

## THE INVESTIGATION OF MORFOLOGY AND CONFORMATION CHANGES OF THE THIN POLYMERIC FILM, FILLED BY THE THIN-DISPERSION FERROELECTRIC PARTICLES

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The separation method of thin-dispersion ferroelectric particles and their input in the crystallizing polymeric matrix have been described. The morphology of the obtained thin polymer composite films have been investigated. It is shown, that the increase of the part of the crystalline  $\beta$ -phase of the polymer matrix is observed at the volume content of the filler up to 15%, but at the high filler content the tendency to the clusterformation takes place. It is established, that clusterformation and conformation changes in PVDF, observed on the lines 840 and 813  $\text{cm}^{-1}$  are interconnected.

### Introduction

The obtaining and investigation of the properties of thin ferroelectric and electro active polymeric films is the actual problem with the aim of their application in the different converters [1-2]. It is known, that the sizes and volume part of filler particles play the determinative role in the process of the formation of composite material structure [3]. With the increase of the particle sizes, the specific surface increases, therefore the peculiarities of the interphase interaction and the size effects are strongly revealed [4-6]. The character of phase transitions changes at critic sizes of the filler or the thickness of the film, or in a particular, the decrease of the particle size leads to the decrease of tangent of dielectric loss angle [5]. It is need to note, that the substrate surface, on which these films have been obtained or treated, influences on the physical state of the thin films essentially. We informed about the influence of the substrate type on the submolecular structure (SMS) and showed, that by the choice of the corresponding substrate one can make dielectric properties of ftopolymers better [6].

The study of the structure peculiarities and properties of the thin polymer composite materials (PCM) with the thin-dispersion ferroelectric fillers (particle diameter  $d < 5 \mu\text{m}$ ) opens the possibility of the revealing of the main regularities of the modification influence of surface and distribution of fillers on the electret and dielectric properties [4-8].

The modification influence of filler on the structure and electroactive properties of PCM have been made by different ways: plasmolysis, nanotechnology, using of the Lengmure-Blodjet technology, selection of solvent and e.t.c. The application borders and realization possibilities of these methods are significantly differed. Moreover, as the analysis of the obtained data shows, the PCM can be created with the definite connectivity, morphology and improved electro active properties at the optimal their combinations in the dependence on the filler dispersion degree and polymer type.

In the present work the method of separation of thin-dispersion particles, the obtaining of the polymeric thin films on the base of the polyvinylidene fluoride (PVDF), filled by the thin- and monodispersion particles of ceramic powders by the PZT-19 type and investigation of their morphology and conformation changes in the dependence on the filler volume content, are described.

### The experimental part

It is known, that the base of the sedimentation particle generation, having different sizes, according to which, particles, precipitating in the viscous medium, have constant

velocity, depending on their sizes is the Stocks law [9]. For the spherical particle this velocity is expressed by the

following form:  $u = \frac{4}{3} \pi r^3 (\rho_m - \rho_l) g / 6 \pi r \eta$ , where

$r$  is particle radius,  $\eta$  is dynamic medium viscosity,  $\rho_m$  and  $\rho_l$  are densities of material particle and liquid correspondingly. At the uniform motion  $u = \text{const} = H/\tau$ , where  $H$  is precipitation height of particle,  $\tau$  is precipitation time. Taking into consideration that  $d = 2r$ , so for the determination of the particle diameter the following formulae is obtained:

$d = \sqrt{18H\eta / g(\rho_m - \rho_l)\tau}$  In the practical aims it is necessary to calculate the precipitation time on the fixed height of the particles, having the different diameters, by the formulae:  $\tau = 18H\eta / g(\rho_m - \rho_l)d^2$ .

It is note that the given formulas are correct for the spherical particles and are applied for the diluted suspensions. For the particles of the irregular form, the representation about equivalent radius is used, corresponding to the radius of the spherical particle velocity.

In our case the separation of the particles by the type PZT-19 was carried out in the dimetylformamide medium (DMF) in the measuring glass of 1l volume. The sampling time in the dependence on the choice of ceramic particle sizes is given on the table 1.

Table 1  
The sampling time in the dependence on the particle size for the suspension DMF/PZT-19

Diameter of particle is less, than $\mu\text{m}$	The sampling depth, $\text{cm}$	The sampling time DMF/PZT-19, sec.
50	10	6
10	10	146
5	10	584
1	10	14600
0,5	10	58400

The polymeric composite films with the thickness  $h < 10 \mu\text{m}$  are obtained by the way of thermal evaporation of 1% solution of polymer PVDF in DMF and colloid ceramic suspension with chosen particles at the temperature 370 K on Al substrate. For the obtaining of the homogeneous degree of dispersion the particles are separated in the opposite order, i.e. the beginning of the small sizes. The ceramic particle

concentration in the colloid suspension with chosen sizes of the particles is found by the weighing of the average trial volume. The mass ratio of the filler and polymeric matrix is obtained by adding of the known volume of the colloid ceramic suspension to the known volume of the polymeric solution. The thickness of the samples is found with the help of the thickness meter IZV-2. The samples are treated by the heat treatment at the temperature 393 K during one hour. The micro photos are taken on the scanning electronic microscope (Nanoscope IIIa, Multimode SPM). IR-spectrums of the samples are investigated in the range 950-750  $\text{cm}^{-1}$  on the spectrophotometer Specord 71JR at the room temperature by the reflection absorption spectroscopy method (RAS). The measurements are carried out at the angles of incidents, which are closed to the normal ones ( $\varphi=10^\circ$ ) in the unpolarised light with the help of special reflection device (Shimadzu, Japan). Polymer films were polarized in the field of Corona discharge at polarization voltage of 7kV at room temperature. The distance between the films and electrode was 10mm, polarization duration 180 sec. Surface potential of the electrets were measured by the vibration electrode method. The surface charge density  $\sigma$  and then charge Q were calculated by the formulae:

$$\sigma = U_c \varepsilon \varepsilon_0 / h,$$

where  $U_c$  is the compensation voltage;  $\varepsilon$ , the relative permittivity of the composite;  $\varepsilon_0$ , the permittivity of the free space, equal to  $8.854 \times 10^{-12} \text{ Fm}^{-1}$ ;  $h$ , is the electret thickness.

### The results and their discussion

Earlier we informed, that the more narrow dispersed distribution of the ceramic particles, and the particles of the size 1mkm [10] also, can be obtained at the exact calculation of the parameters, including in the Stocks equation and at the sampling selection in the opposite order. At the small content of such quazimonosize filler (till 15%), on the data of SEM images, the horizontal and vertical clusters are absent. But at the increasing of the filler concentration till 20%, the aggregation process of the ceramic particles takes place that leads to the cluster formation. SEM images of the composite film with the 20% of the filler volume content is represented by fig.1.

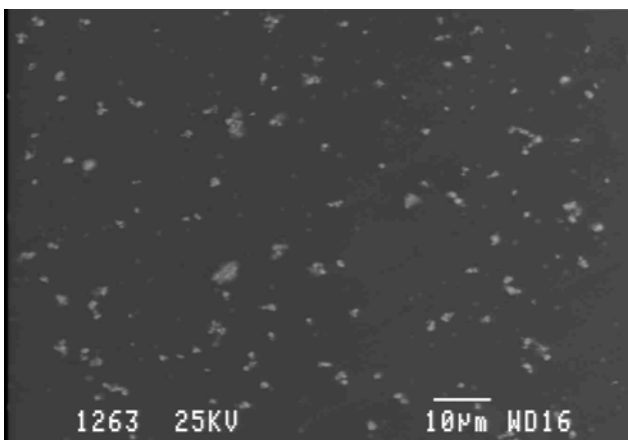


Fig.1. SEM microphotography of the polymeric composite film on the PVDF base and PZT-19 with the particle sizes of the filler  $d \sim 1 \text{ mkm}$  at the volume filler content 20%.

From fig.1 it is seen that particles with the sizes about 1 mkm combine and form the clusters of the form either line chains or lumps. The cluster sizes change from 2 to 10 mkm. SEM images of such a clusters is given in the fig.2.

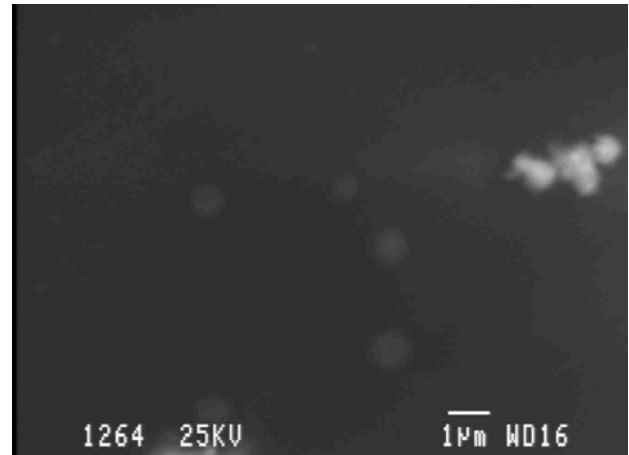


Fig.2. SEM images of the separate cluster of the composite film on the PVDF base and PZT-19 with the particle sizes of the filler  $d \sim 1 \text{ mkm}$  at the volume filler content 20%.

It is seen that the size of this line cluster is about 3 mkm. The appearance of the clusters destroys the morphology of the polymeric film. That's why at increase of filler concentration because of the increase of sum specific surface of the ceramic particles and appearance of the vertical clusters, the composite material with the ratio  $h/d \sim 2$  isn't obtained.

AFM micro photos of free surface and the surface turned to substrate of the composite material with the scanning area  $5 \times 5 \text{ mkm}^2$  on the base PVDF/PZT-19 at 20% of the filler volume content are shown in fig.3 and fig.4.

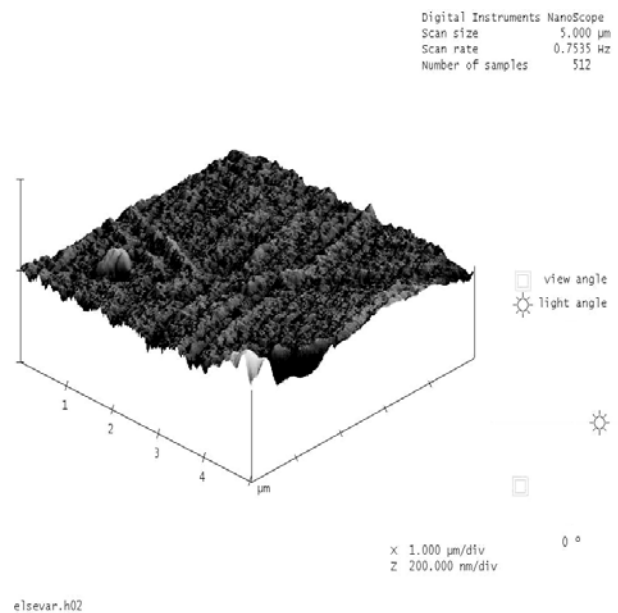


Fig.3. AFM microphotography of the free surface of the composite film PVDF/PZT-19 at the volume filler content 20%.

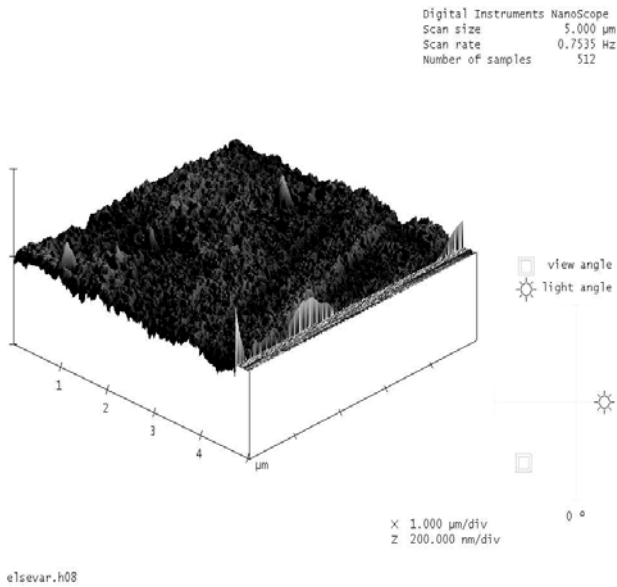


Fig.4. AFM microphotography of the surface, turned to the substrate of the composite film PVDF/PZT-19 at the volume filler content 20%.

From that figures it is seen the formation of the vertical clusters of the ceramic particle in the ledge form that destroys the polymer structures – the ferroelectric particle – polymer. Indeed, these morphological offences will influence on the dielectric properties of the composite as a whole. From the comparison of these images we can see that the surface composite-substrate is rougher than the surface composite-air, i.e. the surface of the substrate also deposit in the formation of the near-surface layer. From the references it is known that the surface tension of the film from side of the solid substrate differs strongly from the surface bounded by air [10]. In this work it is established by authors that the solubility parameter of the near-surface layer differs also from the solubility parameter in the polymer volume that leads to the change of the polymer density in the near-surface region.

Thus, the surface state of the film depends on the volume content of the filler, energetic parameters of the substrate, solubility parameter of the polymer, parameter caused by adhesive properties and etc.. The morphology of the near-surface region formed by such complex method plays an essential role in the formation of a submolecular structure as the polymer film, so the composite material on the base of these polymers and therefore influences on the dielectric properties [6].

The doping of the thin-dispersion filler to the polymeric matrix allows also revealing the structure transformations caused by interphase interactions with the help of IR-spectroscopy. Taking into consideration that the sum of specific filler surfaces causing the interphase interaction between the polymer and the doped particle can purposefully change by the change of the volume content of the filler of the determined size. So it is possible to observe the change of the conformational transformations. The IR-spectrums of the initial film (1) and composite films, filled by the thin-dispersed particles ( $d \sim 1$  mkm) with the volume content 10 (2) and 15% (3) are given in fig.5.

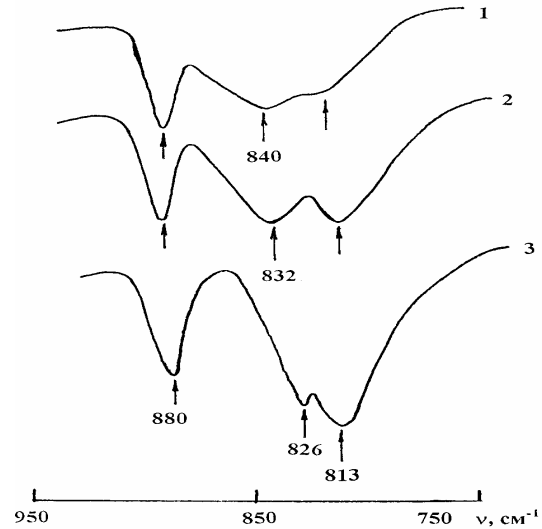


Fig.5. IR-spectrums of the initial film (1) and composite films, filled by the thin-dispersed particles ( $d \sim 1$  mkm) with the volume content  $\Phi=10(2)$  and  $15\%(3)$ .

From fig.5 it is seen that the optical absorption of the conformational sensitive band is  $840 \text{ cm}^{-1}$ , which characterizes the crystal  $\beta$ -phases, increases with the increase of the volume content  $\Phi$ . This increase accompanies with the shifting of the maximum of this frequency and decrease of the half-width. The band  $880 \text{ cm}^{-1}$  is conformational insensitive, but the band  $813 \text{ cm}^{-1}$  characterizes the amorphous phase [10]. The data, reflecting the band changes  $840 \text{ cm}^{-1}$  are given in the table 2.

Table 2  
The change of the parameters of the crystalline  $\beta$ -phase (band  $840 \text{ cm}^{-1}$ ) from the volume content

Sample	Volume content $\Phi$ , %	$D_{840}$	$\nu_{1/2}$ of the band $840 \text{ cm}^{-1}$	$\nu_{max}$ of the band $840 \text{ cm}^{-1}$
1	0	0,025	50	840
2	5	0,05	40	832
3	10	0,065	32	830
4	15	0,075	15	826
5	20	0,068	22	823

The dependence of the optical absorption  $D$  and the half-width of the frequency  $840 \text{ cm}^{-1}$  ( $\nu_{1/2}$ ) on the volume content  $\Phi$  is shown on the fig.6. From the plot it is seen, that both dependencies have the extreme characters. The content of the

crystal  $\beta$ -phase increases and the increase of the crystallinity takes place at the volume content of the filler till 15%. Evidently, the fillers in the form of the thin particles in the polymeric matrix behave themselves as the crystallinity

centers. However, the value of the optical absorption of the frequency  $813\text{ cm}^{-1}$  also increases, that shows the simultaneous appearance of the crystallinity and amorphization processes (growth  $\beta$  and  $\gamma$  phases).

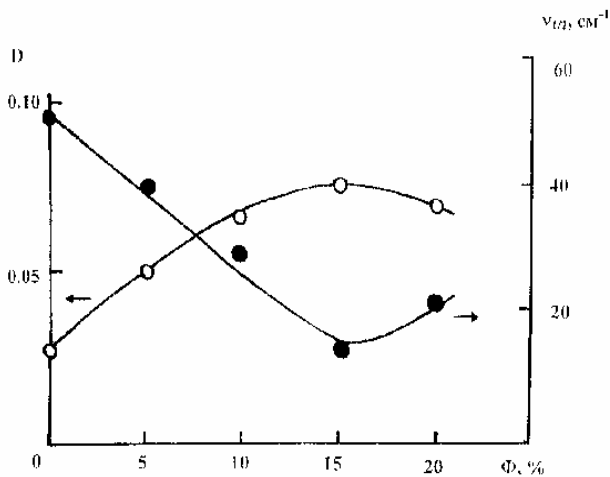


Fig.6. The dependence of the optical absorption  $D$  and frequency half-width  $840\text{ cm}^{-1}$  ( $\nu_{1/2}$ ) on the volume content  $\Phi$ .

The crystallinity change directly influence on the electret properties, in a particular, on the effective electret charge of Corona polarized composite films. The dependence of the relative initial electret surface charge  $Q/Q_0$  on the volume content of the filler  $\Phi$  is given in the fig.7.

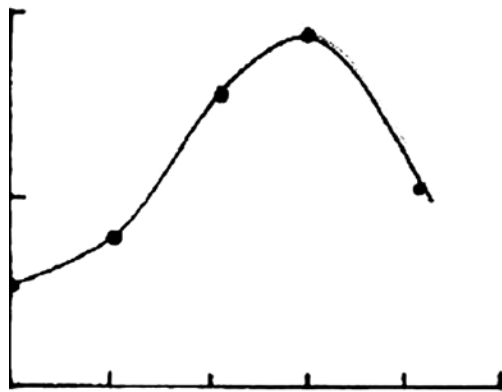


Fig.7. The dependence of the relative initial electret surface charge  $Q/Q_0$  on the volume filler content  $\Phi$ .

From fig.7 it is seen, that the initial electret surface charge achieves its maximum value at the volume content  $\Phi=15\%$ . The comparison of the figures 6 and 7 shows, that the direct correlation, which is proved by our experiments takes place between the crystallinity of the polymer matrix,

volume content of the filler and electret properties of the composite material.

The external form of the dependence of crystallinity on the volume content corresponds to other reference data. In particular, in the work [7] at the studying of the electret properties of polystyrol with the thickness 1,2mm, filled by silicooxides, the extremum dependence of the effective surface charge  $Q$  on the volume content of the filler  $\Phi$  is obtained by authors and is shown that  $Q$  has the maximum value at  $\Phi=12\%$ . This probably can be connected with the change of the conductivity of the surface layer and decrease of the quantity of the polarized polymeric material.

On our opinion, in the case of the thin films, the observable extreme dependence can be explained by the change of the submolecular structure. The near-surface layer forms around the doping particle and it can be proposed that the crystallization process of the polymer takes place in the near-surface layer of this particle. The sum specific surface of the particles increases with the increase of the filler concentration increase that leads to the increase of the polymer crystallization region. However, at the volume content of the filler 20%, as it is seen from the fig.1-4, the clusters form. This is caused the decrease of the sum specific surface of the particles. And in the result, the crystallization region of the polymer decreases. That we can observe on the IR-spectrums.

From the other side, the each particle in the polymer matrix behaves itself as the center of the mechanical stress, acting in the near-surface region, the size of which changes in the dependence on the particle size and filler volume content [11]. These changes cause the change of the mechanical stress in the disperse volume of polymer, that leads to the change of the conformation state. In the work [12], the change of the conformation states, oriented by PVDF films with the width 28 mkm by IR spectroscopy methods the different degrees of deformation, is investigated. These data prove our prediction about the interphase interaction takes place with the help of the mechanical stresses forming in the near-surface layer of the doping particle in the thin filled polymers.

Thus, the separation technique of the thin-dispersed ferroelectric particles with their following doping in the polymer matrix is treated. It is shown, that the surface morphology of the obtained composite materials changes under the influence of the substrate and the change of the filler volume content. By the studying of the conformation changes, obtained by this method of the PVDF films, filled by the thin-dispersed ferroelectric particles it is established, that by the variation of the filler volume content, the content of the crystalline  $\beta$ -phase can be modified and improved of the electret properties of the polymer composite materials. The authors thankful to the scientists of Norwegian University of Science and Technology Kjell Evjen and Tanem S.Bern for realization of SEM and AFM images.

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### **XIRDADİSPERSLİ SEQNETOHİSSƏCİKLƏRLƏ DOLDURULMUŞ NAZİK POLİMER TƏBƏQƏLƏRİNDƏ MORFOLOJİ VƏ KONFORMASIYA DƏYİŞİKLİKLƏRİNİN TƏDQIQI**

Xırdadispersli seqnetoelektrik hissəciklərinin ölçüyə görə ayrılması və onların polimer matrisasına daxil edilməsi üsulu təsvir edilmişdir. Alınan kompozit materialların morfoloji tədqiqatı aparılmışdır. Göstərilmişdir ki, doldurucuların həcm payı 15 % olduqda polimer matrisanın kristallik  $\beta$ -fazasının miqdarının artması və yüksək həcmi faizlərdə isə klasterlərin yaranması müşahidə olunur. Müəyyən edilmişdir ki, PVDF təbəqələrində 840 və 813  $\text{sm}^{-1}$  zolaqlarına görə öyrənilən dəyişikliklər və klasterlərin yaranması qarşılıqlı surətdə əlaqədardır. Göstərilmişdir ki, doldurucuların həcm payını seçməklə elektret xassələrini yaxşılaşdırmaq olar.

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### **ИССЛЕДОВАНИЕ MORFOLOGИИ И КОНФОРМАЦИОННЫХ ИЗМЕНЕНИЙ ТОНКИХ ПОЛИМЕРНЫХ ПЛЕНОК, НАПОЛНЕННЫХ ТОНКОДИСПЕРСНЫМИ СЕГНЕТОЭЛЕКТРИЧЕСКИМИ ЧАСТИЦАМИ**

Описан метод сепарации тонкодисперсных сегнетокерамических частиц и их введение в кристаллизующуюся полимерную матрицу. Исследована морфология полученных тонких полимерных композитных пленок. Показано, что при содержании наполнителя до 15% об. наблюдается увеличение доли кристаллической  $\beta$ -фазы полимерной матрицы, а при высоком содержании наполнителя – тенденция к кластерообразованию. Установлено, что образование кластеров и конформационные изменения в ПВДФ, прослеживаемые по полосам 840 и 813  $\text{cm}^{-1}$  взаимосвязаны. Показано, что электретные свойства могут быть улучшены выбором оптимального значения объемного содержания наполнителей.

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