

Plasticizer Effect on Rheological Behaviour of Screen Printing Pastes Based on Barium Titanate Nanopowder

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Abstract. The dependence of rheological behaviour of pastes based on BaTiO₃ nanopowder vs. plasticizer content has been investigated. All pastes prepared for research can be divided into groups by structure types and viscosity. Such a grouping has been explained by different interaction between nanoparticles and binder in the pastes. Particles with molecules of binder form clusters – the representative units in the volume of paste where particles are uniformly distributed. Plasticizer adding effects on binder molecule conformation and change clusters size. Bond strength between clusters can be specified with rheopexy in the area of low shear stress and low strain rates. Rheopexy degree increasing authenticates interaction intensification between clusters. Rheopexy structure destruction leads to separate clusters formation and initiation of the pseudoplastic flow stage. The end of pseudoplastic flow corresponds to structure with clusters assembled into separated layers. Further shear stress increasing leads to inter-clusters bonds appear which can be deformed elastically and the temporary local linkage is possible. Such a phenomenon fully discloses the features of thixotropic structure destruction in plasticized pastes.

1. Introduction

The miniaturization of electronic devices such as multilayer ceramic capacitors supports the global trend of downsizing their dimensions and gradual application of nanosize particulate components. The specific capacity of the multilayer ceramic capacitors is reversely proportional to square of dielectric layer thickness and directly proportional to number of electrodes. Thickness of metallic and dielectric layers can be decreased to 100-200 nm by using of nanosize particles in combination with new techniques for layer manufacturing. Screen printing technology is one of the promising one for thin and dense dielectric layers obtaining, high precision, rapidness, low cost [1]. The method allows printing with print's thickness in the range 100 nm – 100 μm [2] complex geometry and high thin line resolution [3]. But such properties as roughness, evenness and film thickness, print geometry strongly depend on viscosity and rheological behavior of pastes and screen printing process parameters [1, 3, 4]. In accordance with [2-8], the main requirements to rheological behavior of pastes are pseudoplastic or pseudoplastic-thixotropic flow type and viscosity value must be low enough for paste retention on screen and free smoothing of pattern surface after deposition.

Accordingly to our previous investigation [9-10], ethyl cellulose has considerable affinity to BaTiO₃ nanopowder. This leads to sizeable paste densification, rheological behavior change and solid content decrease to 10 – 15 % wt of nanopowder as compared to typical amount for submicron powders of 50 – 70 % wt. One more important factor directly effecting on rheology is plasticizer content. Thus,



present paper is aimed at investigation of dependence of rheological behavior of screen printing pastes based on BaTiO₃ nanopowder from plasticizer content.

2. Materials and Methods

Screen printing pastes have been prepared by using of BaTiO₃ nanopowder with mean particles size of 20 nm, ethyl cellulose with viscosity of 5 wt. % toluene-ethanol solution 10 mPa·s (Merck) as a binder, terpineol (Merck) as a solvent and dibutyl phthalate (Merck) as a plasticizer. Solid and binder content in pastes were invariable during experiments of 10 and 3 wt. % respectively.

Pastes have been prepared in planetary ball mill Pulverisette 6 (Fritsch) with rotating velocity of 450 rpm. Pastes have been characterized with rheological viscosity analysis in shear stress range of 1 – 1000 Pa using 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 – 3, Table 1 and Fig. 4 show that the plasticizer content increasing determines the viscosity and rheological properties indirectly because the molecule of ethyl cellulose changes conformation with addition of plasticizer. First, the change in molecule conformation directly effects on adsorption of polymer molecules on nanoparticle. In general, several adsorption types may be realized in this systems, for example polymer adsorption on the nanoparticles surfaces, nanoparticles adsorption on polymer molecule, polymer molecule bonding to nanoparticle surface through one part or whole molecule. Adsorption type determines possible structuration type and viscosity of the system.

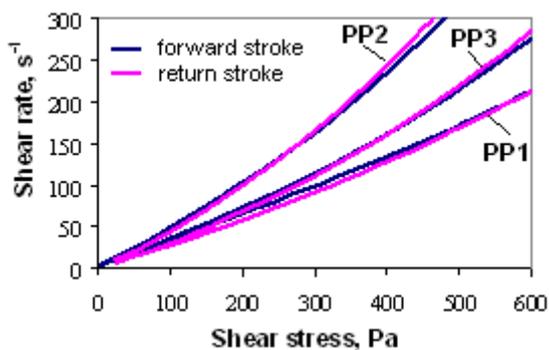


Figure 1. Flow curves of pastes PP1 – PP3

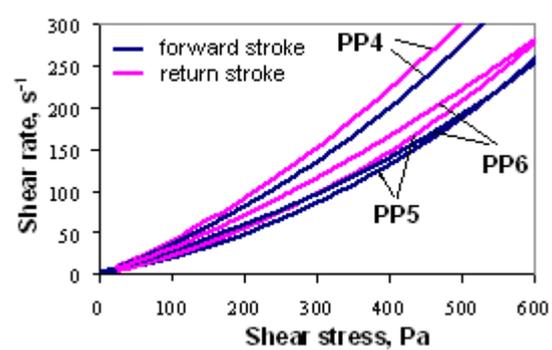


Figure 2. Flow curves of pastes PP4 – PP6

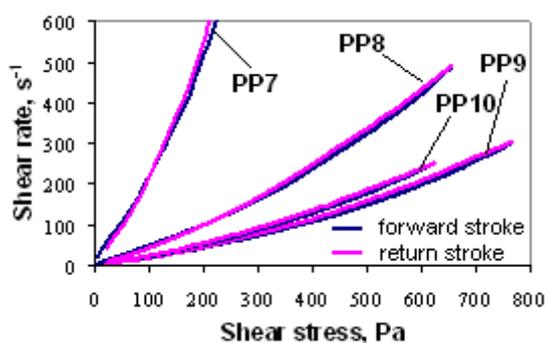


Figure 3. Flow curves of pastes PP7 – PP10

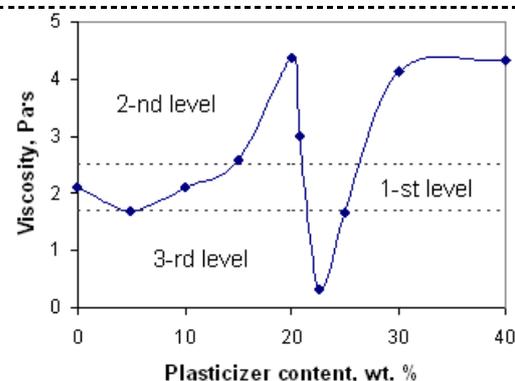


Figure 4. Viscosity dependence on plasticizer content

Table 1. Composition and rheological properties of pastes based on BaTiO₃ nanopowder and plasticizer (ethyl cellulose 10 mPa·s)

Paste	Plasticizer content, wt. %	Yield stress, Pa	Dilatant flow finishing, s ⁻¹	Maximum viscosity of dilatancy, Pa·s	Thixotropy degree, MPa/s	Dilatancy degree, a.u.	Rheopexy degree, Pa·s	Degree of equilibrium structure destruction	Pseudoplastic flow start, Pa
PP1	0.0	185.28	100.90	3.04	0.0002	0.4408	0.0033	2.1628	584.40
PP2	5.0	262.15	31.78	2.04	0.0041	0.2000	0.0009	0.5000	248.60
PP3	10.0	254.72	47.69	2.76	0.0012	0.3019	0.0014	0.8101	362.10
PP4	15.0	243.57	23.60	2.87	0.0100	0.1124	0.0000	0.2164	0.00
PP5	20.0	320.00	14.40	4.91	0.0081	0.1261	0.0000	0.1864	25.33
PP6	20.8	294.09	32.23	3.54	0.0130	0.1761	0.0000	0.3557	23.64
PP7	22.5	156.99	137.00	0.48	0.0080	0.3988	0.0008	0.7351	0.00
PP8	25.0	259.64	33.46	2.05	0.0039	0.2202	0.0008	0.5211	212.90
PP9	30.0	307.57	23.68	4.95	0.0041	0.1985	0.0001	0.3402	140.60
PP10	40.0	230.88	16.16	4.62	0.0026	0.0670	0.0000	0.1349	20.13

In general, all pastes of Table 1 can be divided into 4 groups in concordance with structuration types. For the pastes PP1, PP2, PP3, PP8 and PP9, the rheopexic pseudoplastic flow regime succeeded by pseudoplastic and thixotropic pseudoplastic regimes. In the PP5, PP6, PP10, the pseudoplastic flow regime succeeded by thixotropic pseudoplastic one. The PP4 has demonstrated thixotropic pseudoplastic flowing type only and in the PP7, the rheopexic pseudoplastic flow regime succeeded by thixotropic pseudoplastic one. In addition, three viscosity levels have been considered (Fig. 4). For the pastes PP1, PP2, PP3, PP8, an unbreakable structure viscosity was 1.7 – 2.5 Pa·s (1-st viscosity level), for the pastes PP4, PP5, PP6, PP9, PP10, unbreakable structure viscosity was over 2.5 Pa·s (2-nd level) and for the paste PP7, the viscosity was found less than 1.7 Pa·s (3-rd level). Pastes have been classified by different structural types and by viscosity levels in accordance with the interaction between structural particles and organic components in the pastes.

Existence of the dilatant flow interval on the curves for all pastes is considered the best evidence for 3D-net structure formation. At low shear stresses the structural bonds of such net elongate and viscosity increases. In this case, the dilatancy degree characterizes dimension rising and initial structure strength. Rheopexic or pseudoplastic flow is the evidence of 3D-net disintegration as a result of critical shear stress reaching. Existence of rheopexy is explainable with strong interaction between elementary structural clusters consisting of nanoparticles with polymers tailored into net. Breaking of these bonds requires significant energy to allow destruction dominate over structure reduction processes under shear stress applied (Fig. 5). In substitution pseudoplastic flow interval indicates the bounds braking between clusters as result of lattice volume increasing because of solvent molecules penetration in structure. According to adsorption theory, free functional groups in ethyl cellulose molecules can be observed in rheopexy structures. For the pastes PP1 – PP3, this may be explained with insufficient plasticizer quantity and for the PP8, PP9, with the presence of such groups in the separate molecule parts. In the case of pseudoplastic structuration, the polymer remains bonded with BaTiO₃ nanoparticles in that conformation, where all free functional groups are used. Such an adsorption type strongly increases the viscosity of pastes as result of more uniform cluster distribution in the volume of pastes (2-nd viscosity level). This behavior corresponds to decreasing of dilatancy degree (Fig. 6) and dilatant flow interval on flow curves (Fig. 7).

The destruction of rheopexic structure leads to separate clusters formation. This corresponds to initiation of the pseudoplastic flow stage. The rheopexy degree increase shifts the beginning of pseudoplastic stage to higher stress range (Fig. 8) due to reinforcement of bonds between clusters in the initial 3D-net. The end of pseudoplastic flow corresponds to structure with clusters assembled into separated layers. Further increasing of shear stress leads to difference between strain rates of adjacent cluster layers. Thus, the arrears of intercluster bonds are observed clearly. In this case, the interclusters bonds appear which can be deformed elastically and the temporary local linkage is possible.

Such a phenomenon fully discloses the features of thixotropic structure destruction in plasticized pastes and determines the reduction degree for the structure right after unloading.

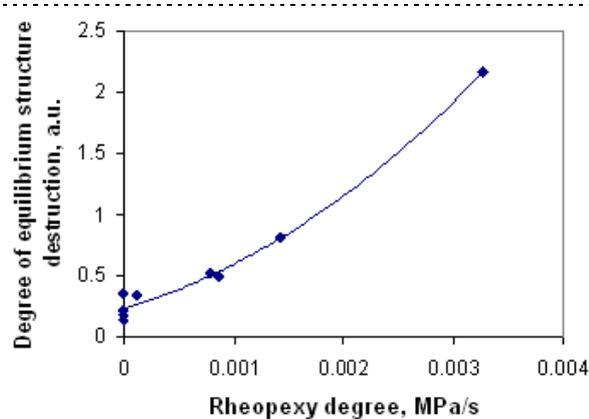


Figure 5. Dependence of degree of equilibrium structure destruction from rheopexy degree for plasticized pastes

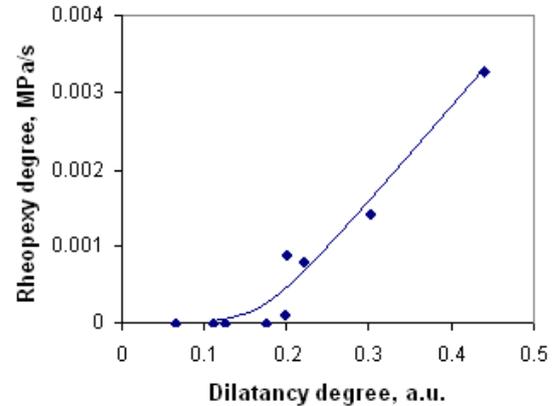


Figure 6. Rheopexy degree dependence on dilatancy degree for plasticized pastes

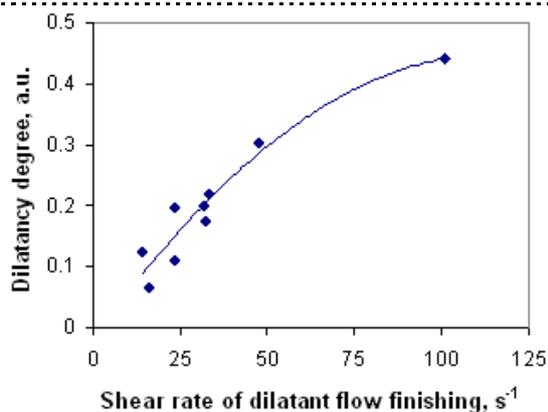


Figure 7. Dilatancy degree dependence on dilatant flow finishing

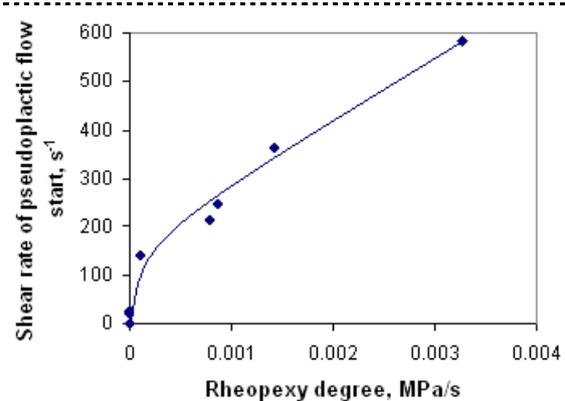


Figure 8. Dependence of pseudoplastic flow start from rheopexy degree

4. Conclusions

The dependence of rheological behavior of pastes based on BaTiO₃ nanopowder vs. plasticizer content has been investigated. Plasticizer addition leads to changing of molecule conformation and adsorption mechanism of ethyl cellulose on BaTiO₃. Interaction degree of polymer-plasticizer determines the viscosity for unbreakable structure and system stability under various conditions, which are specified for various flow types under adjusted shear stress range. Dilatant flow region has been observed for all nanopowder-polymer-plasticizer structures and related to the 3D-net in the pastes. Paste dilatancy degree determines the critical destruction stress for structure and structure strength. Interaction strength between system clusters is specified with existence of rheopexy at low shear stresses. The rheopexy degree increasing authenticates interaction between clusters. Rheopexy structure destruction leads to separate clusters formation and initiation of the pseudoplastic flow stage. The end of pseudoplastic flow corresponds to structure with clusters assembled into separated layers. Further shear stress increasing leads to inter-clusters bonds appear which can be deformed elastically and the temporary local linkage is possible. Such a phenomenon fully discloses the features of thixotropic structure destruction in plasticized pastes.

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