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Rheology and Printability of Pastes Based on BaTiO₃ Nanopowder Depending on Ethyl Cellulose Viscosity

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This paper is about rheology of pastes based on BaTiO₃ nanopowder with ethyl cellulose 100 cP (paste P1) and 10 cP (paste P2) as organic binder. It was established, that P1 was pseudoplastic – thixotropic system and P2 was rheopexic - pseudoplastic – thixotropic one. The reduction of EC viscosity led to changing of paste structurization type from pseudoplastic (P1) to plastic one (P2). Structurization of P1 can be explained with excess of polymer in the paste composition and with dominance of the polymer – polymer bonds. Unlike P1, P2 has some elastic properties due to strong structural links because of polymer – nanoparticle bonds. Moreover, the value of initial viscosity of P2 (2.11 Pa·s) was much less than of P1 (37,5 Pa·s). It was found, that the viscosity of polymer influences the paste printability. In particular, P2 was more prone to form thinner and smoother prints. Thus, composition of P2 was more promising one for obtaining prints with good quality and subsequent assembly into a multilayer object due to its elastic properties during low deformation

Keywords: pastes, rheology, rheopexy, pseudoplasticity, thixotropy

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1. INTRODUCTION

It is known that pastes are high-concentrated suspensions of inorganic particles in organic solvent. Rheological behavior of pastes is important area of research because it provides rich information concerning their viscosity and printability during printing operation. Rheological tests are model the printing process, where investigated paste is subjected to increased shearing.

There are many publications focusing on rheology of polymer concentrated suspensions filled with metal oxide powders of various particle diameters. The rheological properties depend on solid phase concentration [1 – 3], particle size [2, 4 - 6], concentration and molecular weight of polymer [1 - 3, 5 - 7] and also interaction between particles, solvent and polymer molecules [2, 5, 9]. Because of rapid development of microelectronics, the suspensions based on nanopowders represent the most promising objects for rheological investigations. Herewith, nanosized particles allow obtaining «green» ceramic layers with thickness 700 – 800 nm and surface parametr Ra commensurable with size of nanoparticle [10].

It is known that screen printing pastes based on micron powders are generally required to be shear thinning, thixotropic over definite time scale and shear rate, stable for screen/shelf-life and low solvent evaporation [11 - 13]. Therefore, terpineol and its derivatives are used as a solvent, ethyl cellulose EC as an organic binder because of their ability to form thixotropic systems with suspensions of particles of various origination [14]. So, pastes based on micron powders are typical non-newtonian pseudoplastic liquids with decreased viscosity under increased shear stresses. Herewith, the structural elements suspended in a liquid are orient along the flow direction and order their mutual arrangement. But if non-newtonian liquid has yield stress it is plastic system [15]. Plastic liquids have the initial 3-D network formed by particles or molecules due to Van der Waals or polar interactions etc. Such interactions limit the movement of structural elements and form the system with some properties of solid. If applied external shear stresses are lower than strength of structural bonds, the system deforms elastically. Exceeding of yield stress leads to destruction of initial 3-D network and rearrangement of structural elements. The system begins to flow like a liquid.

If disrupted system in a quiescent state restores its own structure it is thixotropic liquid. Graphically, it is expressed in hysteresis loop between up- and down flow curves. Hysteresis loop area is the energy per volume of deformed liquid, i.e. thixotropy degree T. Thus, T is the energy expended on disrupting of thixotropic structure.

The viscosity growing with increasing of shear stresses manifests in rheopexy. Rheopexy is expressed in hysteresis loop due to mismatch of up- and down flow curves, but in this case the hysteresis is counter-clockwise and rheopexy degree R is also determined as hysteresis loop area. Thixotropy and rheopexy are two opposite states of structured liquids.

Present paper is aimed to establishing the difference in rheology between pastes P1 and P2 with EC 100 cP and 10 cP as organic binder. Herewith, the complication of paste flow with decreasing of polymer viscosity from 100 to 10 cP (5 wt. % EC solution in toluene-ethanol mixture) is expected.

2. MATERIALS AND METHODS

Screen printing pastes have been prepared by using

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of BaTiO$_3$ nanopowder with mean particles size about 20 nm, polymer ethyl cellulose (100 and 10 cP, Merck GmbH) as an organic binder and terpineol (mixture of α- and β-terpineol isomers, Merck GmbH) as solvent.

The rheological tests of pastes has been carried out using rotary rheometer «Rheotest RN4.1», Medingen at shear stresses from 1 to 1000 Pa and gap between coaxial cylinders of 1.48 mm. All measurements were carried out at 20±0,5ºC. Herewith, we studied rheology of two pastes with ethyl cellulose 100 cP and 10 cP respectively.

Thixotropy and rheopexy degrees were determined from the hysteresis loop areas between up- and down-curves.

A criterion of equilibrium degree of structure dstruction (EDSD) is effective viscosity determined as follows:

$$EDSD = \frac{\eta_{\max} - \eta_{\tau}}{\eta_{\max} - \eta_{\infty}} \qquad (1.1)$$

where η_{τ} - is the effective viscosity at given shear stress; $\eta_{\max}$ - is a maximal viscosity corresponding to nonvolatile initial structure; η_{∞} - is the less viscosity, corresponding to breaking point [16]. When EDSD < 1 the recovery processes prevail destruction processes and vice-versa when EDSD > 1.

Dilatancy degree D is characterized by the strength of sheared initial structure [17] and determined as:

$$D = \frac{\eta_{\max} - \eta_{\tau}}{\eta_{\tau}}, \qquad (1.2)$$

where $\eta_{\max}$ - is the maximal viscosity corresponding to nonvolatile initial structure; η_{τ} - is the effective viscosity at given shear stress.

Both pastes were printed through nylon screen with 38x38 mm patterns using precision screen printer MPS-485 (AMI). Films thickness and roughness parameters R_a and R_z have been identified by optical profilometry method using Non-contact 3D interference profilohraf "Micron - alpha". Microscopic analysis was conducted by using SEM.

3. RESULTS AND DISCATION

3.1 Rheology of paste P1 with EC (100 cP) as an organic binder

Under increased shearing paste P1 was demonstrated pseudoplastic - thixotropic structurization (fig.1): during pseudoplastic flow region (from 0.1 to 52 Pa) a sharp drop in viscosity value was observed (fig.2).

Further increasing of shear stresses up to strength stress value (741 Pa) led to viscosity gradually reducing during thixotropic structural state. Herewith, thixotropy degree T was about 0.058 MPa/s (tab. 1).

Such structurization of P1 could be explained as follows. Because of abcense of yield stress the initial 3-D network of P1 begins to break down at once up to two-dimensional state due to orientation of structural elements along the flow direction. During pseudoplastic flow region structural cross links disrup and system flow layerwise. In the pseudoplastic region, the system was in equilibrium state because of balance between recovery

and destruction processes. Further shearing led to difference in shear rates between structural layers and to disrupting of longitudinal bonds. Thus, the system becomes thixotropic one-dimensional structural state. Thixotropic distruction was characterized by gradual viscosity decreasing due to simultaneous destruction and violation of the molecular orientation. The elementary units of structure (clusters) were moved with the average velocity of the gradient flow and rotated in a perpendicular direction. The clusters were collided and mutually shielded, affecting the rotating rate. The final destruction of system became after achieving and exceeding of strength stress value (tab.1).
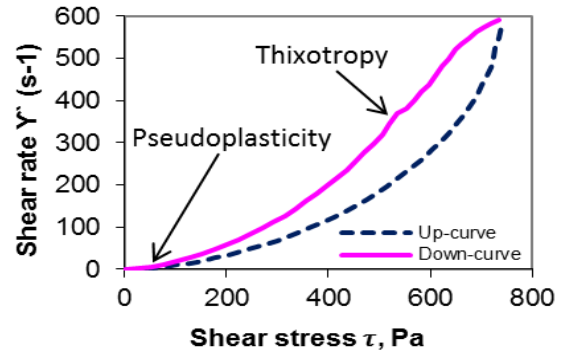

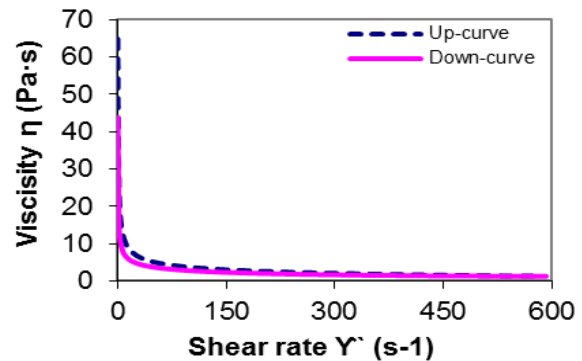**Fig. 1** – Flow curves of paste P1 with EC (100 cP) as an organic binder

Fig. 2 – Viscosity profiles of paste P1 with EC (100 cP) as an organic binder

3.2 Rheology of paste P2 with EC (10 cP) as organic binder

It was established that paste P2 gradually was in rheopexic – pseudoplastic – thixotropic structural states (fig. 3). Unlike P1, paste P2 has shear thickening region up to shear rate Vd 101 s^{-1} (307 Pa). Further deformation led to achieving and exceeding of Vd value and the systems viscosity started to decrease. So, Vd value was yield stress of investigated structure and paste P2 was a plastic liquid.

Structural transitions of P2 could be explained as follows. Because of the plastic nature and presence of yield stress, under relatively low shearing (up to 307 Pa) the initial structure of P2 deforms elastically. Herewith, the additional molecular engagements were formed and there was the additional resistance of initial network to deformation. Graphically it could be observed in shear thickening during dilatant region (fig. 4) and in rheopexic

structural state (fig. 3). But increasing of shear stresses and exceeding Vd value led to occurrence of overstrain condition of transverse structural links. The system becomes pseudoplastic two-dimensional state (fig. 3) due to forced orientation of structural elements. During the pseudoplastic flow region (from 584 to 620 Pa) the system was in equilibrium state and flowed layerwise. Next
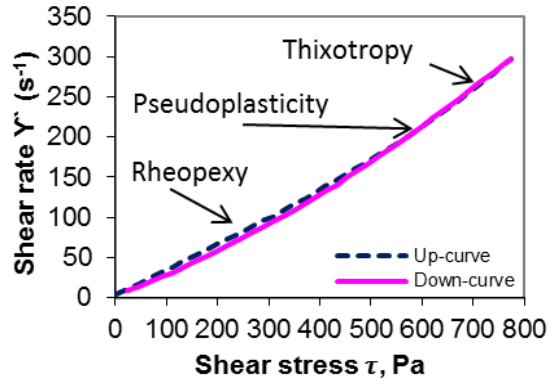
rising of shear stresses led to the gradient flow velocities in the structural layers. Longitudinal structural links overstrained and started to disrupt. The system became one-dimensional thixotropic state. Thixotropic properties were reflected in viscosity value decreasing (fig. 4). The final destruction of system became after achieving and exceeding of strength stress value (tab. 1).
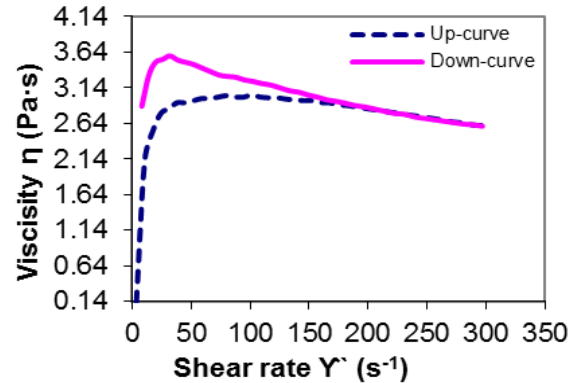

Fig. 3 – Flow curves of paste P2 with EC (10 cP) as an organic binder

Fig. 4 – Viscosity profiles of paste P2 with EC (10 cP) as an organic binder

Table 1 – Rheological properties of pastes P1 and P2

Paste	Viscosity $\eta_{0.1}$, Pa·s	Dilatant flow Vd, s^{-1}	Maximum viscosity of dilatancy η_{max}, Pa·s	Thixotropy degree T, MPa/s	Dilatancy degree D, $\Delta\eta/\eta$	Rheopexy degree R, MPa/s	Equilibrium degree of structure destruction EDSD, r.u.	Pseudo-plastic flow start, Pa	Strength stress, Pa
P1	37.50	-	-	0.0580	-	-	-	0.7	741
P2	2.11	101	3.04	0.0002	0.44	0.0033	2.16	584	773

Common feature for both pastes is the nature of thixotropy phenomena in such high-filled systems. Polymer molecules form in the solution loops which are randomly entangled. A certain length of chemical bonds and the angles between them form zigzag shape chain molecule. In a quiescent state the molecule has energy minimum. Under shearing the molecule or its segments are stretched in the direction of the applied force. The distension of molecule deforms the angles between chemical bonds and increases the energy potential of the molecule. After removing shear stresses the molecule relaxes and restores its initial structure.

Thus, structurization of P1 can be explained with excess of polymer in the paste composition. Some fraction of molecules interacts with BaTiO$_3$ nanoparticles. But the remaining part of polymer is sufficient to form the initial pseudoplastic 3-D structure due to the dominance of the polymer – polymer bonds. Unlike P1, addition of EC 10 cP was sufficient to dominance of the polymer – nanoparticle bonds. So, P2 was plastic system with elastic properties due to strong structural links.

3.3 Optical profilometry and SEM of prints of the pastes P1 and P2

Prints of both investigated pastes were characterized by optical profilometry method (tab. 2). It was established that using of low-viscosity polymer as organic binder allows obtaining prints with less thickness and smoother surface. According to the fig. 5, the bigger value of parameter Rz of P2 can be explained with distinct
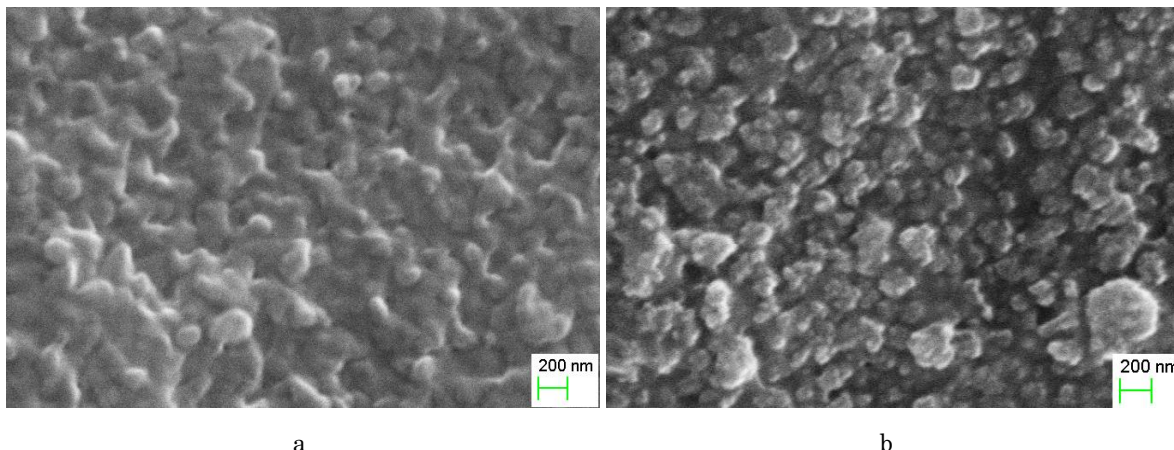
nanopowder agglomerates on the surface (fig.5, b). Unlike P2, the P1 surface is characterized by the tops of nanopowder agglomerates surrounded by excess of polymer (fig.5, a).

Table 2 – Optical profilometry of prints of the pastes P1 and P2

Paste	Thickness, µm	Ra, nm	Rz, nm
P1	1.57	51	160
P2	1.30	36	173

4. CONCLUSIONS

It could be concluded, that the replacement of EC 100 cP to EC 10 cP has significantly complicated the flow character of paste. Firstly, the reduction of EC viscosity led to changing of paste structurization type from pseudoplastic to plastic one. Herewith, the appearance of rheopexy for P2 was observed. So, P2 demonstrates elastic properties due to more solid structure. Moreover, the value of initial viscosity of P2 (2.11 Pa·s) was much less than of P1 (37,5 Pa·s) (tab. 1). This testifies the thickening of P1 because of excess of polymer in the paste composition. It was found, that the viscosity of polymer influences the paste printability. In particular, P2 was more prone to form thinner and smoother prints. Thus, composition of P2 was more promising one for obtaining prints with good quality and subsequent assembly into a multilayer object due to its elastic properties during low deformation.

a   b

Fig. 5 – SEM of prints of investigated pastes: a – P1; b – P2

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