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L.S. Dzubenko, S.M. Makhno, O.O. Sapyanenko, P.P. Gorbyk

The Influence of High-Dispersed Barium Titanate, in Films With Addition of, and Based on Poly(Vinylidene) Fluoride), on Structure and Electrophysical Properties of Ones

Institute of Surface Chemistry named after. O.O. Chuyko of the National Academy of Sciences of Ukraine,
General Naumov St., 17, 03164 Kiev-164, e-mail: ryash@i.ua

With the aim of creation of effective electret materials, the composite films, based on poly(vinylidene fluoride) (PVF), in addition with segnetoelectric of barium titanate ($BaTiO_3$) were obtained in concentration range of 0.5 – 5.0 %vol. It is established, that presence of $BaTiO_3$, at low content of, leads to increase of crystallinity degree, and, practically, have no influence on, when at content of 1.0 – 5.0 % vol. of. There are PVF's melting temperature range becomes narrower, when at 0.5 – 1.0 % vol. of, and, this pointing on more homogeneous crystallite formation by dimensions in. When at high content (5.0 % vol.) of $BaTiO_3$, there is decrease of crystallization temperature observed (at 5 °C), and then, there is temperature range broadening exists, and this pointing on forming of larger, but less homogeneous crystallites by dimensions in. It is determined, when in composite films of PVF - $BaTiO_3$, that surface charge is more stable at $BaTiO_3$ content of 4.0 %vol. in, and then, one reaches value of $10^{-}6$ Cl/m^2, when at conditions of treatment with electric field and crown discharge, and, at film charge value of 500 kV/m in. There are non-linear dependence of dielectrical permittivity exists, either when at low, or very high frequencies, and this may be linked with influence of high-disperse addition on polymer's crystalline structure formation, and sub-surface layers of one.

Key words: poly (vinylidene fluoride), barium titanate, crystallinity degree, electret, dielectric permittivity, surface charge.

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Introduction

Lately, there are number of polymer electrets uses increasingly – that is, the dielectric materials, those are creating the powerful electric field in the external space around. Those are used in the many life's spheres, from devices for home use to those ones for special purposes, such as electroacoustical devices (the electret-based microphones, surdophones), the electromechanical convertors (the electret-based sound pickupers, the sensor switches, the knock detectors), and the electret-based air filters etc. There is actual the aim for polymer materials improvement, in area of those electret properties in.

There are known several methods to govern to electrophysical polymer properties, including the electret ones of. Those are the additon of disperse fillers to polymer [1, 2], the polymer surface modification with different techniques [3], and blending of different polymers [4]. There is the polymer modification via addition of different nature's fillers, plastifiers, and others of purpose additions, which giving the possibility for governing in composite properties, in the simple way relatively, including to give for those the segneto- or piesoelectrical properties [5] of. There are purposes of work given, when consisting in the formation's and holding features for surface charge determining for composite films, based on PVF, and when those are content-dependently ones from high-disperse addition of barium titanate.

I. The experimental part

There was poly(vinylidene) fluoride-2M(E), made by Kirovo-Chepetz chemical factory (Russia), and one has had chosen for preparation of the electret-based composite films, as polymer in. There was the powder-like barium titanate also, made by Fluka ($BaTiO_3$ content of 98.0 %), and particle size of 3 mkm in.

There were the polymer compositions, of PVF-2M(E) and barium titanate $BaTiO_3$ in, prepared with polymer and disperse addition, with combining through

Table 1

The temperature characteristics for melting, and those for crystallinity degree, in composite films of poly(vinylidene) fluorude — barium titanate

The $BaTiO_3$ contents in compositions, % vol. of	The temperature characteristics for melting, T °C				
	T_1	T_m	T_2	ΔT_m	DC, %
0	126	158	182	56	17.9
0.5	128	162	182	54	19.3
1.0	126	161	180	54	17.8
2.0	125	161	183	58	17.4
3.0	128	160	187	60	17.6
4.0	127	160	186	59	17.6
5.0	128	160	187	59	17.6

Table 2

The temperature characteristics for crystallization, and those for its degree, in composite films of poly(vinylidene) fluorude — barium titanate

$BaTiO_3$ contents in compositions, % vol. f	The temperatures for crystallization, T °C of				
	T_3	T_c	T_4	ΔT_c	DC, %
0	127	122	111	16	22.8
0.5	128	124	113	15	23.3
1.0	128	124	113	15	23.1
2.0	129	124	112	17	22.2
3.0	129	125	112	14	22.8
4.0	130	125	113	17	20.5
5.0	133	127	114	19	21.1

suspension in the ethyl alcohol, and, when at conditions of grinding, in the mortar of porcelain, during 30 min. There were $BaTiO_3$ contents of 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 in. There were mixtures on air at room temperature of 23 ºC dried, during 12 hrs., and then, those were post-dried in the drying hood, at temperature of 80 ºC during 5 hrs. after. There were samples pressed, at temperature of 200 ºC and pressure of 30 MPa, during 5 min., and cooling on air, at one's speed of 9 ºC /min in. There was sample thickness approximately of 200 mkm in.

There were DTA, TG, and DTG curves, and those registered with Q-1500D derivatograph by MOM, Budapest. There were the platinum crucibles used in, and Al_2O_3 as standard also. There were films dispersed, and the probe studying was approximately of 200 mg in. There were thermograms of melting process registered, at heating speed of 5 ºC /min, in the temperature range of room one to 200 ºC, and then the crystallization curves were recorded, at cooling speed of 1.5 ºC/min in.

There were temperatures of melting beginning (T_1), melting itself (T_m), the temperature range for melting (ΔT_m), and those of crystallization beginning (T_3), crystallization itself (T_c), and temperature range of crystallization (ΔT_c). There was the determination error of 2 ºC, for melting temperature and crystallization ones. There was melting enthalpy, determined with known technique [5]. There was calibration of peak squares by p-aminobenzoic acid, with one of 36.3 cal/g, to calculate enthalpy with.

There was crystallinity degree, and one's value calculated in, when proceeding from melting enthalpy of fully crystallized polymer, as follows in equation:

$$A = \Delta H/\Delta H_{cr}\cdot 100,$$

where is ΔH_{cr} as melting enthalpy of fully crystallized polymer, and one's value of 25 cal/g for PVF [6]; H- the melting enthalpy of specimen given.

There were real component (*ε'*) and imaginating (ε") one for complex dielectrical permittivity of composites studied both, and this has performed in UHF range of 8 - 12 GHz, using the interferometer, which is principle-based on RFK2-18 measurer of phase differences, and R2-60 measurer of slacking coefficients for standing waves, by non-electrode technique [7], and when at low frequencies, of 0.1, 1, and 10 kHz [8] – by two-contact one with E7-14 immitance measurer. There was measuring error, and one not exceeding value of 5% in.

There was surface charge density (*σ*), one is determined with non-contact induction technique (the electret vibrations in capacity clearance) [9]. There was setup for, and one combined with two plane and static condensors of covers as themselves in. There were specimens, in the frames fixed on, and those were attached to the mechanical vibrator, which doing harmonical vibrations, directed in destination, from normal one to condensor covers both. There was surface charge of samples determined, by the way of comparation of amplitude voltage, when on the specimen and known calibrated electret both. When using this technique, there was surface charge of PVF films and composites, based on addition of $BaTiO_3$ determined with.

II. The results and discussion

There are temperature characteristics of melting, crystallization processes, and crystallinity degree respectively, when dependently to $BaTiO_3$ content (Table 1 and 2) in.

As it seen from Table 1, there is presence $BaTiO_3$, at low content of (0.5 % vol.), which leads to increase of crystallinity degree in, and, practically, have no influence on this parameter at content of 1.0 – 5.0 % in. There is melting temperature range of PVF becomes narrower, at 0.5 – 1.0 % of addition, and this pointing on forming more homogeneous crystallites by dimensions, explaining with nucleation-forming influence on, by particle surface of addition, when at homogeneous particle dispersion, and, at low content of. There is broadening of melting temperature range observed, at higher addition's content in, of 2.0 – 5.0 % vol., pointing on that, there were crystallites of PVF formed in, and ones are more less homogeneous by dimensions. This can be caused with increase of polymer's macromolecule part, which contacts with surface of disperse addition in, and those having lower mobility in, then, the crystallization process goes at higher temperature, when comparing with pure one, and, it means, at conditions, which are more closely to equilibrium state in. In general, and it is worth noticing here, that introduction of hard and high-disperse addition have not suitable influence on crystallinity degree (DC) of PVF-2M(E) in.

When using DTGA technique, then, there was thermal stability of films, based on PVF-2M(E) and $BaTiO_3$, at heating speed of 10 ºC/min performed also. This is important characteristic to choose the temperature range of electret-forming process in.

As it seen from Table 3, there is $BaTiO_3$ presence decreases the temperature values of thermal polymer stability, however, the temperature for beginning of intensive polymer's part destruction, in the composite based on (390 ºC), is suitably overcomes T_m (160 ºC) of polymer, and, this means that, there is possibly to perform the electret-forming process at temperature, as high as T_{Curie} for $BaTiO_3$ the segnetoelectric (120 ºC), and T_m of polymer in.

There are on Fig. 1, the dependencies of real component for complex dielectric permittivity from $BaTiO_3$ volume content, at low frequencies (a) and ultra-high ones (b) shown.

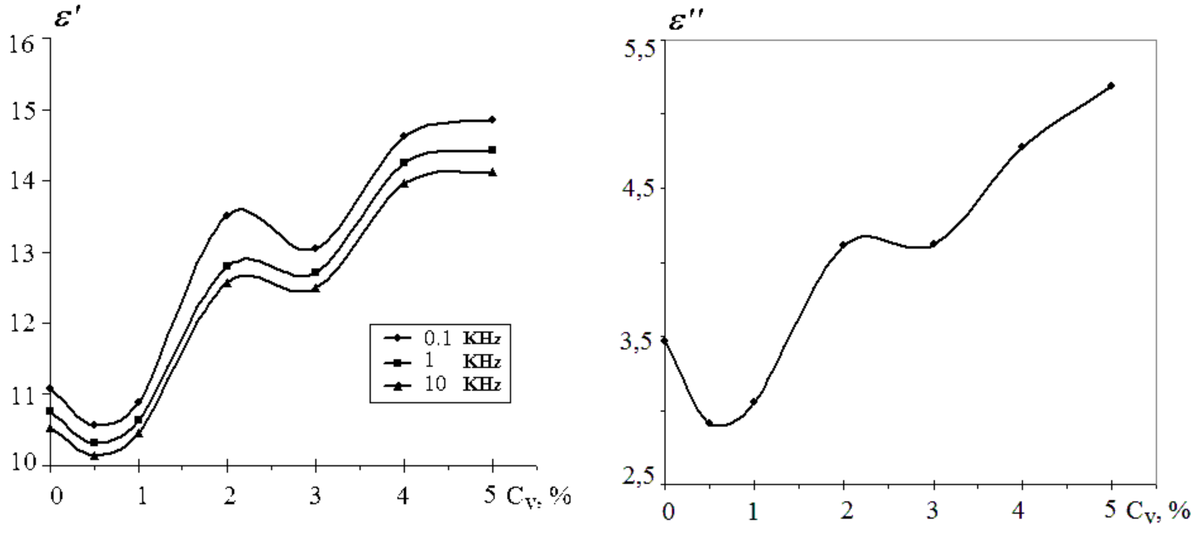
Here it seen that, at low content of hard addition in composite (up to 1% vol.), there is decrease of ε', one is possibly linked with more finely-crystallic structure of its

Table 3

The thermal stability in poly(vinylidene fluoride)-based films

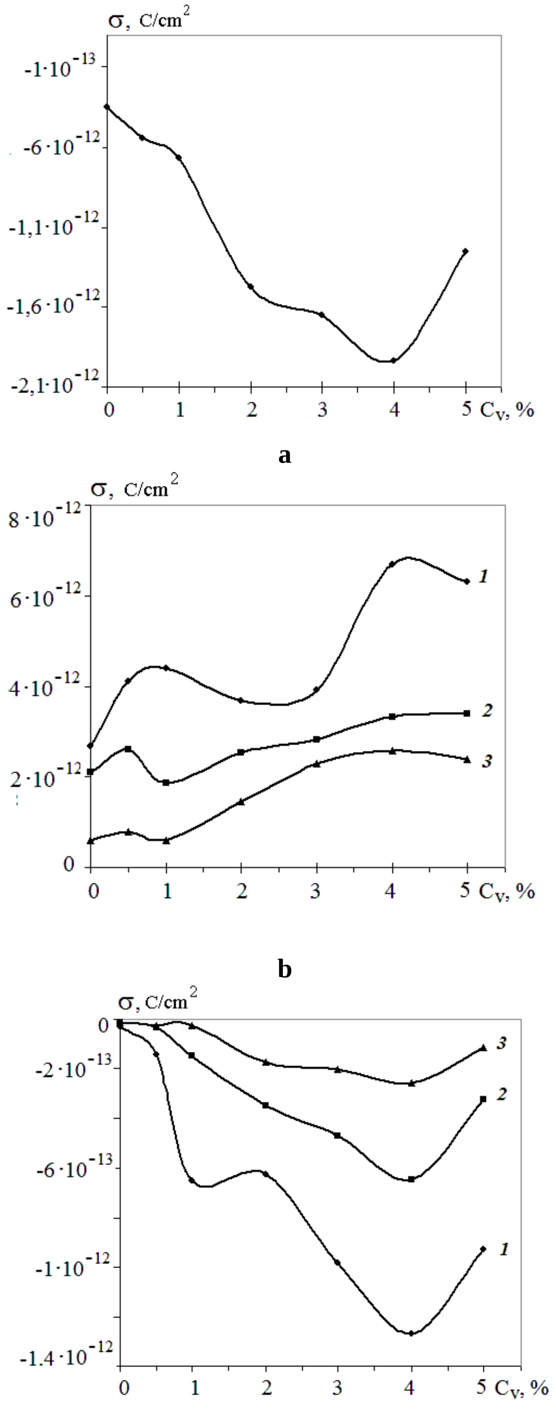
$BaTiO_3$ contents in the compositions, % vol. of	Temperature characteristics for process, T °C in			
	T_{beg}	T_1	T_2	$T_{10\%}$
0	400	485	575	460
0.5	390	480	575	450
5.0	390	440	560	440

T_{beg} — the temperature of beginning for intensive decomposition; T_1 — the temperature of main and (first) destruction's peak by DTG's curve; T_2 — the temperature for second and the same process in; $T_{10\%}$ - the temperature for 10% mass lost of polymer.



a **b**

Fig. 1. The dependence for real part of complex dielectrical permittivity, from value contents of $BaTiO_3$, in films of PVF–$BaTiO_3$,on the low frequencies (*a*) та and those of UHF in 9 GHz (*b*) ones.



a

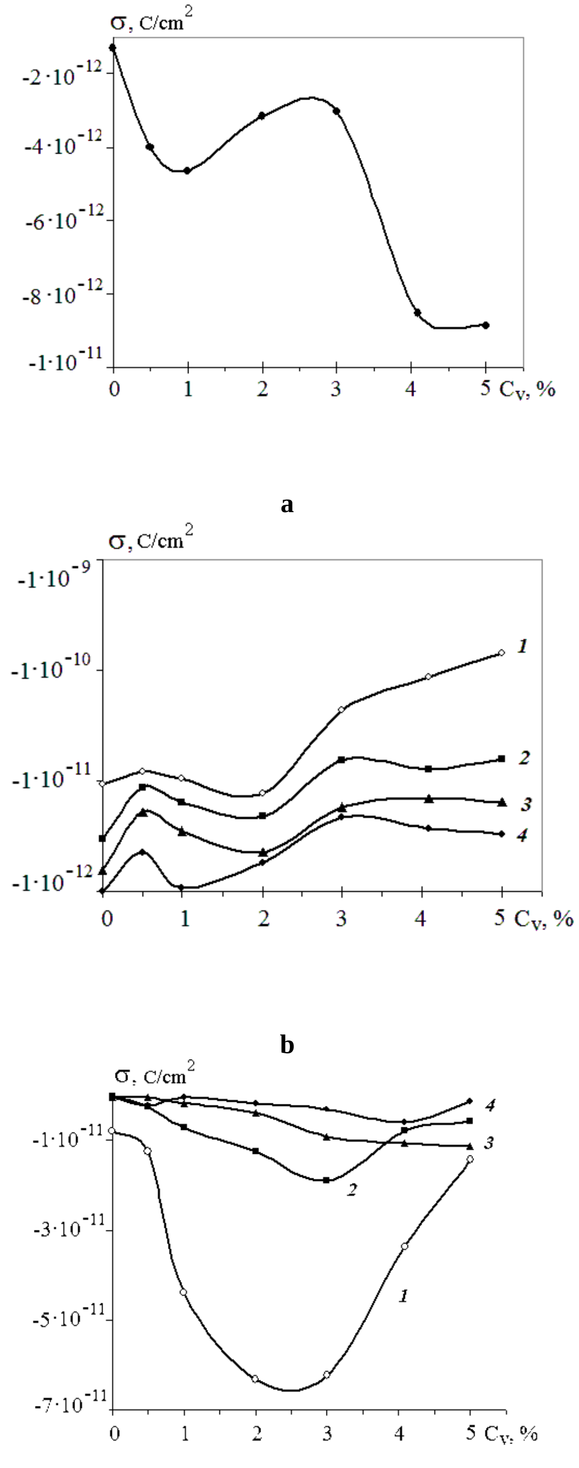
b

c

Fig. 2 The dependence of surfacial charge (σ) for PVF–BaTiO$_3$ films, from BaTiO$_3$ contents, until action of external electric field (*a*), and after that, when at charge with intensity of 0,5 kV/cm of positive (*b*) potential, negative(*c*) one, and at temperature of 22 °C, during 5 (*1*) , 10 (*2*) and 15 min (*3*), after charging off.

films inside. There is further decrease of ε', at conditions of BaTiO$_3$ content's increasing, this linked with structural change on molecular level, and in the amorphous regions of. There is linear dependence, at further increase of addition content (3.0 – 5.0 % vol.), and one induced with contribution of addition itself, so that BaTiO$_3$ have significantly values of ε' in.

As it seen, from data presented here, that initial samples are having surface charge in, when without pre-



a

b

c

Fig. 3 The dependence of surfacial charge (σ) for PVF–BaTiO$_3$ films, from BaTiO$_3$ contents, until act of external electric field (*a*), and the same after, when at charge with crown discharge conditions, with intensity of 5 kV/cm of positive (*b*) potential, negative (*c*) one, and at temperature of 90 °C, during 5 (*1*) , 10 (*2*) and 15 (*3*), and 20*(4)* min after charging off.

treatment with electric field (Fig. 2, *a*) of. There is initial polymer, and one have the lowest values for surface charge (σ), but, possibly, one decreases due to positive and negative charges, in composites of. When after remaining of samples, in electrical field of crown discharge during 1 min, then those surface was charged with positive potential (Fig. 2, *b*), as well as negative one (Fig. 2, *c*). When at room temperature of sample treatment, there are the charges in composite of PVF – 3.0 % vol. $BaTiO_3$ saving more stable ones, and, at positive potential in.

When at sample treatment in electrical field, and at temperature of 90 °C, there the same trend for charge stability after cooling stays (Fig. 3, *b*, *c*), but, there is level for *σ* values increases more, in compare with previous measures, up to 10 degree of value in. There is increase in formation temperature for surface charges, when in crown discharge, making the same for specific charge in polymer composite, and, when after cooling, owing to fixing of charges in.

There is the temperature of pre-heating must be higher one, than those of T_m and segnetolectric's T_{Curie} are, but, then cooling must be performed in the crown discharge of. This is technique, which will give the possibility for polymer-, disperse-, and segnetoelectric-as-filler-based preparation, of stable electret properties itself.

Conclusions

There are poly(vinylidene fluoride)- and segnetoelectric-based (barium titanate) composite films, at concentration range of 0.5 – 5.0 % vol., prepared. It is established, that $BaTiO_3$ presence, when at low content of 0.5% vol., leads to increase of crystallinity degree in, and, practically, have no influence on one, when at content of 1.0 – 3.0% vol. in. There is the temperature range for melting in PVF narrows, at filler concentration of 0.5 – 1.0% vol., pointing on crystallite formation, being more homogeneous ones by dimensions in. When at high content of $BaTiO_3$ (5.0 % vol.), there is increase of crystallization temperature observed, up to 5 ºC, and for temperature range also, pointing on crystallite forming, being larger, but less homogeneous ones by dimensions in. It is detected, that, when in composite films of PVF–$BaTiO_3$, there is surface charge more stable, when at $BaTiO_3$ content of 4.0 % vol., and one reaches value of 10^{-6} Cl/m^2, and when at intensity of electric field of crown discharge of film charge of 500 kV/m in. There is non-linear dependence for dielectrical permittivity, on lower frequencies, as well as on UHF ones, and one can be linked with influence of high-disperse addition on the crystallic structure, and on one in sub-surface layers of polymer in.

Dzubenko L.S. **-** candidate of chemical sciences, senior researcher;
Makhno S.M. **-** candidate of physical and mathematical sciences, head of laboratory of electrophysics of nanoobjects;
Sapyanenko O.O. **-** junior research fellow;
Gorbyk P.P. **-** professor, doctor of physical and mathematical sciences, chief scientist.

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Л.С. Дзюбенко, С.М. Махно, О.О. Сап'яненко, П.П. Горбик

Вплив високодисперсного титанату барію на структуру та електрофізичні властивості плівок на основі полівініліденфториду

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України, вул. Генерала Наумова, 17,
03164 Київ–164, e-mail: ryash@i.ua

З метою створення ефективних електретних матеріалів одержано композитні плівки на основі полівініліденфториду (ПВФ) із сегнетоелектриком титанатом барію ($BaTiO_3$) в інтервалі концентрацій 0,5 - 5,0 об. %. Встановлено, що присутність $BaTiO_3$ за низького вмісту (0,5 об. %) призводить до зростання ступеню кристалічності і практично не впливає на нього за вмісту 1,0 - 5,0 об. %. За низьких концентрацій (0,5 - 1,0 об. %) звужується температурний інтервал плавлення ПВФ, що вказує на формування більш однорідних за розмірами кристалітів. За високого вмісту (5,0 об. %) $BaTiO_3$ спостерігається зростання температури кристалізації на 5 °С та розширення температурного інтервалу цього процесу, що вказує на формування крупніших, але менш однорідних за розмірами кристалітів. Визначено, що поверхневий заряд в композитних плівках ПВФ–$BaTiO_3$ найбільш стабільний за вмісту $BaTiO_3$ 4,0 об. % і досягає значення 10^{-6} Кулон/м^2 при обробці за напруженості електричного поля коронного розряду зарядки плівок 500 кВ/м. Нелінійна залежність діелектричної проникності як на низьких, так і на надвисоких частотах може бути пов'язана із впливом високодисперсної добавки на формування кристалічної структури, а також на будову приповерхневих шарів полімеру.

Ключові слова: полівініліденфторид, титанат барію, ступінь кристалічності, електрет, діелектрична проникність, поверхневий заряд.