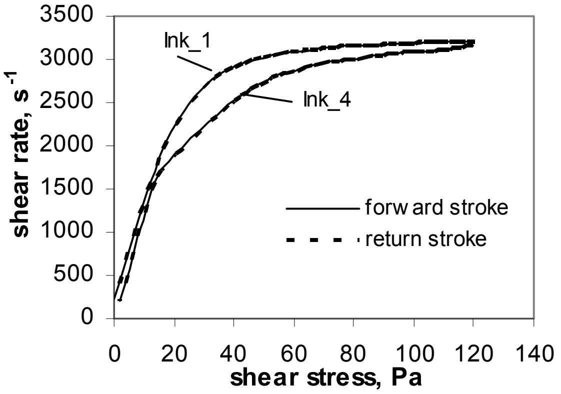

Figure 1. Flow curves of Ink_1 and Ink_4

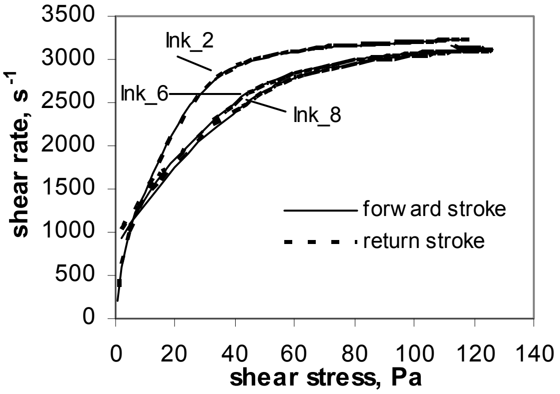

Figure 2. Flow curves of Ink_2, Ink_6 and Ink_8

Probably, Ink_5 structure is characterized by thinning the ink adsorption solvate shells due to the increasing specific surface area particles of the barium titanate volume fraction, resulting in a more compressed condition interaction. This assumption is confirmed by complete degradation newtonian plot on the corresponded flow curve and appearance the rheopectic-thixotropic hysteresis loop (fig.4).

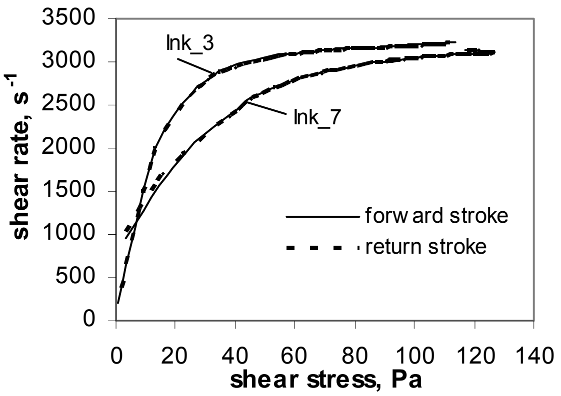

Figure 3. Flow curves of Ink_3 and Ink_7

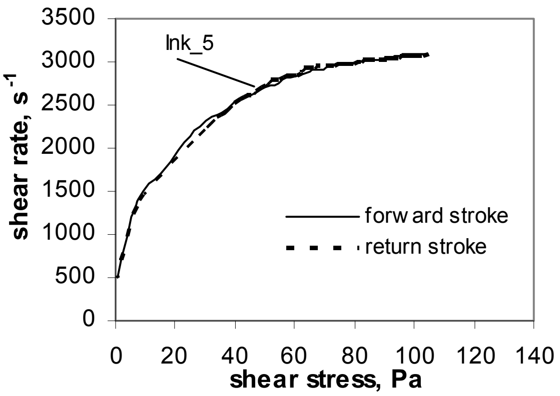

Figure 4. Flow curves of Ink_5

With further reduction of the dispersant concentration on the interval Ink_5 - Ink_8 thinning solvent protective layer take place that enhances the processes of aggregation and coagulation. This is expressed in sharp difference in the concentration dependences and is accompanied by a display of the dilatant flow with thixotropic viscosity hysteresis on the initial period of curves Ink_6 - Ink_9 that caused by the strengthening of colloidal structure under the influence of directional flow due to destruction of the original compact aggregates. Besides, there is take place a destruction this aggregates with their simultaneous peptization under the influence of hydrodynamic forces. As a result, structural elements formation with more compact aggregates occurred during system relaxation. A typical hysteresis loop rupture between the forward and reverse curves indicates that the structural change of the system proceeds irreversibly [8].

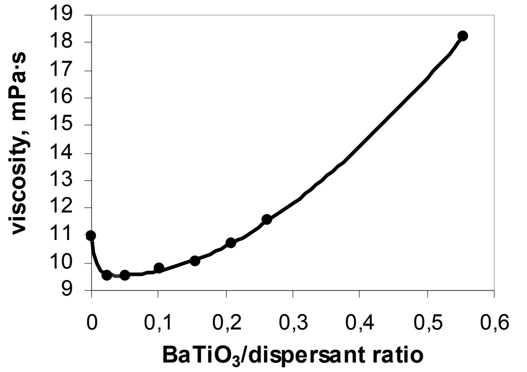

Figure 5. Dependence of viscosity from $BaTiO_3$–dispersant ratio

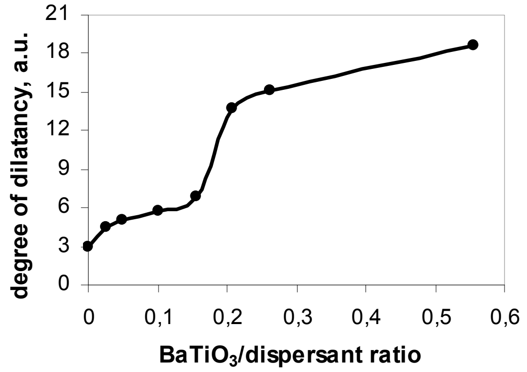

Figure 6. Dependence of dilatancy degree from BaTiO3–dispersant ratio

These results suggest that in the ink volume take place the formation periodic colloidal structures (PCS). In this case, structural constitution of the Ink_1 - Ink_4 in the system represented as PCS_2, that contains solid particles in deflocculated that stabilized by the presence of adsorption-solvate layers. Dilatant structure formation for such inks explained by constrained conditions of the interaction. At the same time, despite the demonstration of the rheological hysteresis effects, structure of the Ink_5 also belong to ordered PCS_2. This is explained by the fact that the system is more rheopectic than thixotropic, indicates that the dominance of repulsive forces under the forces of attraction between the structural elements. Therefore, one could argue about the overwhelming action of disjoining pressure $\pi_2 > 0$, that typical for the second kind of colloidal structures. Most probably that the formation of relaxation effects on the Ink_5 flow curve related to thinning of the solvation shells due to increasing value of the $BaTiO_3$–dispersant ratio.

In turn, the structure nature of samples Ink_6 – Ink_8 has been classified as PKS_1. This assumption evidenced by the formation of structurally defining hysteresis and anomalous effects such as initial loop breaking and disrupts the flow. Dilatant properties of the PKS_1 lead to stabilization of the colloidal structure as a result of its rearrangement under the influence of the flow. The end of tixotropic flow corresponds to formation completely deflocculated structure. The initial structure of the Ink_6, Ink_7 and - Ink_8 presented in the form of the compact aggregates [7].

Thus, during increasing of $BaTiO_3$-dispersant ratio to the values that lies between Ink_5 and Ink_6 (0.10 – 0.15) the formation systems with inverse properties take place. In other words, there is conversion PKS_2 to PKS_1. And summing all of the above, we can conclude that the dispersant content of Ink_5 (19.4 wt. %) corresponds to the critical concentration stabilization system.

4. Conclusions

The relationship between rheological properties of ceramic inkjet inks based on $BaTiO_3$ nanopowder and solid phase concentration has been investigated. Formation periodic colloidal structures (PCS) take place in the ink volume. The determining factor of structure formation is ratio powder-dispersant. At low powder concentrations system behaves as a dilatant periodic colloidal structure of the second type with a limited volume of the medium (PCS_2) in which a positive disjoining pressure $\pi_2 > 0$ operates. In turn, the nature of the highly loaded samples refers to PKS_1, as evidenced by the formation of hysteresis, and manifestation anomalous effects such as break the loop and disrupt the flow. In the region of values powder-dispersant ratio of about 0.10 – 0.15 take place conversion PKS_2 to PKS_1 and ink structure transform to destabilize monodisperse to aggregate state. Notably, critical solvation shell volume reached at the dispersant concentration 6.5 wt. %. All formulated inks demonstrate dilatant flow with an established rate of dilatant deformation. It follows that at high shear rates samples as completely deflocculated PKS_2.

5. Acknowledgments
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