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Chap. 15 : BaTiO₃ films for multilayer devices by tape casting

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Abstract : The diversity of the applicational scope of modern printed electronics relentlessly requires the improvement of operational properties simultaneously with reducing the overall dimensions of devices. One of the most effective ways to overcome this major obstacle is the reduction of functional layers thickness in respect to the size of the device. In the present article, we are discussing a simple way of practical implementation of miniaturization concept through the application of a well-known high-productive industrial method of tape casting for obtaining thin nanostructured ceramic layers based on BaTiO₃ nanopowders for MLCC. Using of nanosized powders per se imply a new approach of developing suspensions with suitable rheology for tape casting. We demonstrate, that a length of polymer molecule defines the size of floccules and therefore influences the thickness and surface quality of tape casted films. A certain nanopowder/polymer ratio contributes to the formation of the tapes with the surface roughness comparable with the size of one nanoparticle (20-25 nm). Moreover, it was established that developed suspensions are extremely sensitive to temperature changes. Lowering the temperature significantly affects the flow character of suspension and thus the thickness of casted tapes. Considering this fact, we propose an effective self-developed pre-cooling method of nanopowder suspension casting, which allows obtaining extremely thin and smooth tapes with a thickness of less than 1 μm and surface roughness of 20–25 nm by tape casting method.

Keywords: BaTiO₃ TAPE CASTING, NANOPARTICLES, RHEOLOGY, TEMPERATURE, ROUGHNESS

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I. Introduction

Barium Titanate (BaTiO_3) is a perovskite material of excellent dielectric, piezoelectric and ferroelectric properties with wide application in multilayer electronics. Because of high dielectric constant values, Barium Titanate finds its application as a material for dielectric layers of MLCC (Multi-Layer Ceramic Capacitors). Production of multilayer devices requires a thin tapes and a smooth interface between them because it is the most efficient way to increase its specific capacity. A challenging goal is to overcome the limitation of the known high-performance methods of tapes production for parameters like thickness and roughness of individual layers. The use of nanopowders as the basis for dielectric tapes are promising because they allow thinning the films and decreasing their surface roughness values up to the size of one nanoparticle (1). It is a guarantee of improving the performance of multilayer devices without increasing their dimensions, which is consistent with the tendency of miniaturization. In particular, it arises an interest to study the high shear stress (1) effect on the viscous flow of liquid powder suspension containing polymer binder during colloidal forming processes and other parameters, like suspension temperature, that can allow thinner layers to be obtained.

Nowadays, printed electronics fields almost completely rely on the tape casting and screen-printing¹ technologies due to their high-productivity what makes this methods the basis of the passive electronic components production. These methods are widely studied, but the minimum thickness of the layers (tapes or prints) formed by these methods with traditional approaches remains 1-3 microns (2), (3), (4). To create layers thinner than 1 μm , other methods like Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) are commonly used. These methods are usually less productive, much more complex, and more expensive (5). Also, most of the high-productive technologies use micro-powders for film-forming. The composition and the peculiarities of film formation from suspensions of nanopowders require more detailed coverage. The use of the nanopowders will not only reduce the thickness and roughness of the films but also increase their green density. This can be achieved due to the denser packaging of nanoclusters formed by polymer molecules and nanosize particles (6).

¹ Screen printing is a printing method in which a grid is used to transfer ink onto a substrate. Some print areas may be covered with a blocking screen to produce a print of a certain shape. The blade moves around the screen to fill the mesh holes with ink.

A few works describe the temperature dependence of rheological² properties and the character of the flow of the suspensions (7). Seal *et al.* (8) have described an influence of ambient temperature during tape casting and recommend taking this parameter into account. The use of low temperature as an instrument for obtaining porous films described by Sofie (9). But none of these works describe the influence of the suspension temperature on the thickness and surface parameters of the films.

There are a few approaches that allow the casting of thin tapes (2), (10), (11). They are proper suspension composition, casting conditions, and the influence of external factors during the process. Proper suspension composition means an amount and type of each component and technique of suspension preparation (12). Most attention must be given to powder because it determines all functional properties of the sintered tape. Other components play a role of temporary additives needed for tape formation and in the majority of cases will be removed on drying and burning-out stages of the process. The use of fine nanopowder is promising because of the unique properties of tape given by small particle size. For example, high electric (13), (14), (15) or optical properties (16) can be obtained due to smaller grain sizes in the sintered body as well as the ability to reach high density at low sintering temperatures (17). But high specific surface area and tendency to agglomeration cause numerous complications in the suspension preparation (18). To use all advantages of nanopowders it is important to preliminary separate particles one from another and to reduce their agglomeration. To prevent re-agglomeration, the special surfactant must be used. The best results were achieved by covering each particle with a monomolecular layer of surfactant (10) because this creates repulsion forces which can overcome Van der Waals attraction. A choice of a suitable polymer (19), (20), (21) and the addition of a thermodynamically compatible plasticizer is important to build a strong and flexible polymer matrix filled with particles (22) which provides flexibility and mechanical strength for green tape.

Tape casting machines use a simple process of a covering substrate (carrier) with liquid suspension (fig. 1) but differ in some basic principles (2), (23). The blade that regulates the thickness of the tape is stationary or mobile. Machines with a moving blade (without reservoir) are usually more suitable for obtaining a tape with a thickness corresponding to the distance from the blade to the carrier. The advantage of this machine construction is the ability to cast one layer upon another. Machines with a stationary blade and reservoir allow the suspension to permanently flow inside the reservoir and cover carrier only in a small region beneath the blade. It allows obtaining thin tapes with uniform density distribution. The thickness of tape in the machines with

² Rheology is the study of flow and deformation of materials (mostly fluids) under applied forces

a stationary blade is usually in the range of 10 - 20% of the blade gap (24). The thickness also depends on the carrier speed (25), (26) and rheological properties of suspension (27). A higher tape thickness requires an additional pressure in the reservoir provided by the height of a liquid or external compressor.

Figure 1: Schematic representation of the tape casting process with a single stationary doctor blade and moving substrate

The analysis of suspension flow nature via rheological study allows predicting the suspension behavior under the blade of the casting machine (27). Traditionally a pseudoplastic³ type of flow is considered preferable for tape casting because of suspension viscosity decrease under applied shear (2). But the influence of nanoparticles in suspension often tends to dramatically and complex change of flow character. Even though rheopexy⁴ has been considered a non-desirable type of flow, most of thinnest tapes, described in previous works, were obtained from suspensions

³ Pseudoplasticity or shear thinning is the non-Newtonian behavior of fluids whose viscosity decreases with an increasing shear load independently of the time of shear action.

⁴ Non-Newtonian behavior of time-dependent shear thickening fluids. Sometimes called negative thixotropy. In rheopectic materials, the structural strength increases while shearing and recovers after a certain rest period (52).

with a small degree of rheopexy (1), (28). All the conditions listed above make it possible to obtain films about one micron thick. The suspension temperature is another important parameter that influences tape properties but it is poorly described in the literature. According to the literature search, altering the suspension temperature to obtain films with better properties is not a common practice. Our previous studies describe the influence of BaTiO₃ nanoparticle suspension temperature on its rheology and structure (1). It was found that casting of the cooled suspension gives benefit in tape thickness comparing to the casting of the same room-temperature suspension.

The purpose of this work is to study the effect of BaTiO₃ suspension composition and temperature on its rheology and tape properties to predict and alter these properties. This study is important not only for a particular application in dielectric MLCC layers but in general for tape casting of films for a wide variety of multilayer devices. Rheological analysis of BaTiO₃ suspensions behavior also can be applied to suspensions of other materials because it depends more on the shape, density, and particle surface properties⁵ than on the chemical composition of the material. Another important goal is to establish criteria that allow casting tapes with a thickness of less than 1 μm and surface roughness comparable with the size of 1 nanoparticle which enables its application in modern multilayer devices. Also, to describe and explain previously discovered phenomena of tape thickness decrease with the decrease of suspension temperature.

II. Materials and methods

The BaTiO₃ nano-sized powder (NanoTechCenter LLC) with a particle size of 25-30 nm and micro-sized powder (Ferro Corporation) with a particle size of 0,5-0,7 μm were used for the suspensions. The size and shape of the particles are shown in fig. 2. Preparation of polymer solutions was carried out by dissolving powdered Polyvinyl Butyral (PVB) Movital B75H (Kuraray GmbH) and Ethyl Cellulose (EtCII), (100 cP 5 % in toluene/ethanol 80:20 (lit.), Merck GmbH) in Isopropyl Alcohol (IPA) for 30 minutes under constant stirring on a magnetic stirrer RCT basic (IKA) at the temperature of 45°C. Dibutyl Phthalate (DBP) by Merck GmbH was used as a plasticizer. A planetary mill Pulverisette 6 (Fritsch) was used for initial powder deagglomeration and mixing with polymer solution at the rotation speed of 450 rpm. Rheological measurements were performed with the rheometer Rheotest RN 4.1 (Rheotest Medingen GmbH) using a cylindrical measuring system S2 with the gap between coaxial cylinders of 1.4 mm. Flow curves and viscosity profiles were evaluated in the range of shear stress

⁵ However, powder surface charge can influence on a choice of solvent and surfactant for stabilization of particles in suspension

from 20 to 1000 Pa. Before measurement, each liquid was pre-sheared for 100 s with a shear stress of 20 Pa to obtain the equivalent measurement pre-history.

Figure 2: TEM microstructure of BaTiO₃ nanopowder (a) and micropowder (b)

To achieve a stable temperature during measurements and test the effect of heating and cooling on suspension rheological properties a ministat 125 (Hauber) thermostat was used. The liquids that represent suspension components were studied. It includes reference suspension of solid-phase particles in the solvent, plasticized and non-plasticized polymer solution, and tape casting suspension. Measurements were conducted in the temperature range from 5 to 20 °C (measurement error 0.1 °C) with a 20 min pause between measurement sequences for temperature stabilization. Films from BaTiO₃ suspensions were formed on a TTS-1200 (Richard E. Mistler, Inc) machine with a maximum carrier speed of 55 cm/min and a doctor blade with an adjustable blade gap with an accuracy of 10 microns. A polyethylene terephthalate film with silicone anti-adhesive coating “Mylar” (DuPont) has been used as the carrier. Silicon coating not only increases lyophobic properties of the carrier’s surface but also smoothening it, resulting in reducing the roughness of the bottom side of the green tape. 2D and 3D surface profiles, thickness, and roughness parameters Ra and Rz of raw films were determined using the contactless interfacing 3D profilometer Micron-alpha (Micron-System) and atomic force microscope TT-AFM (AFM Workshop). Ra – the arithmetical mean of the absolute values of the profile deviations from the mean line of the roughness profile. Rz is a roughness parameter that represents a mean value of the sums of the heights of the highest-profile peaks and the depth of the deepest profile valleys, relative to the mean line, within a sampling length. Both parameters were calculated by 20 baselines, with a length of 200 μm, perpendiculars

to casting direction. JEOL USA Transmission Electron Microscope was used to obtain powder images (fig. 2).

The shear rate for fluids that flows between two parallel plates, one of which moves at a constant velocity, while the other is fixed motionless (the Couette flow) is determined by the equation 1 (29):

$$\gamma = \frac{v}{h} \quad (1)$$

Where γ - shear rate, s⁻¹, v – velocity of the moving plate, m/s, and h – the gap between parallel plates, m

According to the equation (1), assuming a stationary blade and a moving substrate as two parallel plates, it is clear that with a decrease in the height of the blade gap to minimum values, the shear rate will increase significantly. Equilibrium degree of structure destruction (EDSD) is a dimensionless viscosity, which characterizes a quasi-equilibrium suspension state. EDSD can be found from the equation 2 (30):

$$EDSD = \frac{\eta_{max} - \eta_r}{\eta_{max} - \eta_{\infty}} \quad (2)$$

Where η_r is an apparent viscosity at given shear stress, η_{max} is the maximal apparent viscosity corresponding to non-volatile initial structure, and η_{∞} is the less apparent viscosity at flow curves breaking point. EDSD shows a balance between structure destruction and recovery. When EDSD>1 the destruction prevails and when EDSD<1 the recovery process becomes dominant (7).

Suspension flow curves are plotted in shear rate - shear stress coordinates. Forward and reverse flow curves are corresponding to measurement with increasing and decreasing stress respectively. The presence of thixotropy⁶ or rheopexy in suspension can be easily revealed from the hysteresis loop between the forward and reverse flow curves. Thixotropy and rheopexy degrees can be numerically represented by the calculation of the hysteresis area between forward and reverse flow curves (31). These areas can be found using definite integral. In this work, we have used a trapezoid integration applied to a flow curve table data. In the case when the forward

⁶ In thixotropic materials, the structural strength (and therefore viscosity) decreases while shearing and recovers completely after a certain rest period.

flow curve is situated above the reverse flow curve, the hysteresis area is positive and will represent a suspension thixotropy degree. When the forward curve is below the reverse curve, the hysteresis area is negative and represents a rheopexy degree.

A Peclet number Pe is calculated by the following equation 3 (7), (32):

$$Pe = \frac{\tau a^3}{k_b T} \quad (3)$$

Where τ is the shear stress, a is a particle hydrodynamic radius, and $k_b T$ is thermal energy. The floccules⁷ hydrodynamic radius a can be calculated from roughness parameter Rz (equation 4) assuming that agglomerates on tape surface have a spherical shape (7):

$$a = \frac{Rz}{\pi} \quad (4)$$

The real floccules hydrodynamic radius a_2 (6) is calculated by equation 5 (7):

$$a_3 = \sqrt[3]{\frac{a_1^3 Pe_2}{Pe_1}} \quad (5)$$

Where a_1 is a hydrodynamic radius of the structural element of the reference suspension and Pe_1 is the Peclet number of the reference suspension⁸. Pe_2 is the Peclet number of the corresponding casting suspension. Thus, comparing the reference suspension (where a radius of structural elements are known) and the corresponding tape casting suspension, the real hydrodynamic radius of the structural elements (floccules) of casting suspension can be found. A more detailed methodology of this calculation and formulas derived has been previously reported by Umerova and Ragulya (7). The formulation of the suspension was based on previous tape casting experience (12). The weight percent of components remains constant, to study the influence of these components on slurry's rheology (table 1).

⁷ In this case floccule is a one or several powder particles covered with polymer chain

⁸ Suspension that consists only of particles, surfactant, and solvent.

Table 1: Suspensions composition

Suspension name	S-1	S-2	S-3
Powder	BaTiO ₃ (nano)	BaTiO ₃ (nano)	BaTiO ₃ (micro)
Solvent	IPA	IPA	IPA
Binder	EtClI cP100	PVB B75H	EtClI cP100
Plasticizer	DBP	DBP	DBP

Only binder and powder were differing in suspensions. The content of the solid phase and binder was 21 and 3 weight % respectively. A ratio of binder to plasticizer was 1:1.

III. Results and discussion

III.1 Influence of temperature on rheological properties of suspension and its components

To establish optimal suspension composition it is essential to study the rheological behavior of suspensions based on nano and micropowders of BaTiO₃ with different polymer binders. In this section represented data of all calculated values for suspensions, its corresponding binder solutions and reference suspensions with temperatures of 20, 15, 10, and 5 °C. This data is needed for a better understanding of the impact of gradually temperature change on on the flow character of casting suspension, corresponding binder solution, and reference particle dispersion. Overall tendencies that share all suspensions and binder solutions are viscosity increase and shear thickening degree decrease with a cooling. While the increase of viscosity is expected, a decrease of shear thickening can be explained by lowering of Brownian motion and overall mobility of suspensions components (long and short polymer chain molecules of binder and surfactant, particles, etc.). Shear-thinning degree increase for the majority of measured liquids (except casting suspension S-1). So, while studied liquids become more viscous with cooling, they also become thinner easily in reaction to applied shear. This behavior is characteristic of liquids with the ability to arrange its structure in the direction of flow (42), (46).

III.1.a Suspension of BaTiO_3 nanopowder in ethyl cellulose binder solution (S-1)

A great change in the nature of the suspension flow can be observed when adding different components to its composition (fig. 3).

Figure 3: Flow (a) and viscosity (b) curves for reference BaTiO_3 nanoparticles suspension in IPA (1), non-plasticized (2) and plasticized (3) Ethyl cellulose binder solutions in IPA and S-1 casting suspension (4) with the temperature of $20\text{ }^{\circ}\text{C}$ ⁹

A reference suspension is consisting of BaTiO_3 nanoparticles dispersed in a solvent with the same ratio as in suspension with binder and plasticizer. The reference suspension shows low viscosity and low maximum shear stress¹⁰ because particles are not bonded together. A shear thickening can be explained by the internal tension of particles. With the increase of shear stress and shear rate, a layer of liquid between particles is thinning allows interaction between particles or their clustering. Both non-

⁹ Data for the other temperatures represented in tables 2, 3 and 4.

¹⁰ Maximum shear stress is the value that depends on the type of rheometer and measuring system used, suitable only for comparison of suspensions measured under the same conditions

plasticized and plasticized binder solutions exhibit a shear thickening in the range of low shear stresses and almost Newtonian flow when shearing increases. The addition of plasticizer slightly reduces the viscosity and maximum shear stress. This behavior indicates a result of molecular plasticization. Plasticizer penetrates inside polymer chains. Chains become softer and break, thus the chain length is reduced (2).

The addition of nanoparticles to plasticized binder solution makes the suspension a highly viscous shear-thinning thixotropic¹¹ liquid. Both thixotropy presence and viscosity increase indicate the formation of polymer transient network (33) and formation of particles-polymer structure (31). Attention must be given to the increase in maximum shear stress after nanoparticles addition. This behavior can be explained by some sort of reinforcing properties (interaction between particles and polymer chains) that particles bring to a system (19). A similar behavior and viscosity increase in the system of TiO₂ nanoparticles in the ethyl cellulose solution was described by Sanson *et al.* (34). Long polymer chains are much larger than nanoparticles (35) and can flocculate a few of them at the same time by the polymer bridging mechanism (36). A bonding of polymer-particle that is stronger than polymer-polymer thus created. All measured liquids exhibit an increase in viscosity with temperature decrease (table 2). Shear-thinning degree of casting suspension S-1 an order of magnitude higher than of polymer solutions and tend to decrease with cooling. In general, it means that this cooled casting suspension is harder to make fluent. This behavior can be explained based on the S-1 suspension structure. Casting suspension S-1 consists of long-chain polymer and nanoparticles, so as it was mention above, the polymer can flocculate few nanoparticles. Created floccules can become more rigid with cooling, which can make it harder to stretch and align in flow direction with shear provided by rheometer. All measured liquids show insignificant rheopexy except casting suspension which shows a considerable thixotropy degree. Reduction of shear-thinning and thixotropy degree, as well as the increase of strength stress¹², can be evidence of the structure change to one, that better resists applied shear. It should be mentioned, that rheometer's shear rate operation diapason is limited and real shear during the casting process can be much higher. So, the behavior of suspensions under high shears can change. EDS (that can be calculated for liquids with both presences of shear thinning and shear

¹¹ Thixotropy is the Non-Newtonian behavior of some structured disperse systems with the ability to restore their initial structure that was destroyed under the action of the mechanical forces

¹² From a hardware point of view, increase in strength stress (maximum shear stress) with temperature decrease detected because of an increase of viscosity, so liquid stays in measuring diapason of the rheometer under higher stresses.

thickening under stresses) shows a balance between structure destruction and recovery. When EDSD parameter remains <1 , it means that the structural recovery prevails over destruction. Destruction substantially exceeds structure recovery at close-to-room temperatures for binder solution and tends to equilibrium at low temperatures. The balance is shifted to structure destruction for polymer solutions at 20 °C. Suspension cooling leads to a significant decrease in this parameter.

Table 2 : Rheological characteristics of S-1 suspension and its components

$T, ^\circ\text{C}$	Viscosity $\eta_0, \text{Pa}\cdot\text{s}$	Shear thickening degree $D, (\eta_{\max1} - \eta_0)/\eta_0$	Shear thinning degree $Dn, (\eta_{\max1} - \eta_\infty)/\eta_\infty$	Thixotropy degree $T, \text{Pa/s}$	Strength stress $\tau_{\max}, \text{Pa}$	Equilibrium degree of structure destruction EDSD, r.u.
Plasticized Ethyl cellulose binder solutions BS-1						
20	0.278	0.633	0.115	-0.731	366	4.537
15	0.580	0.430	0.133	-1.119	449	1.875
10	0.907	0.269	0.242	-0.973	525	1.121
5	1.312	0.273	0.273	-0.428	604	1.022
Non-plasticized Ethyl cellulose binder solutions BS-1						
20	0.322	0.467	0.116	-0.388	397	4.462
15	0.650	0.333	0.172	-0.720	476	1.825
10	0.930	0.468	0.267	-0.389	552	1.429
5	1.446	0.292	0.257	-0.230	630	1.088
BaTiO ₃ nanoparticles reference suspension in IPA						
20	0.014	2.544	-	1.924	111	-
15	0.014	2.529	-	-0.878	115	-
10	0.016	2.105	0.024	0.476	120	0.878
5	0.019	1.685	0.050	1.293	123	0.855
S-1 Casting suspension						
20	1.726	-	2.984	11.043	381	-
15	2.038	-	1.942	4.590	451	-
10	2.843	-	2.128	4.116	519	-
5	3.927	-	2.175	3.137	592	-

Processes of structure destruction/restoration find equilibrium near 5 °C. Processes of structure restoration prevail only in reference suspension at lower temperatures. At 20 and 15 °C EDS of reference suspension can't be measured because liquids show a pure shear thickening. Vice versa for casting suspension at all temperatures because the liquid exhibits shear-thinning in all measured diapason.

III.1.b Suspension of BaTiO₃ nanopowder in polyvinyl butyral binder solution (S-2)

The polymer solution based on the PVB binder shows a lower viscosity than its ethyl cellulose-based analog. This can happen because of the lower molecular weight of the PVB and a shorter polymer chain (fig. 4). Rheopexy behavior can be explained by the formation of tangles of polymer chains. These tangles do not tend to form a strong regular network and act in a solution like solid particles. After plasticizer addition, a rheopexy degree decreases presumably. This behavior of the system indicates a lubrication effect of the second plasticization mechanism (2). Due to this mechanism, the intermolecular interaction (tension) between polymer tangles decreases (fig. 4). Unlike S-1, an addition of BaTiO₃ nanoparticles leads to an almost two-time decrease in viscosity, a significant decrease in maximum shear stress, and an increase in rheopexy degree. The high rheopexy degree can be caused by frictional contacts that initiate stresses proportional to normal stresses that lead to thickening (37). High molecular weight polymers are more susceptible to flocculation by polymer bridge formation (38). Nanopowder-based suspensions are more likely to form its structure by this mechanism (39). An assumption can be made, that rheopexy appears because PVB has slightly shorter polymer chains than ethyl cellulose. So PVB flocculates individual BaTiO₃ particles or particle groups without the formation of polymer bridges. This also explains a significant viscosity drop of the binder solution as compared to the cast suspension (fig. 4, b). Shear thickening degree gradually decreases with temperature decrease for all measured S-2 components including tape casting suspension. This behavior is opposite to observed in S-1 casting suspension, probably because of the different structure formed by shorter PVB chains and nanoparticles. Shear-thinning degree increase for all liquids including casting suspension. This happens because cooled liquids are more viscous and more susceptible to shear. Base on this observation, we can assume that with the increase of shear to high values at certain point liquids with different temperatures will thin to a similar viscosity.

Figure 4: Flow (a) and viscosity (b) curves for reference BaTiO₃ nanoparticles suspension in IPA (1), non-plasticized (2) and plasticized (3) Polyvinyl Butyral binder solutions in IPA and S-2 casting suspension (4) with the temperature of 20°

It is interesting, that at a temperature of 5 °C shear-thinning degree is higher than a shear thickening degree. In this case, cooling significantly changes the suspension's flow character. All measured liquids show significant rheopexy degree at temperatures near 20 °C which decreases with cooling. A decrease of rheopexy degree can indicate structure ordering. Strength stress increase with temperature decrease. EDSD show structure destruction prevails at higher temperatures and its gradual decrease with cooling. Prevail of structure restoration only observed in reference suspension and casting suspension at temperatures near 5 °C. Cast suspension tends to the structural equilibrium with a temperature decrease and shows an anomaly increase of destruction at 20 °C (table 3).

Table 3 : Rheological characteristics of S-2 suspension and its components

$T, ^\circ\text{C}$	Viscosity $\eta_0, \text{Pa}\cdot\text{s}$	Shear thickening degree D, $(\eta_{\text{max1}} - \eta_0)/\eta_0$	Shear thinning degree Dn, $(\eta_{\text{max1}} - \eta_\infty)/\eta_\infty$	Thixotropy degree T, Pa/s	Strength stress $\tau_{\text{max}},$ Pa	Equilibrium degree of structure destruction EDSD, r.u.
Plasticized Polyvinyl Butyral binder solutions BS-2						
25	0.073	2.883	0.020	-2.689	260	27.753
20	0.172	1.531	0.030	-2.581	301	11.064
15	0.266	1.382	0.099	-0.182	392	5.977
10	0.297	1.232	0.161	0.249	456	4.544
5	0.702	0.761	0.193	-0.346	535	2.447
Non-plasticized Polyvinyl Butyral binder solutions BS-2						
20	0.177	1.471	0.019	-5.549	329	13.940
15	0.319	0.820	0.113	-1.859	388	4.402
10	0.517	0.442	0.131	-1.015	460	2.840
5	0.799	0.392	0.229	0.933	528	1.671
BaTiO ₃ nanoparticles reference suspension in IPA						
20	0.014	2.544	-	1.924	111	-
15	0.014	2.529	-	-0.878	115	-
10	0.016	2.105	0.024	0.476	120	0.878
5	0.019	1.685	0.050	1.293	123	0.855
S-2 Casting suspension						
25	0.027	4.070	0.064	-4.276	133	4.851
20	0.092	1.128	0.039	-6.253	200	13.535
15	0.142	0.671	0.130	-5.251	276	4.668
10	0.224	0.668	0.146	-1.718	302	3.419
5	0.480	0.146	0.303	-0.082	369	0.965

III.1.c Suspension of BaTiO_3 micropowder in ethyl cellulose binder solution (S-3)

An interesting observation can be made from the flow curves analysis of S-2 (fig. 4) and S-3 (fig. 5) cast suspension. These suspensions based on different polymers and consist of BaTiO_3 particles of different sizes but show a noticeable similarity in flow character. It can be seen in two specific peaks in the first half of the S-2 and S-3 flow curves (fig. 3, b, curve 4 and fig. 4, b, curve 4). The addition of solid particles leads to a decrease in viscosity, reduction of maximum shear stress, and rheopey behavior. A ratio of polymer chain size to particle diameter can be an explanation of the similarity of flow curves. An assumption can be made that a short-chain polymer and nano particles form a floccule that behaves in a flow like a that formed by long-chain polymer and micro particles.

Figure 5: Flow (a) and viscosity (b) curves for the reference BaTiO_3 microparticles suspension in IPA (1), non-plasticized (2) and plasticized (3) Ethyl cellulose binder solutions in IPA and S-3 cast suspension (4) at the temperature of 20 °C

Table 4 : Rheological characteristics of S-3 suspension and its components

$T, ^\circ\text{C}$	Viscosity $\eta_0, \text{Pa}\cdot\text{s}$	Shear thickening degree D , $(\eta_{\max 1} - \eta_0)/\eta_0$	Shear thinning degree D_n , $(\eta_{\max 1} - \eta_\infty)/\eta_\infty$	Thixotropy degree T , Pa/s	Strength stress $\tau_{\max}, \text{Pa}$	Equilibrium degree of structure destruction EDSD, r.u.
Plasticized Ethyl cellulose binder solutions BS-3						
20	0.284	1.011	0.122	-1.341	359	4.087
15	0.475	0.507	0.162	-0.579	424	2.157
10	0.774	0.338	0.250	-0.490	492	1.166
5	1.062	0.281	0.036	0.631	562	1.105
Non-plasticized Ethyl cellulose binder solutions BS-3						
20	0.322	0.467	0.116	-0.388	397	4.462
15	0.650	0.333	0.172	-0.720	476	1.825
10	0.930	0.468	0.267	-0.389	552	1.429
5	1.446	0.292	0.257	-0.230	630	1.088
BaTiO ₃ microparticles reference suspension in IPA						
25	0.009	4.081	-	-1.457	99	-
20	0.009	3.964	-	-1.522	103	-
15	0.010	3.744	-	-0.299	107	-
10	0.012	2.943	-	-0.240	113	-
5	0.015	2.161	-	2.014	118	-
S-3 Casting suspension						
25	0.082	1.500	0.207	-5.731	170	3.089
20	0.169	1.029	0.269	-1.978	198	1.496
15	0.264	0.372	0.466	1.109	251	1.037
10	0.504	0.076	0.609	3.360	312	0.372
5	0.883	0.054	0.985	7.734	377	0.196

The conclusion can be made that the interaction between the polymer and solid-phase particles plays a major role in suspension's structuring and flow. A number and strength of polymer-polymer/polymer-particle bonds and the ratio of particle size to polymer chain length define this interaction. Change of ratio of particle size to polymer chain length can be used as an instrument of obtaining desirable rheological character during suspension preparation, therefore, making the design of desirable flow possible.

According to measured parameters (table 4), suspension S-3 behaves similarly to S-2. The significant difference is observed in the Equilibrium degree of structure destruction parameter which is few times lower for temperatures near 20 °C but the overall tendency to EDSD decrease with cooling is preserved. EDSD for the casting suspension S-3 reaches quasi-equilibrium state at the temperature of 15 °C. As temperature decrease further, a structure restoration begins to prevail.

III.2 Influence of suspension composition on tapes properties

The creation of multilayer devices requires thin layers and a smooth interface between them. The reduction of a tape roughness can be achieved by a decrease of solid-phase particle size. To understand how the suspension composition and particle size influence the properties of the tapes, all three suspensions were cast under similar conditions. The blade gap was set to 100 µm, carrier speed was 0.508 m/min. These parameters equal to the shear rate of 84.66 s⁻¹. The temperature inside the laboratory was thermostatically controlled at 10 °C. Thickness and roughness parameters of all tapes were measures in four points of each sample. 2D and 3D profiles of casted tapes are shown in fig. 6. The table data indicates a minor difference in tape thickness (table 5).

However, particle size has a great influence on tape roughness. Tapes cast from S-3 suspension which consist of micro powders has a *Ra* parameter two times and *Rz* three times bigger than other nanopowder-based tapes. Also, there is a good correlation between the *Ra* parameter and the calculated floccule radius (equation 4). This indicates that the suspension was well dispersed and the tape forms the best surface roughness, corresponding to the size of one nanoparticle.

Table 5 : Casting conditions and tape properties

Suspension name	Tape thickness h , μm	Roughness parameter Ra , nm	Roughness parameter Rz , nm	Floccules hydrodynamic radius a , nm
S-1	4.94	22.17	35.90	11.43
S-2	5.21	24.95	54.43	17.33
S-3	4.85	44.25	124.25	39.57

Figure 6: 2D and 3D profiles of tapes casted from S-1 (a), S-2 (b) and S-3 (c) suspensions

III.3 Influence of suspension temperature on properties of casted tapes

One of the main goals of this work was an establishment of a possibility of using the temperature of suspension during casting as an additional instrument to change the properties of the casted tape. Overall tendencies that share all suspensions and binder solutions are viscosity increase and shear thickening degree decrease with a cooling. While the increase of viscosity is expected, a decrease of shear thickening can be explained by lowering of Brownian motion and overall mobility of suspensions components (long and short polymer chain molecules of binder and surfactant, particles, etc.). Shear-thinning degree increase for the majority of measured liquids (except casting suspension S-1). So, while studied liquids become more viscous with cooling, they also become thinner easily in reaction to applied shear. This behavior is characteristic of liquids with the ability to arrange its structure in the direction of flow (42), (46).

For further studies, the S-1 suspension has been chosen because of its suitable shear-thinning ability, thixotropic flow character, and ability to form tapes with the lowest surface roughness. Also, a high thixotropy degree of S-1 suspension (table 2) indicates the presence of a strong polymer network structure (31), (33), (40).

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The study of S-1 suspension flow curves corresponding to different temperatures has shown more than double increase in viscosity, significant thixotropy degree drop, and maximum shear stress increase between 20 and 5 °C suspension (fig. 7). A great decrease in the thixotropy degree is occurring most likely due to the repetitive mechanical stress rather than temperature change. The first measurement was carried out at 20 °C and time between measurements was not enough for the suspension to restore the initial structure. The increase of maximum shear stress can be explained by the influence of the temperature on the polymer chain. This makes it more rigid and stress-resistant.

An assumption can be made that the suspension at low temperature can preserve the structure that was formed during shearing. At higher temperatures, the structure of the

Figure 7: Flow (a) and viscosity (b) curves for BaTiO₃ suspension S-1 at different temperatures: 1 - 20, 2 - 15, 3 - 10, 4 - 5 °C

suspension will be completely destroyed. To analyze an influence of suspension temperature during casting on tape properties a series of casting experiments were performed. The casting of tapes from S-1 suspension was provided under similar conditions. Suspension temperature was the only variable. For the first series of experiments, a doctor blade gap was set to 200 microns and carrier speed was 0.508 m/min which creates a shear rate of 42.33 s⁻¹. Suspensions were divided into four equal parts of 5 ml and thermostated at temperatures of 20, 15, 10 and 5 °C. The four fragments of green tape with approximately 10x10 cm dimensions were obtained. Thickness and roughness were measured by optical profilometer in three different points of each fragment. The result shows a gradual decrease in tape thickness with temperature decrease (fig. 8).

To achieve a tape thickness below one micron, a high shear was applied to suspensions at temperatures of 25 and 5 °C. These two temperatures were chosen to show clearly the difference between the properties of tapes that have been cast from suspension at near-room temperature and cooled suspension. Also, it is important to study how suspensions with a significant difference in temperature behave under different shear rates.

A blade gap was set to 20 μm , carrier speed was 0.508 m/min what equals a shear rate of 423.33 s^{-1} . Under these regimes, two tapes were cast at 5 and 25 $^{\circ}\text{C}$, respectively. The thickness of the film obtained from pre-cooled suspension was almost two times lower (690 nm for 5 $^{\circ}\text{C}$ suspension against 1210 nm for 25 $^{\circ}\text{C}$ suspension). The surface roughness parameter Ra of the thinner film also decreased to value compared to the size of one nanoparticle (table 6).

Figure 8: Temperature dependences of the tape thickness (a) and roughness (b) for the suspension S-1

To achieve a minimum possible tape thickness a doctor blade gap was set to zero. In this case, liquid suspension due to the action of capillary forces lifts the whole doctor blade during the casting process. To achieve a higher shear stress an additional weight was added to the doctor blade. S-1 suspension with a temperature of 5 $^{\circ}\text{C}$ was cast under this condition. The thickness of tapes near 300 nm is approved by optical profilometry and atomic force microscopy (fig. 9).

This experiment confirms previous research when an effect of the decrease of tape thickness with suspension temperature decrease was noticed and described (1). A suggestion can be made, that this behavior happens due to internal suspension structure deformation that occurs under high shear. Long-chain polymer molecules tend to form floccule structure curling up around small BaTiO_3 particles. Floccules can

be reversibly destroyed under high shear due to the action of hydrodynamic forces. A similar effect of shear rate on the floccule structure can lead to shear-thinning and appearance of yield strength point.

Table 6 : Casting conditions and tape properties

Blade gap, μm	Carrier speed, m/min	Shear stress, s^{-1}	Suspension temperature T , $^{\circ}\text{C}$	Tape thickness h , μm	Roughness parameter Ra , nm	Roughness parameter Rz , nm	Real floccules hydro-dynamic radius a_2 , nm
200	0.508	42.33	20	6.95	25.3	36.9	11.87
			15	6.81	24.0	46.3	14.81
			10	6.42	27.9	39.4	12.60
			5	6.06	28.8	71.2	22.70
20		423.33	25	1.21	45.8	189.8	60.76
			5	0.69	26.0	121.7	38.80
0		-	25	0.52	29.8	115.4	36.91
			5	0.27	24.0	71.5	22.87

At the same time, the decrease in the floccule size has been observed corresponding to the decrease in the resistance of the system to the applied stresses (41). Presumably, under high shear, the molecular chains can be stretched and aligned in casting direction (42) corresponding to the orientation effect observed in suspensions with elongated particles (43), (44), (45), (46), (47), (48). The use of a highly volatile solvent leads to a high viscosity increase during suspension drying. We can assume that the fascination of the stretched structure happens almost instantly. This results in lower tape thickness and surface roughness.

The represented above technique can be used as a new thin tape formation method which involves a suspension pre-cooling. This is a complex process, which combines the movement of particles and macrostructure elements under capillary forces within suspension during the tape casting and the solvent evaporation processes. (49), (50), (51). Because of the valuable advantages inherent in this method, the studies of the physical mechanisms competing through the process should be continued and extended.

Figure 9: 2D profiles of a green tape obtained from pre-cooled S-1 suspension. a – image from the optical profilometer, b – image from the atomic-force microscope

IV. Conclusion

The tape casting method appears to be applicable and effective for producing thin films of barium titanate when using nanopowder suspension and modified casting process. As an alternative to existing micro-powder based suspensions, suspensions based on BaTiO_3 nanopowder have been developed. A combination of nanopowder and the plasticized long-chain polymer solution allows achieving a shear-thinning flow character with four times viscosity decrease under the shear rate of 1000 s^{-1} . Tapes that were cast from obtained suspension shows a decrease of surface roughness parameter R_a twice and R_z parameter up to five times. In addition to the efficiency of nanopowder use, it was found that by the preliminary cooling of the suspension before tape casting a suspension's flow character and tape thickness can be altered. For

thick tapes, lowering the temperature from 20 to 5 °C allows decreasing tape thickness from 7 to 6 µm with other process parameters unaltered. In thinner tapes obtained under high shear stresses, pre-cooling allows obtaining films with a twice lower thickness (from 0,52 to 0,27 µm). Thus, by combining nanoscale functional material, cooling and a high shear rate during casting process, a tape with a thickness of approximately 300 nm and roughness of 20-30 nm was cast, which previously was never reported obtaining by a tape casting method. These results are very promising because it expands the application field of the tape casting method, can simplify and reduce the cost of production of multilayer and functional gradient devices and improve their properties.

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