

Formation Features of Thin Bilayer Objects «Conductor-dielectric» Obtained by Screen Printing Method

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This paper is about formation features of thin layers for different multilayered nanocomposites obtaining. It is well-known that screen printing technology is more promising one for thin layers obtaining, but films thickness and parameters of surface are determinate by viscosity and rheological behavior of pastes. Plasticizer addition has positive influence on thickness and prints parameters of surface of corresponding dielectric pastes based on BaTiO₃ nanopowder because of rheological properties changing during adsorption type modification between nanoparticle and plasticized polymer molecule: rheopexy degree R increasing leads to surface parameter Ra value decreasing (from 83 nm to 20-25 nm); shear stress of pseudoplastic flow start increasing leads to thickness growing. It was found that opportunity of bilayer objects formation «conductor - dielectric» is conditioned by dielectric pastes rheological behavior: dilatancy rate Vd increasing leads to dielectric film thickness growing. Here, Ra parameter of conductive layer determines with EDSD criteria value of appropriate dielectric paste and should not be equal to 0.5.

Keywords: Screen printing technology, Pastes, Rheological properties, Surface parameters

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1. INTRODUCTION

Developing of modern electronics leads to dimensions downsizing of the devices. In this connection there was a necessity to decrease the films thickness and surface parameters values for the most multilayered nanocomposites. Therefore, thinning nature investigation is more promising rout for objects obtaining with prescribed properties. According to this problem, thickness of dielectric layers can be decreased to 100-200 nm by using of nanosize particles and new techniques of layer manufacturing. Screen printing technology is more promising one for thin dielectric layers obtaining, but roughness, evenness and thickness of films and are determined by the viscosity and rheological behavior of pastes. Thus, investigations of film characteristics depending on screen printing pastes based on BaTiO₃ nanopowder composition, rheology and viscosity are very important.

2. MATERIALS AND METHODS

Screen printing dielectric and conductive pastes have been prepared by using of BaTiO₃ and Ni/NiO nanopowders with mean particles size about 20 and 8 nm correspondently, ethyl cellulose as binder and terpineol as solvent and dibutyl phthalate (DBP) as plasticizer for dielectric pastes.

Initial three-component solutions and dielectric pastes have been characterized by rheological viscosity analysis. Dielectric and conductive pastes printed through nylon screen with 38 × 38 and 1.5 × 2 mm patterns. Films thickness and roughness parameters R_a and R_z have been identified by optical profilometry. Cross-section analysis was conducted by using SEM.

3. RESULTS AND DISCUSSION

3.1 Rheological Properties of Initial Two-component Solution

Under shear rate increasing the initial two-component solution «ethyl cellulose + terpineol» P1 has alternately 3 structural states: pseudoplastic rheopexic, pseudoplastic and pseudoplastic thixotropic. In this case, rheopexic degree R was almost equal to thixotropic degree T.

It was established, that plasticizer addition into the initial two-component solution lead to rheological properties changing of appropriate three-component solution because of plastification features. First of all, there was a necessity to understand the specificity of polymer solving in solvent. Inherently polymer chain has some flexibility. Hence, macromolecules are bent and therefore polymer has a loose structure with big intermolecular voids. Further, solvent volume increasing leads to polymer macromolecule moving apart and their conformation changing due to effective radii of polymer coils and distance between their mass centers changing. Wherein, polymer body continuity doesn't occur. Eventually, there comes a moment when polymer molecules are moved apart sufficiently and start to break away from each other. Thus, polymer molecules pass into the solution.

PP1 is polymer macromolecules dispersion in organic solvent which has elastic properties. But separate macromolecules and their spherical shaped segments (globules) are in Brownian motion. During small shear deformation of the system globules are collide, partially overlap and create molecular engagements. The process is manifested in dilatants flow section. During viscosity increasing simultaneously with shear stress growing

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structure formation takes place because of formed linear and crosslink bonds lead to some group's formation which can wove like separate flow units. Wherein system hardening occurs and three-dimensional chaotic arrangement of the molecules takes place. Further shear rate increasing to Vd value exceeding leads to Newtonian flow section appearance owing to crosslink bonds breaking down and the system goes into the layered flow regime. The initial structure destruction beginning corresponds to rheopexical hysteresis loop. The final system passing into two-dimensional state reflected in pseudoplastic flow appearance during which destruction and recovery processes are compensate. Further shear stress increasing (high values region) leads to shear rates difference appearance between crosscut macromolecular layers whereupon the bonds between globules appear. Simultaneously it is possible to molecular formation existence with lots of links. In addition, they can be deformed elastically and create instantaneous local clutches. Such phenomenon is accompanied by gradual viscosity decreasing and expressed in thixotropic system structuring.

3.2 Plasticizer Addition Influence on the Rheological Properties of Corresponding Three-component Polymer Solutions

In general, plasticizer addition has an ambiguous effect on three-component solutions viscosity and rheological properties because of ethyl cellulose molecule conformation changing during its partial or full deployment. Besides, rigidly chained ethyl cellulose has no clearly defined molecular weight, so the plasticizing fullness can not be predicted. Fig. 1 and Tab. 1 show that three-component solutions PP8 and PP9 (25 and 30 wt. % correspondently) have several larger values of R , D , $EDSD$ simultaneously with T lower values. In addition, pseudoplastic flow starts at higher shear stress values. But structuring character of these systems is identical to initial two-component solution PP1. Consequently, DBP addition acts as a lubricant, namely moves up polymer molecules and facilitates chains mutual slippage. This is reflected in Newtonian flow

region length increasing simultaneously with DBP content growing.

However, three-component solutions PP2, PP6 and PP7 (5, 20.8 and 22.5 wt. % correspondently) also have structuring character like initial two-component solution PP1. Unlike PP8 and PP9, thixotropy degree T of these solutions increases. In addition, in PP2, PP6 and PP7 systems are no Newtonian flow region and Vd increasing are observed. Hence, plasticizing process passed. Obviously, plasticizer quantity was enough to partial or full molecule deployment and at the beginning the initial structure of these three-component solutions was continuous spatial three-dimensional network. Consequently, PP2, PP6 and PP7 flow curves show destruction of initially structured system.

However, PP3 and PP4 three-component solutions greatly differ from described above. 10 wt. % DBP addition leads to 2 structural states realizing: pseudoplastic and pseudoplastic thixotropic. Unlike PP1, pseudoplastic rheopexic region missing is explained by the higher D and η_{max} values at almost equal Vd and η_0 (Table 1). In this case, initial PP3 structure has been more stretched than PP1 during dilatancy region at the same deformation conditions. Besides, when the Vd has been reached the system was in more elastic state than PP1. That's why destruction of such overstretched system occurs instantaneously with disintegration into certain molecular groups. In turn, these groups become Newtonian layered flow at shear stress increasing.

Interestingly, three-component solution PP4 with 15 wt. % DBP also has 2 structural states but there are pseudoplastic rheopexic and pseudoplastic thixotropic one. In this case initial deformation stage of PP4 occurs similar to PP1. But when the Vd has been reached the system was in more stretched state than PP1 because of higher D and Vd values. Hence the high R value indicates the destruction process even during Newtonian flow region. Thereby, equilibrium state can not be established due to initial structure breaking down almost to initial elementary constitutes and with further shear stress increasing the system immediately becomes pseudoplastic thixotropic one because of bigger energy advantage.

Table 1 – Composition and rheological properties of initial two- and three-component solutions

Solution	DBF content, wt. %	Viscosity η_0 , Pa·s	Dilatant flow Vd , s^{-1}	Maximum viscosity of dilatancy η_{max} , Pa·s	Newtonian flow end $Vn2$, s^{-1}	Newtonian flow region length ΔVn , s^{-1}	Thixotropy degree T , Mpa/s	Dilatancy degree D , r.u.	Rheopexy degree R , Mpa/s	Equilibrium degree of structure destruction $EDSD$, r.u.	Pseudoplastic flow start, s^{-1}
PP1	0	2,11	78	2,81	108	30	0,0008	0,33	0,0007	2,12	407
PP2	5	1,83	109	2,58	0	0	0,0012	0,41	0,0008	2,68	363
PP3	10	2,20	103	3,19	117	14	0,0036	0,45	0	2,54	0
PP4	15	1,46	172	2,18	189	17	0,0004	0,49	0,0030	4,50	0
PP5	20	1,59	108	2,15	127	19	0,0098	0,35	0	1,47	0
PP6	20,8	2,13	130	3,18	0	0	0,0008	0,49	0,0011	3,75	435
PP7	22,5	0,46	198	0,67	0	0	0,0060	0,48	0,0003	1,75	134
PP8	25	1,40	146	2,00	165	19	0,0004	0,43	0,0036	4,00	528
PP9	30	1,82	109	2,57	133	25	0,0003	0,41	0,0023	3,41	535
PP10	40	1,88	77	2,53	110	33	0,0044	0,35	0	1,86	0

3.3 Plasticized Dielectric Pastes Based on BaTiO₃ Nanopowder

The same BaTiO₃ nanopowder quantity was added into the initial three-component solutions composition. As can be seen from Table 2, the general features of all pastes were pseudoplastic flow character and Newtonian flow region absence. Pastes P1, P2, P3, P8 and P9 successively became in 3 structural states: pseudoplastic rheopexic, pseudoplastic and pseudoplastic thixotropic. In contrast, pastes P5, P6 i P10 became in pseudoplastic and pseudoplastic thixotropic structural states. General exception was P7. The system becomes in pseudoplastic rheopexic and pseudoplastic thixotropic states successively. Also, P7 has the lowest viscosity η_0 value (Table 2).

Thus, nanopowder addition into the plasticized solutions for P3, P4, P5, P6, P7 and P8 pastes leads to reversal systems structuring changing in comparison with corresponding initial solutions. It occurs due to plasticizer addition leads to ethyl cellulose conformation changing because of adsorption type modification between polymer molecules and nanoparticles. Thereby, next variations could be possible: polymer molecule adsorption on nanoparticle surface; nanoparticle adsorption on the polymer; polymer molecule joining by one end to the nanoparticle surface; polymer molecule adsorption by the main part on the nanoparticle surface, etc.

From the adsorption position ethyl cellulose molecules in pseudoplastic rheopexical structures have free functional groups. Evidently, in P1, P2 and P3 cases this is due to insufficient plasticizer quantity; for P8 and P9 – due to such group's presence on the molecule separate parts. However, pseudoplastic structures have such polymer molecule conformation that its joining with BaTiO₃ nanoparticle closes the free functional groups.

In general, systems possibility to be in several structural states successively could be explained by structural-strength properties. It is known that structural system begins steady flowing at some shear stress value τ reaching. Exceeding this value to shear stress value τ_s leads to initial three-dimensional network break down. Here, under shear stress value τ_s the system deforms elastically. For investigated pastes τ_s corresponds to V_d .

Consequently, size and strength of initial structure are determined by dilatancy degree D . Destruction beginning of initial structure corresponds to rheopexical flow region appearance. During all rheopexical flow existence the initial three-dimensional network continues to break down right up to clusters form. In turn, clusters formation leads to system approaching into some equilibrium state providing that structure temporarily unable changing under shear stress increasing. Then, destruction processes stop and clusters became move like autonomous flow units. Such phenomenon expressed in pseudoplastic flow appearance during which shear stress increasing leads to clusters dimension decreasing.

It was established that presence in the system of several structural states transitions from one state to another during shear stress increasing could be explained predominantly with η_0 value (Tab. 2). Figure 1 shows that η_0 is determined by plasticizer content in the paste and has ambiguous character. However, there are 3 viscosity levels can be distinguished: the first one is η_0 from 1.7 to 2.5 Pa s (P1, P2, P3 and P8 – pseudoplastic rheopexic - pseudoplastic - pseudoplastic thixotropic), the second one is $\eta_0 > 2.5$ Pa s (P4, P5, P6 and P10 – pseudoplastic - pseudoplastic thixotropic). Despite the presence of three structural states P9 may be refer to the second viscosity level because of very low rheopexy degree value. In this case systems being in pseudoplastic and pseudoplastic thixotropic states will be predominantly. Lastly, the third viscosity level is $\eta_0 < 1.7$ (P7 – pseudoplastic rheopexic - pseudoplastic thixotropic).

3.4 Influence of Rheological Properties of the Dielectric Pastes on Thickness and Surface Characteristics of Obtained Prints

Possibility of obtaining complete rheological flow curve of all investigated systems and their describing by specific parameters mentioned above permit to establish the affection of separate structure states on prints thickness and surface characteristics. Such correlation is explained with rheological test and screen printing method similarity.

Table 2 – Composition and rheological properties of dielectric pastes based on BaTiO₃ nanopowder

Paste	DBF content, wt. %	Viscosity η_0 , Pa s	Yield stress, Pa	Dilatant flow V_d , s ⁻¹	Maximum viscosity of dilatancy η_{max} , Pa s	Thixotropy degree T , Mpa/s	Dilatancy degree D , $\Delta\eta/\eta$	Rheopexy degree R , Pa s	Equilibrium degree of structure destruction EDSD, r.u.	Pseudoplastic flow start, s ⁻¹
P1	0	2,11	185,28	101	3,04	0,0002	0,44	0,0033	2,16	584
P2	5	1,7	262,15	32	2,04	0,0041	0,20	0,0009	0,50	249
P3	10	2,12	254,72	48	2,76	0,0012	0,30	0,0014	0,81	362
P4	15	2,58	243,57	24	2,87	0,0100	0,11	0,0000	0,22	0
P5	20	4,36	320	14	4,91	0,0081	0,13	0,0000	0,19	25
P6	20,8	3,01	294,09	32	3,54	0,0130	0,18	0,0000	0,36	24
P7	22,5	0,341	156,99	137	0,48	0,0080	0,40	0,0008	0,74	0
P8	25	1,68	259,64	33	2,05	0,0039	0,22	0,0008	0,52	213
P9	30	4,13	307,57	24	4,95	0,0041	0,20	0,0001	0,34	141
P10	40	4,33	230,88	16	4,62	0,0026	0,07	0,0000	0,13	20

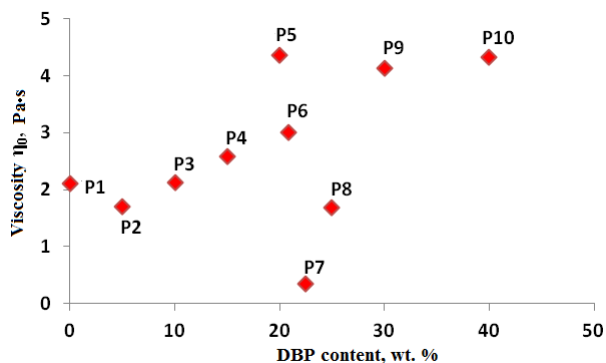


Fig. 1 – Plasticizer DBP content influence on the viscosity of pastes based on BaTiO₃ nanopowder

Rheopexy degree increasing leads to surface parameter Ra decreasing (Fig. 2). Among plasticized pastes the biggest Ra value was established for P4, which has pseudoplastic thixotropic structural type during all applied shear stresses region. Also it was found that in general plasticization phenomenon has positive influence on the smoother surface formation.

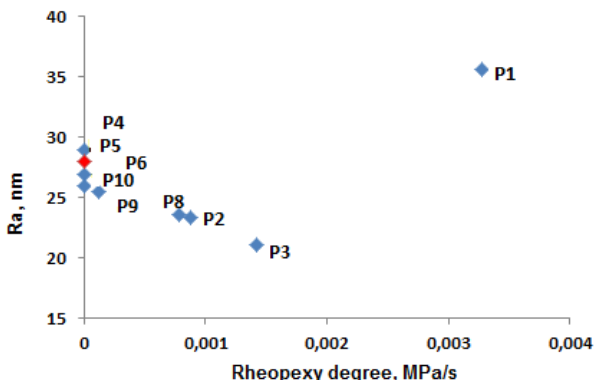


Fig. 2 – Rheopexy degree influence on the parameter Ra value of corresponding dielectric pastes prints

Shear stress value which determines systems becoming in separate clusters state, mainly defines the film thickness. Fig. 3 shows the second viscosity level pastes P4, P5, P6 and P10 with pseudoplastic rheopexic flow region absence, the growing of shear stress values of pseudoplastic flow region beginning on 0.1 to 200 Pa range leads to films thickness increasing. In turn, the growing of shear stress values of pseudoplastic flow region beginning on 200 to 600 Pa range for the first viscosity level pastes P1, P2, P3 and P8 leads to prints thickness increasing to. Such tendency is explained with shear stress values of pseudoplastic flow region beginning determine the degree of cluster system ordering and systems ability to laying in a thinner layer.

In addition, the length of pseudoplastic flow region practically determines clusters finite size on the surface – Rz parameter (Fig. 4). Region length increasing from 0 to 40 Pa leads to Rz value decreasing. However, further region extension to 50 Pa leads to some clusters consolidation. Interestingly, in P10 and P2 cases clusters size increasing or decreasing may occur at the same pseudoplastic flow region length. This is due to polymer – plasticizer interaction features. Besides, clusters size of pseu-

doplastic thixotropic paste P4 is determined just by initial structure strength, therefore has the biggest Rz value. Lower Rz sizes were established for P8, P9 and P2 due to pseudoplastic rheopexic state presence. And the lowest clusters size was measured for P3 paste because of the biggest rheopexy degree value among all investigated pastes.

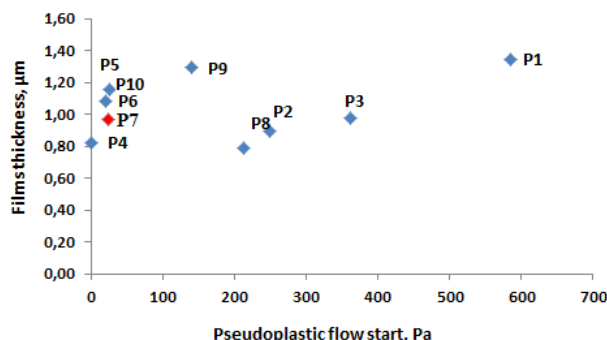


Fig. 3 – Shear stress values of pseudoplastic flow region beginning influence on the films thickness of pastes based on BaTiO₃ nanopowder

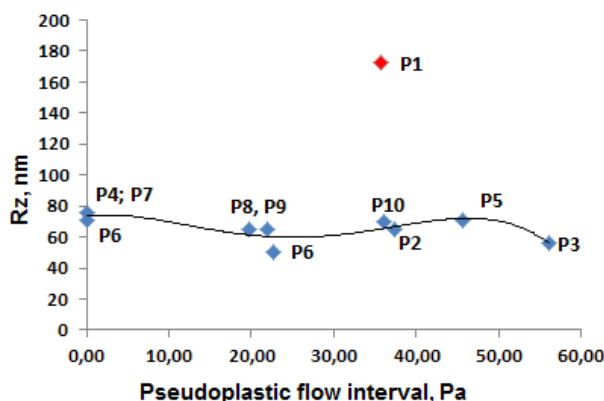


Fig. 4 – Pseudoplastic flow region length influence on the parameter Rz value of corresponding dielectric pastes prints

4. FEATURES OF BILAYER «CONDUCTOR – DIELECTRIC» OBJECTS FORMATION

4.1 Influence of Rheological Properties of the Dielectric Pastes on Thickness and Surface Parameters Values of Bilayer «Conductor-dielectric» Objects

Conductive paste based on Ni/NiO nanopowder was printed on the films surface of all investigated dielectric pastes by screen printing method. It was established that during printing process the green dielectric body undergoes to some deformation. In this case, prints structure resistance degree was determined by Vd value of correspond dielectric paste initial structure (Fig. 5). Moreover, the Ra parameter of conductive layer was determined by EDS criteria value of correspond dielectric paste. Fig. 6, all plasticized pastes have EDS < 1. But for conductive layer, Ra value dependence has extreme character: around EDS = 0.5 the distinct maximum at the highest Ra can be observed. And deviation to higher or lower values leads to Ra decreasing. Consequently, EDS = 0.5 is a limit value and demonstrates

that recovery processes occur in two times faster than destroying ones leading to affection on the Ra parameter value.

It was found that during screen printing both conductive and dielectric layers change its thickness. In addition, these changes are so essential relatively to initial values that lead to all composition thickness changing. Besides, it occurs both in the positive and negative sides. Fig. 7 shows, that such tendency is explained with dielectric systems possibility to be in several structural states. Here, the pastes of first viscosity level P1, P2, P3 and P8 form a separate dependence during which pseudoplastic flow start stress increasing leads to dielectric layer thickness growing after conductive layer printing. However, the second viscosity layer pastes P5, P6, P9 and P10 in lowest correspond stresses values range are characterize with dielectric layer thickness decreasing due to stresses growing to 25 Pa. Further stresses values increasing to 140 Pa (P9) leads to less dielectric layer thickness decreasing. Obviously, bigger P4 layer thickness is associated with pseudoplastic flow region absence.

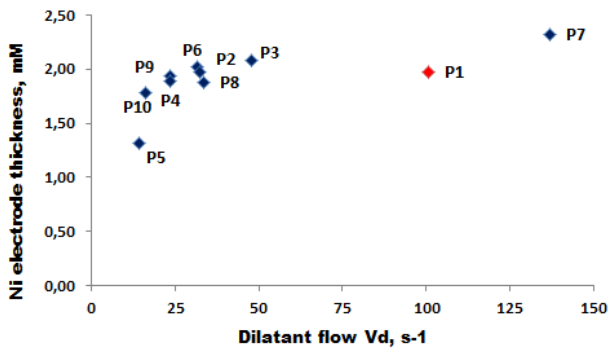


Fig. 5 – Dilatant flow rate influence on the Ni electrode thickness

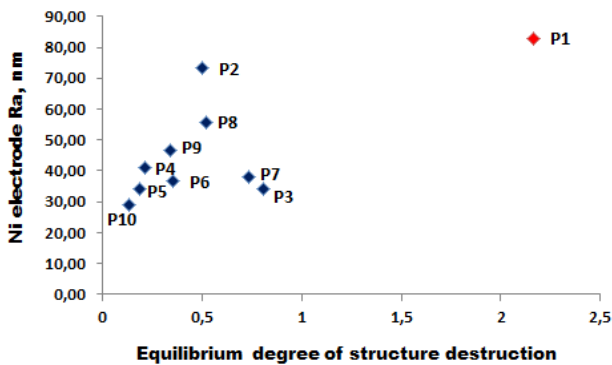


Fig. 6 – Equilibrium degree of structure destruction influence on the Ni electrode Ra parameter value

4.2 Conductive Layer Thickness Changing due to Plasticizer DBP Content in Dielectric Paste Composition

Dielectric layer thickness changing occurs both in the positive and negative sides to. Fig. 8 shows that DBP content in dielectric pastes composition influences the conductive layer thickness. Here, DBP content in ranges from 0 to 15 and from 25 to 40 wt. % leads to

almost similar thickness increasing. However, P5 and P6 pastes

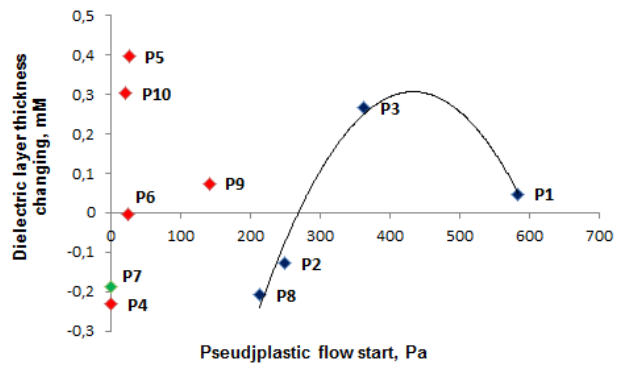


Fig. 7 – Pseudoplastic flow start influence on the parameter thickness value of corresponding dielectric pastes prints after conductive layer printing

form some transition region with two extremes: 20 wt. % DBP addition leads to great thickness decreasing and 20.8 wt. % DBP leads to conductive layer thickness increasing in comparison with initial values. Such phenomenon can be explained with cross-section analysis of correspond bilayer objects.

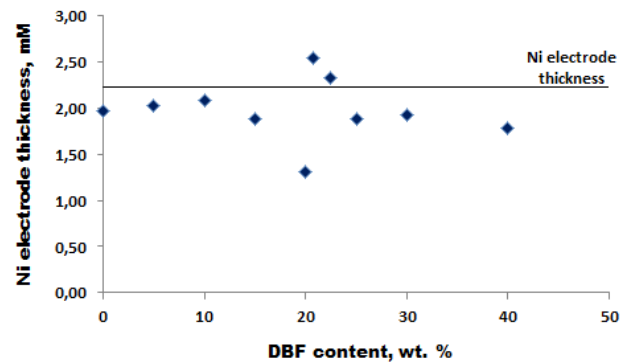


Fig. 8 – DBP content influence on the conductive layer thickness

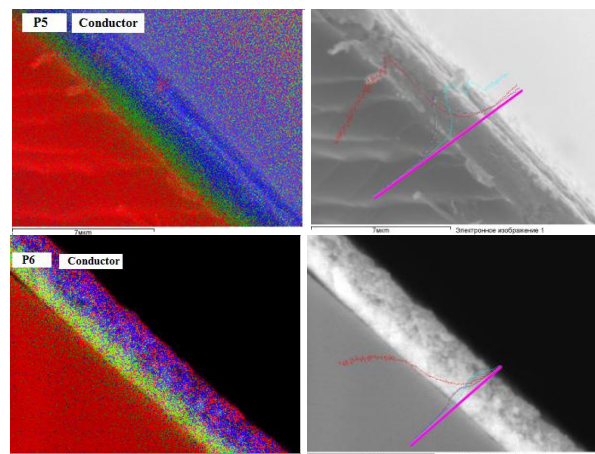


Fig. 9 – Cross-section analyses of bilayer objects «P5 - conductor» and «P6 - conductor» correspondently

Fig. 9 shows, that conductive layer of bilayer object «P5 – conductor» is separated into two parts: directly continuous and subsurface lamellar. Corresponding

spectrum of elements mutual penetration shows that as it approaches the ceramic base the continuous part gradually compacted and Ni content increasing tendency is observed. Thus, conductor penetration into the dielectric layer takes place. Besides, the conductor – dielectric interface is not clear.

Bilayer object «P6 – conductor» has clear interface between functional layers and has sufficiently dense and uniform layer structure.

5. CONCLUSIONS

1. Rheological properties of initial two- and three-component solutions are determined by partial or full ethyl cellulose macromolecule deployment during plasticization which determines systems possibility to become in several structural states, also strength and deformation resistance.

2. Nanopowder addition into plasticized polymer system changes its rheological behavior fully in comparison with initial appropriate solutions. In this case, it can be due to adsorption type modification between polymer molecules and nanoparticles. Thus, in rheopexical structures case ethyl cellulose molecule has free functional groups on the surface; pseudoplastic structures has such ethyl cellulose molecule conformation that during its joining with BaTiO₃ nanopowder free functional groups closing take place. In general, it leads to aggregates formation by plasticized polymer systems like to structured suspensions. Moreover, it can be doublets and chains too. Then they unite into special three-dimensional network

which has great elastic properties and is able to be deformed like a solid.

3. In general, plasticization has positive influence on the smoother surface formation of dielectric layers because of several structural states presence in the system. Rheopexy degree R increasing leads to surface parameter R_a value decreasing (from 83 nm for P1 to 20-25 nm for the plasticized pastes). Independently of systems structuring type shear stresses values increasing, which determine ordering degree of clustered system and its possibility to layering into a thinner layer, uniquely leads to thickness growing of corresponding pastes films.

4. Opportunity of bilayer objects formation «conductor - dielectric» is conditioned by dielectric pastes rheological behavior. Dilatancy rate Vd increasing leads to dielectric film thickness growing. Here, R_a parameter of conductive layer determines with EDS criteria value of appropriate dielectric paste and should not be equal to 0.5 (otherwise R_a increases to 75 nm). During screen printing process the dielectric and conductive layers thickness changing occurs both in the positive and negative sides because of dielectric pastes rheological properties difference due to different plasticizer DBP content.

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