THERMOPHYSICAL, DIELECTRIC AND CONDUCTIVITY PROPERTIES OF PLASMA-MODIFIED COMPOSITES BASED ON PVDF DISPERSED WITH BATIO$_3$ PARTICLES

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The effect of barrier electric discharge plasma on thermophysical, dielectric and conductive properties of PVDF+BaTiO$_3$ based composite has been studied. It is shown that the enthalpy and entropy of melting and solidification decrease sharply when the filler is included, and a relative increase is observed at a concentration of 20%. At the other concentrations, however, except at 10% and 30%, these physical quantities decrease after exposure to barrier electric discharge plasma. This increase is negligible for pure polyvinylidene fluoride but significant for composites. Also the dielectric permittivity increases with increasing concentration. It is shown that the conductivity first increases with increasing filler concentration, reaches a maximum at 20% concentration and then decreases. After exposure to barrier electric discharge plasma, the dielectric permittivity and conductivity decrease.

Key words: barium titanate, polyvinylidene fluoride, dielectric permittivity; electric conductivity, composite material.
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INTRODUCTION

Polymer-inorganic composite materials with high dielectric constant and low losses, combining viscoelastic properties of the polymer with dielectric properties of the filler, are necessary for the creation of numerous devices. One of the most promising materials of this type are composites based on a segmentoelectric filler - barium titanate. The review article [1] presents data on the permeability of ceramics based on barium titanate with different grain sizes. In this work, the influence of calcined barium titanate powders on the electrical properties of barium titanate/polyvinylidene fluoride composites is investigated. The crystal structure of BaTiO$_3$ powders, piezoelectric and dielectric properties of barium titanate/polyvinylidene fluoride composites were systematised. The results showed that the appropriate calcination temperature of barium titanate fillers could improve the electrical properties of the composites. When barium titanate powders were calcined at 950 0C, the dielectric constant εr and piezoelectric strain constant d33 of barium titanate/polyvinylidene fluoride composites reached the maximum values of 166.38 and 25 pKl/N, respectively, while the dielectric loss tan δ was maintained [2]. The frequency and temperature dependences of dielectric permittivity and electrical conductivity of high-density polyethylene with the addition of monodisperse barium titanate particles were studied. It is shown that dielectric permittivity and electrical conductivity increase with increasing filler concentration at all temperatures. In this case, the conductivity has a hopping mechanism described by the Josher theory. The corresponding parameter of degree index and activation energy decrease with increasing concentration of barium titanate [3].

Electrodischarge plasma modification is one of the most efficient methods compared to other methods requiring vacuum conditions. In the process of electro-discharge plasma treatment, a process of functionalisation takes place on the polymer surface with the formation of various polar groups containing oxygen [4, 5]. Various forms of plasma, including corona discharge plasma [6], barrier discharge plasma [7, 8] and low pressure O$_2$ glow discharge plasma [6], have been used to modify the properties of low density polyethylene film. The results obtained indicate good processing uniformity and improved adhesion properties after these processes. The authors of [9] showed that the electric discharge plasma process leads to the formation of deep traps with high concentration in the electret composite and reduces the probability of local centre ionisation during electrothermopolarisation. In [10], porous polyethylene films were treated with dielectric surface-barrier discharge plasma at atmospheric pressure in oxygen or nitrogen, as well as radio frequency discharge plasma. A noticeable increase in the surface energy and polar component of porous polyethylene films modified by all types of plasma was found. In [11], plasma treatment of coated and uncoated polymer films and particles by plasma is considered. The authors suggest that the threefold difference in the processing rate of films in ammonia plasma is a consequence of their quasi-crystalline structure compared to amorphous polyethylene films. In [12], high density polyethylene (HDPE) with semiconducting or dielectric fillers was prepared by hot pressing method. The results showed that an increase in filler concentration is accompanied by a corresponding increase in thermal conductivity. In [13], the crystallisation of "polymer-segnetoelectric/piezoceramic" composites under the action of electric discharge plasma and temperature was investigated. It is shown that this process leads to strong oxidation of polymer chains. Thus, the method of plasma modification of polymers and composites based on them can find a wide practical application.

The practical application of composites requires a fundamental understanding of the interaction properties between the components. One of the most promising materials are composites based on segmentoelectric barium titanate as a filler. Its particles increase the dielectric constant and electrical conductivity of the polymer [14] and form local electric fields in liquid crystals, improving the switching time [15-19].

The present work focuses on the electrical and dielectric properties of composites before and after plasma treatment.

The present report is devoted to the effect of barrier discharge plasma on the thermophysical, dielectric and electrical conductive properties of PVDF-$BaTiO_3$ composites.

2. MATERIALS AND METHODS

Polyvinylidene fluoride (PVDF) was used as a matrix. The melting and softening temperatures of the polymers are 170-175°C and 140-160°C, respectively. Barium titanate particles of 600 nm (USA, Research Nanomaterials, In.) were added to the fine powder of polyvinylidene fluoride at different concentrations (5 vol%, 10 vol%, 20 vol% and 30 vol%.)).

The resulting mixture was shaken in a vortex mixer for 1 hour at room temperature followed by ultrasonic treatment with a NATO CD-4800 Ultrasonic Cleaner (China) for 4 hours. Disc-shaped composite samples were obtained by hot pressing at 165°C and 15 MPa pressure. The pressing time after reaching the selected temperature is 15-20 minutes. The diameter and thickness of the obtained films were 4 cm and 80-90 μm, respectively. Aluminium electrodes with a diameter of 3 cm and a thickness of 10 μm were pressed on both sides of the films.

Nonthermal non-equilibrium plasma, called surface microdischarges (SMD), has been used as electrical discharges. SMD generation at atmospheric pressure is achieved using dielectric barrier discharge (DBD) technology, which belongs to the corona discharge family. In this case, the electric charge voltage in the cells is 8 kV.

A differential scanning calorimeter DSC 204 F1 (Netzsch, Germany) with a CC200 F1 liquid nitrogen flow-controlled cooling system was used to determine the thermophysical parameters. Argon at 50 kPa was used to purge and protect the cell. DSC204F1 and Proteus Analysis software were used to process the results. The rate of temperature change was 10 deg/min over the temperature range from 200°C to 1500°C. The exposure time was 30 min.

The critical temperature Tcr, at which the composite transitions from one state to another, was determined by the local maximum of heat flux, and the enthalpy change ΔH was determined by the expression:

$$\Delta H = k \cdot \Delta A, \tag{1}$$

where k is characteristic for the given device, A is the area under the corresponding peak. The entropy change ΔS during the transition was determined as:

$$\Delta S = \frac{\Delta H}{T_{cr}} . \tag{2}$$

The degree of crystallinity K was found by the expression:

$$K = \frac{\left|\Delta H_h + \Delta H_c\right|}{\Delta H(100\% cryst)} 100\% \tag{3}$$

where ΔH_h and ΔH_c are enthalpy changes at heating and cooling, respectively; ΔH (100% crystal) is enthalpy change at 100% crystallisation of the matrix. For polyvinylidene fluoride, the enthalpy change at 100% crystallisation was assumed to be 105 J/g.

Dielectric measurements were performed using a Precision LCR Meter 1920 (IET Labs. Inc., USA) in the frequency range of 20 Hz to 1 MHz and at 18°C to 70°C. The applied voltage was 0.5 V. The values of dielectric constant ε were determined as follows

$$\varepsilon = \frac{Cd}{\varepsilon_0 S} , \tag{4}$$

where ε_0 is the dielectric constant of free space, *d* and S are the thickness and area of the sample, respectively. The real ε' and figurative ε'' parts of dielectric permittivity and electrical conductivity σ were calculated by expressions:

$$\varepsilon' = \frac{\varepsilon}{\sqrt{1+D^2}} , \tag{5}$$

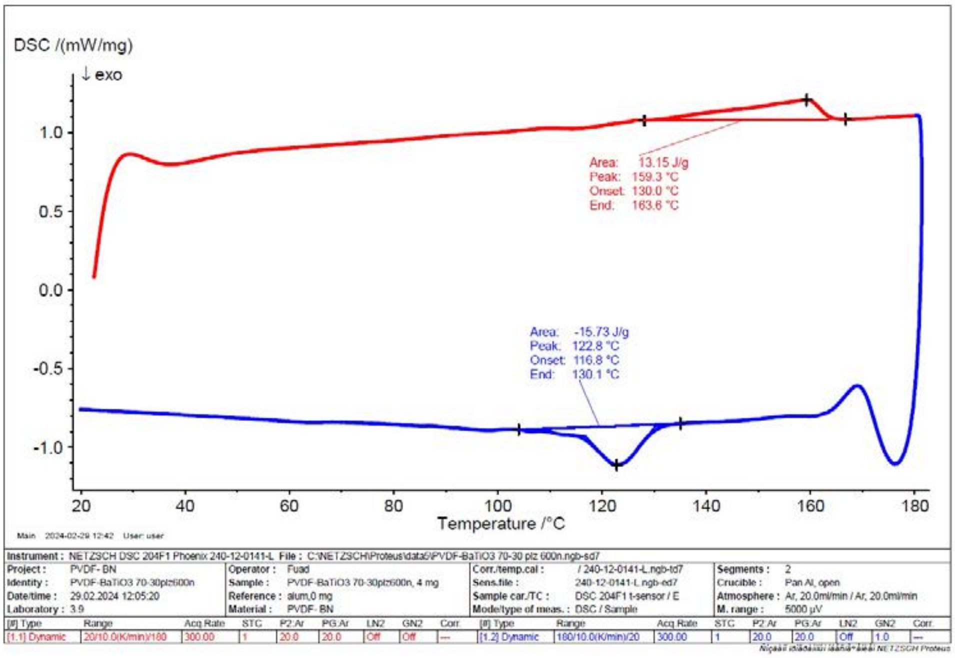
$$\varepsilon'' = \frac{\varepsilon D}{\sqrt{1+D^2}} , \tag{6}$$

$$\sigma = 2\pi f \varepsilon_o \varepsilon'' , \tag{7}$$

3. RESULTS AND DISCUSSION

Figure 1 shows typical dependences of heat flow on temperature (DSC curves). Similar curves are observed for other filler concentrations.

As can be seen, the critical temperature during cooling process is observed at lower temperatures than the critical temperature during heating. This indicates that the composite crystallises at lower temperature. Moreover, the critical temperature decreases with increase in concentration and also after the action of barrier discharge. As the concentration of crystalline $BaTiO_3$ in the composite increases, the crystalline phase also increases. Since the phase transition of the crystalline structure occurs at a lower temperature compared to the amorphous phase, the increase of the crystalline phase also here causes a decrease in the phase transition temperature in the composite.



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Instrument : NETZSCH DSC 204F1 Phoenix 240-12-0141-L File : C:\NETZSCH\Proteus\data5\PVDF-BaTiO3 70-30 plz 600n.ngb-sd7

Project : PVDF- BN
Identity : PVDF-BaTiO3 70-30plz600n
Date/time : 29.02.2024 12:05:20
Laboratory : 3.9
Operator : Fuad
Sample : PVDF-BaTiO3 70-30plz600n, 4 mg
Reference : alum,0 mg
Material : PVDF- BN
Corr./temp.cal : / 240-12-0141-L.ngb-td7
Sens.file : 240-12-0141-L.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / Sample
Segments : 2
Crucible : Pan Al, open
Atmosphere : Ar, 20.0ml/min / Ar, 20.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P2:Ar	PG:Ar	LN2	GN2	Corr.
[1.1] Dynamic	20/10.0(K/min)/180	300.00	1	20.0	20.0	Off	Off	---
[1.2] Dynamic	180/10.0(K/min)/20	300.00	1	20.0	20.0	Off	1.0	---

Fig.1. Temperature dependence of heat flow (DSC curves) for 70% PVDF+30% $BaTiO_3$ composite before and after plasma modification.

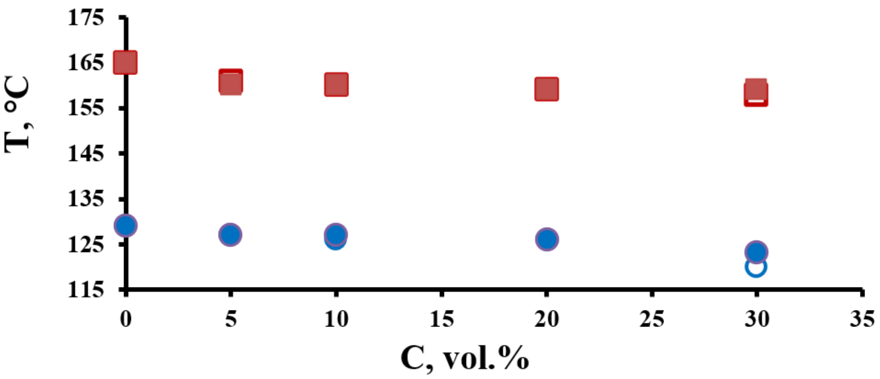

Fig. 2. Concentration dependence of the critical temperature of samples before and after the action of barrier discharge plasma. (empty circles) cooling regime before treatment, (filled circles) cooling regime after treatment; (empty squares) heating regime before treatment; (filled squares) heating regime after treatment.

Figure 2 shows the concentration dependence of the critical temperature of the samples before and after the discharge action.

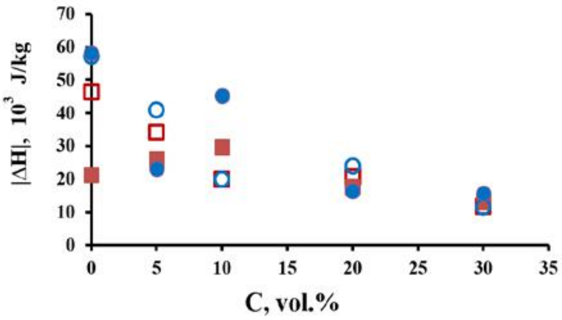

Fig. 3. The enthalpy change as a function of filler concentration: (empty circles) cooling regime before treatment; (filled circles) cooling regime after treatment; (empty squares) heating regime before treatment; (filled squares) heating regime after treatment.

Fig. 3 shows the dependence of the enthalpy of phase transition of samples before and after plasma at heating and cooling on the dispersant concentration. As can seen, with increasing filler concentration in the composite, the enthalpy before and after barrier discharge plasma during heating and cooling decreases. After barrier discharge plasma at heating and cooling processes enthalpy decreases at concentrations of 0, 5, 20% and enthalpy increases at concentrations of 10, 30%.

Fig. 4 shows the dependence of entropy of phase transition of samples on the filler concentration before and after plasma treatment at heating and cooling. As can see, the enthalpy of transition before and after the barrier discharge plasma during heating and cooling decreases with increasing filler concentration in the composite. Moreovere, during the barrier discharge plasma heating and cooling processes, the enthalpy of transition decreases at concentrations of 0, 5, 20% and enthalpy increases at concentrations of 10, 30%.

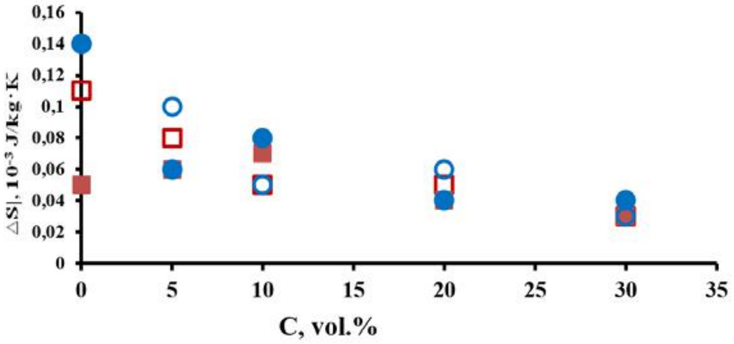

Fig. 4. Entropy change as a function of filler concentration: (empty circles) pre-treatment cooling mode, (filled circles) post-treatment cooling mode; (empty squares) pre-treatment heating mode; (filled squares) post-treatment heating mode.

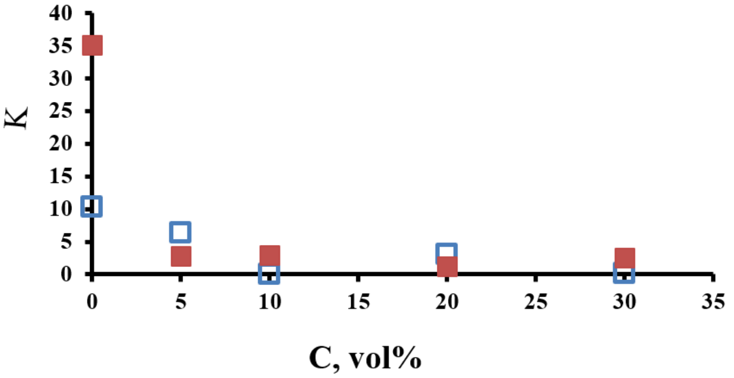

Fig.5. Dependence of crystallinity on dispersant concentration before and after the barrier electric discharge plasma. (empty squares) before treatment; (filled squares) after treatment.

Fig. 5 shows the dependence of the crystallinity on the filler concentration before and after the barrier discharge plasma. It can be seen from here that the crystallinity after plasma increases in pure polymer and composite at filler concentrations of 10 and 30% and decreases at concentrations of 5 and 20%.

The reason why the melting temperature of the polymer and composite is higher than the curing temperature is that the melting process requires the destruction of the ordered structure of the polymer chains, which is energetically more costly than the ordering or crystallisation process during cooling. As the polymer cools, its molecules lose energy and gradually begin to form into a more ordered structure, leading to solidification or crystallisation. This process requires less energy than melting to break down these structures and therefore occurs at a lower temperature.

It is known that the enthalpy of melting of a substance is the energy that is absorbed by the body in the form of heat during the transition from solid to liquid state, and for crystalline substances this occurs without increasing the temperature. It serves to disorganise the intermolecular bonds holding the molecules together. In solidification, the opposite process occurs when heat is removed from the substance. In this case, the intermolecular bonds are restored and the temperature does not change. For crystalline substances, the enthalpy change during melting and solidification has the same value. The degree of crystallinity of polymers is small, so the above laws do not apply to them. Enthalpy is an extensive quantity, i.e. for a composite system it is equal to the sum of enthalpies of its independent parts. Similarly, the enthalpy change of the composite is also the sum of the enthalpy changes of the matrix and filler. When the filler enters the polymer, the intermolecular bonds between individual groups of atoms shift. In particular, the chains in the macromolecule of the polymer are broken. As a result, less energy is required to completely disorganise the polymer chains, i.e. the enthalpy of fusion is significantly reduced. Further increase in the concentration of crystalline filler leads to a slight increase in enthalpy, as more energy is required to break the bonds in a larger volume of filler. A similar process occurs during solidification of the composite.

The entropy of melting and solidification is a measure of the disorder in the material accompanying melting or solidification, not only in the sense of changes in the arrangement of atoms and their configuration, but also in the sense of changes in the nature of chemical bonds. The higher value of the entropy of solidification compared to the entropy of melting is explained by the more ordered state of the composite in the solid phase during cooling. This is also consistent with the lower transition temperature. The entropy and enthalpy of transition are interrelated and their variation with concentration is explained in a similar manner.

These considerations agree well with the experimental curves of enthalpy and entropy change as a function of concentration. It is evident that the overall degree of crystallinity of composites increases with increasing volume of crystalline filler.

The barrier discharge plasma technique used modifies the composite not only on the surface but also in the volume [6, 7]. This type of discharge is accompanied by the formation of accelerated electrons and ions, recombination radiation, active gas products and the occurrence of surface electron-ion effects [11]. The process occurs as a result of polymer chain rupture, which allows such phenomena as cross-linking, free radical formation, etc. to occur, dramatically affecting the final characteristics of polymeric materials. The surface of composites can oxidise when exposed to oxygen environment. According to [14-15], as the concentration of oxygen atoms increases, additional oxidised species appear. In particular, ketone [-(C=O)-] and acetal [-(O-C-O)-] carbons are formed, and the latter is a carboxyl [-(C-O)-O-] carbon. The formation of new bonds favours the increase in the crystallinity of the composite. This is consistent with the experimental concentration-dependent crystallinity curves. At the same time, the decrease in the degree of crystallinity before and after treatment is due to the decrease in the volume fraction of polyethylene with increasing filler volume concentration.

The reason why the melting temperature of both polymer and composite is higher than its curing temperature is that the melting process requires the destruction of the ordered structure of the polymer chains, which is energetically more costly than the process of ordering or crystallisation on cooling. . As the polymer cools, its molecules lose energy and gradually begin to organise themselves into a more ordered structure, leading to solidification or crystallisation. This process requires less energy than melting to break down these structures, so it occurs at a lower temperature.

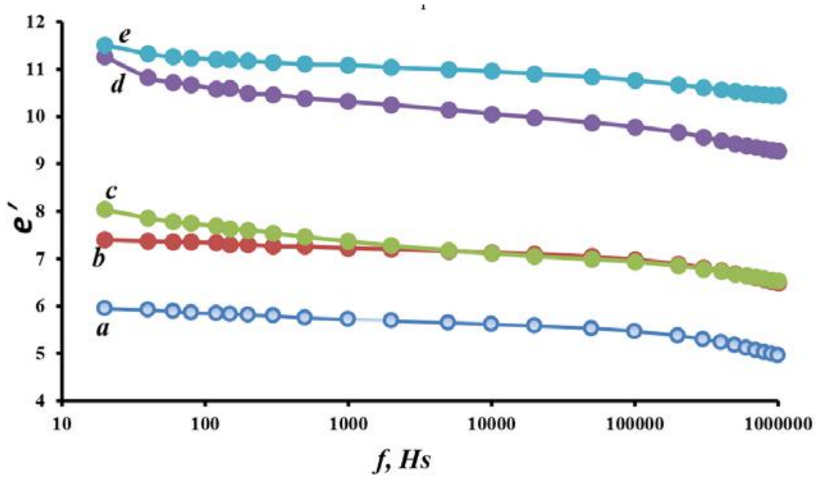

Fig. 6. Frequency dependences of real part of dielectric permittivity before treatment: (*a*) pure PVDF, (*b*) PVDF+ 5 vol.% filler, (*c*) PVDF+ 10 vol.% filler, (*d*) PVDF+ 20 vol.% filler, (*e*) PVDF+ 30 vol.% filler.

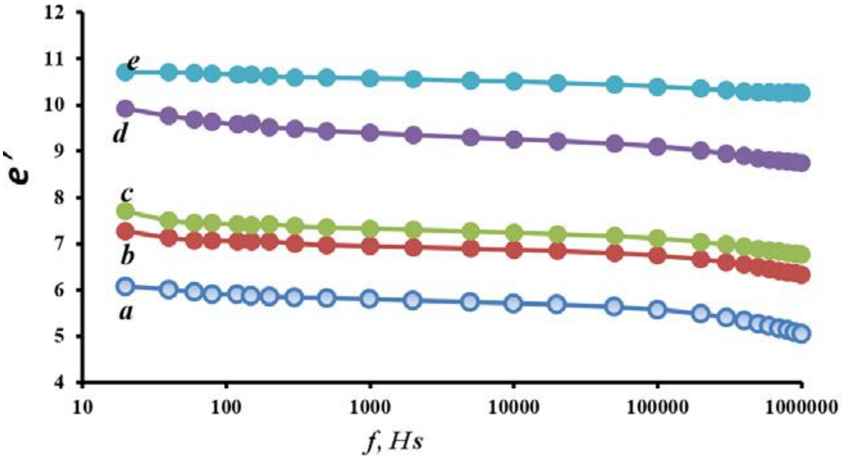

Fig. 7. Frequency dependences of real part of dielectric permittivity before treatment: (*a*) pure PVDF, (*b*) PVDF+5 vol.% filler, (*c*) PVDF+ 10 vol.% filler, (*d*) PVDF+ 20 vol.% filler, (*e*) PVDF+ 30 vol.% filler.

Figures 6 and 7 show frequency dependences of real parts of dielectric permittivity of samples before and after the action of barrier discharge. It can be seen from the figures that with increasing filler concentration the real part of dielectric permittivity of the samples increase. As the frequency increases, these values relatively decrease. As can be seen from this figure, the dielectric permittivity of the composites decrease with increase in frequency. Since the matrix we used is a polar dielectric, this change in the dielectric permittivity is due to the decrease in the number of polarized particles.

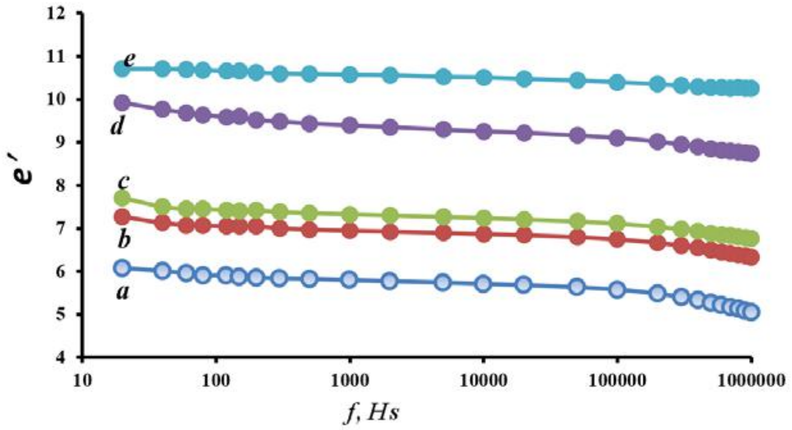

Fig. 8. Frequency dependences of real part of dielectric permittivity after treatment: (*a*) pure PVDF, (*b*) PVDF+ 5 vol.% filler, (*c*) PVDF+ 10 vol.% filler, (*d*) PVDF+ 20 vol.% filler, (*e*) PVDF+ 30 vol.% filler.

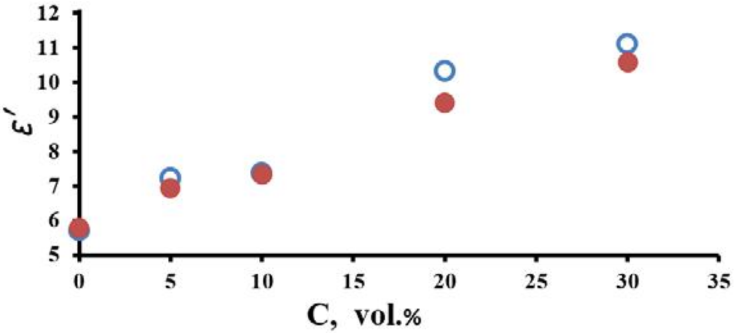

Fig. 9. Concentration dependence of real part of dielectric permittivity of samples before and after barrier discharge plasma at 1 kHz: (empty circles) before the discharge action, (filled circles) after the discharge action.

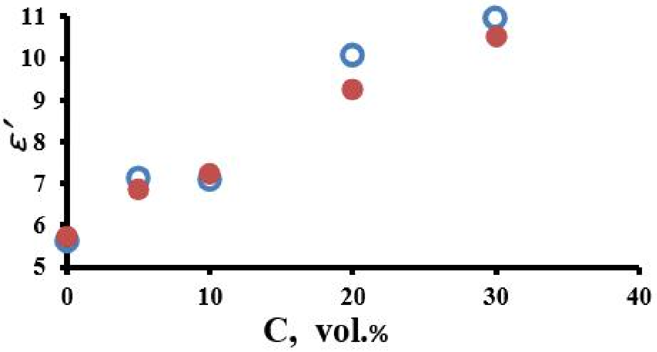

Fig. 10. Concentration dependence of real part of dielectric permittivity of samples before and after barrier discharge plasma at 10 kHz: (empty circles) before the discharge action, (filled circles) after the discharge action.

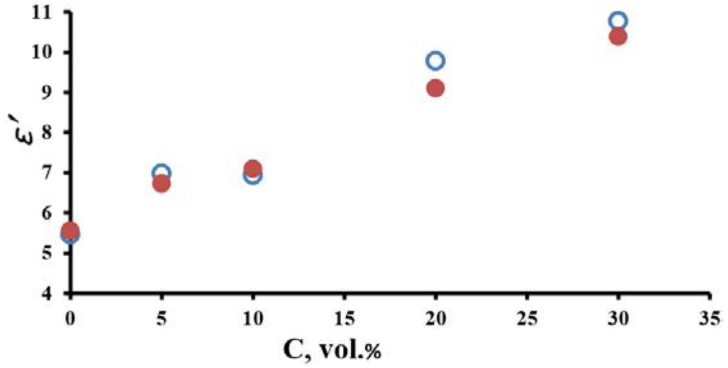

Fig. 11. Concentration dependence of real part of dielectric permittivity of samples before and after barrier discharge plasma at 100 kHz: (empty circles) before the discharge action, (filled circles) after the discharge action.

Figures 9-12 show the real parts of dielectric permittivity of samples before and after plasma treatment at 1 kHz, 10 kHz, 100 kHz and 1 MHz as a function of concentration. It can be seen from the figures that the dielectric constant increases after plasma in pure polymer. As the concentration of filler in the composite increases, the real value of dielectric constant after plasma decreases. When the pure polymer is exposed to plasma, oxygen-containing groups are formed in the air layer. Exposure of barrier electric discharge plasma leads to a decrease in dielectric permittivity of all samples, which is due to the change in the structure of the samples with the formation of new structural elements.

Figure 13 shows the frequency dependence of the conductivity of PVDF+10%$BaTiO_3$ composite before and after plasma. The figure shows that the conductivity decreases after plasma, and with increasing frequency the conductivity increases.

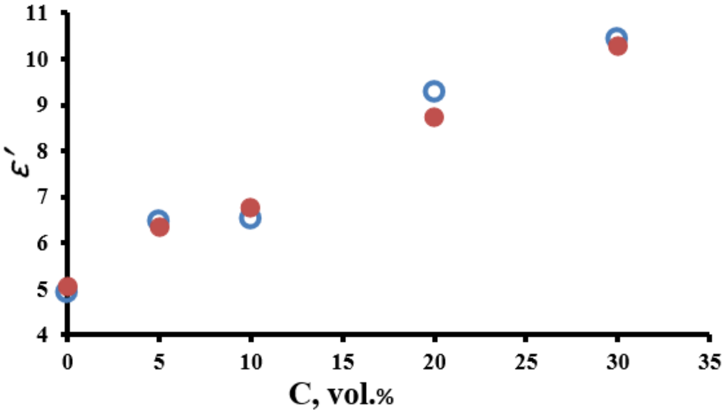

Fig.12. Concentration dependence of real part of dielectric permittivity of samples before and after barrier discharge plasma at 1 MHz: (empty circles) before the discharge action, (filled circles) after the discharge action.

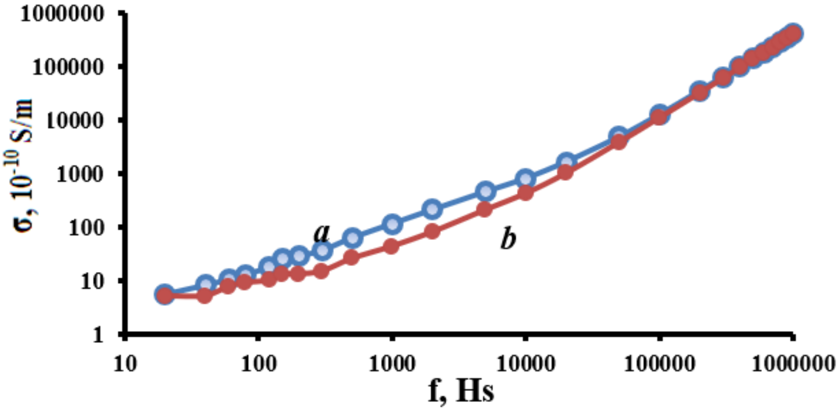

Fig. 13. Frequency dependence of the electric conductance for the composite with 10 vol.% filler: (*a*) before gas discharge treatment, (*b*) after gas discharge treatment.

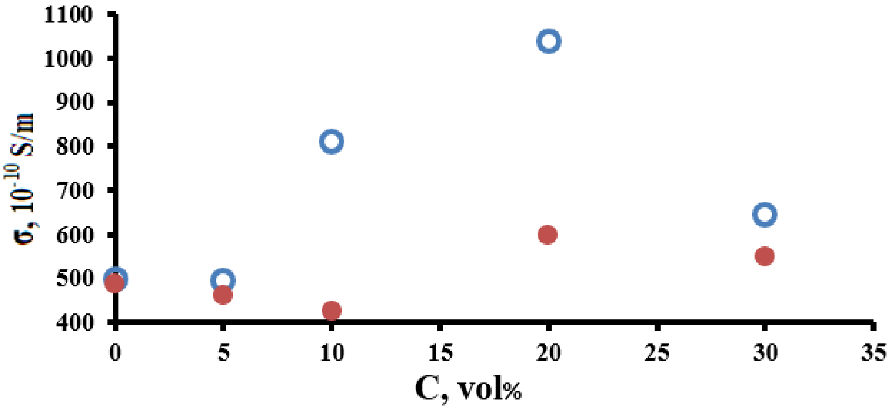

Fig. 14. Composite conductivity as a function of filler concentration at 10 kHz: (empty circles) before gas discharge treatment, (filled circles) after gas discharge treatment.

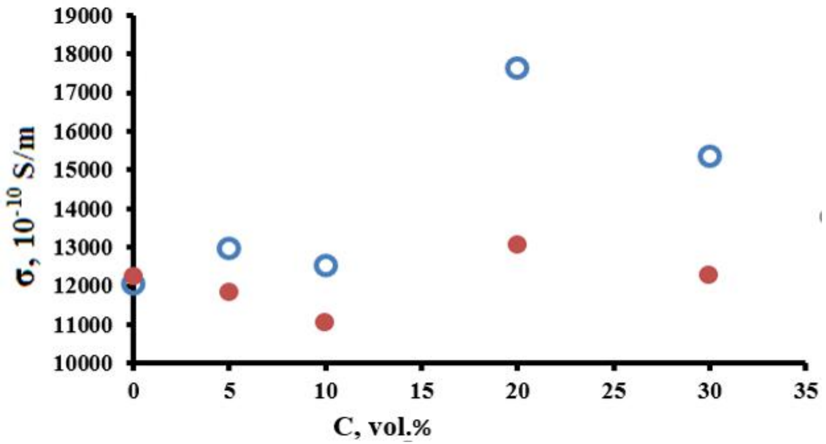

Fig. 15. Composite conductivity as a function of filler concentration at 100 kHz: (empty circles) before gas discharge treatment, (filled circles) after gas discharge treatment.

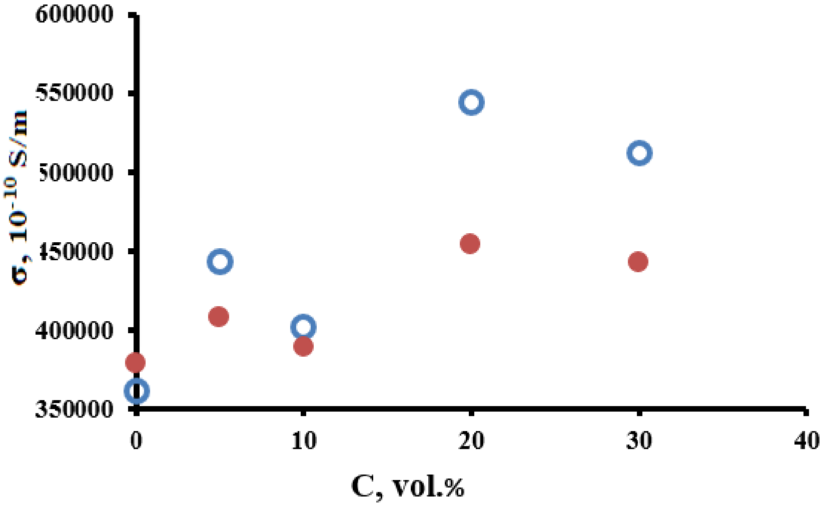

Fig. 16. Composite conductivity as a function of filler concentration at 1 MHz: (empty circles) before gas discharge treatment, (filled circles) after gas discharge treatment.

Figures 14-16 show the concentration dependences of the conductivity of samples before and after plasma at frequencies of 10 kHz, 100 kHz and 1 MHz. From here it can be seen that the conductivity of pure polymer decreases after barrier discharge plasma. As the dispersant concentration increases, the permeability decreases after the plasma. Also as the concentration of dispersant increases, the conductivity of samples before and after plasma first increases, reaches a maximum at 20% concentration and then decreases. When pure polymer is exposed to plasma, the crystalline phase of the polymer increases and the electrons of this phase contribute to the increase in conductivity. When exposed to barrier electric discharge plasma, the oxygen-containing groups formed in the air gap lead to the formation of new traps in the polymer phase [11-15]. These traps impede the movement of electrons and the conductivity decreases.

CONCLUSIONS

It has been found that when $BaTiO_3$ is added to PVDF, the enthalpy and entropy of the phase transition and the crystallinity decrease as the filler concentration increases. This is due to the increase in defectivity of the sample as the concentration increases and the thermal energy required for the transition from one phase state to another decreases. As the filler concentration increases before and after the plasma, the real part of dielectric permittivity of the samples increases, As the concentration of filler in the polymer matrix increases, the number of defects in the sample increases as well as after the action of the discharge. These defects act as traps for charge carriers. As a result, the conductivity decreases.

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[1] *T.D. Ibragimov, I.S. Ramazanova, G.Kh. Guseynova, U.V. Yusifova, A.F. Nuraliyev.* Dielectric properties of polyethylene doped with barium titanate particles. AJP Fizika, 2022 28(1), pp.43-45.

[2] *Rui Li, Zhenhua Zhao, Zixuan Chen, and Jianzhong Pei.* Novel $BaTiO_3$/PVDF composites

with enhanced electrical properties modified by calcined $BaTiO_3$ ceramic powders. Mater. Express, Vol. 7, № 6, 2017, pp.536-540.

[3] *T.D. Ibragimov, I.S. Ramazanova, G.Kh. Guseynova, U.V. Yusifova, A.F. Nuraliyev.* Dielectric and conductivity properties of polyethylene doped with barium titanate particles. UNEC Journal of Engineering and Applied Sciences Vol. 2, № 1, 2022, pp. 5-12

[4] *Novak, M. Steviar, A. Popelka, I. Chodak, J.Mosnacek, M. Spırkova, I. Janigova, A.Kleinova, J. Sedliacik, M. Slouf.* Surface Modification of polyethylene by diffuse barrier discharge plasma. J. Polym. Engineering and Sci. 53 (3), 1, 2012, pp.

[5] *W. Kun, L. Jian, R. Chunsheng, W. Dezhen, W.Younian. Surface* modification of polyethylene (PE) films using dielectric barrier discharge plasma at atmospheric pressure. J. Plasma Sci. and Technol. 10 (4), 433, 2008.

[6] *J.M. Grace, L.J. Gerenser.* Plasma treatment of polymers, J. Dispersion Sci. Technol. 24, 305, 2003.

[7] *S. Guimond, M.R. Wertheimer*. Surface degradation and hydrophobic recovery of polyolefins treated by air corona and nitrogen atmospheric pressure glow discharge, J. Appl. Polym. Sci. 94 (3), 1291, 2004.

[8] *L. Paralı.* The electret effects of crystallized polymer–ferropiezoelectric composite under electric discharge plasma, J. Electrostatics. 76, 89, 2015.

[9] *Novák, G.K. Elyashevichb, I. Chodák, A.S. Olifirenko, M.Števiar, M.Špírková, N. Saprykina, E. Vlasova, A. Kleinová.* Polymer matrix of polyethylene porous films functionalized by electrical discharge plasma, European Polym. Journal 44, 2702, 2008.

[10] *F.Arefi-Khonsaria, M. Tatouliana, F. Bretagnola, O. Bouloussab, F. Rondelez.* Processing of polymers by plasma technologies, J. Surface & Coatings Technol. 200, 14, 2005. DOI:10.1016/j.surfcoat.2005.02.184

[11] *M. Tahara, N.K. Cuong, Y. Nakashima.* Improvement in adhesion of polyethylene by glow-discharge plasma. Surface and Coatings Technol. 174–175, 826, 2003.

[12] *R. Morent, N. De Geyter, T. Jacobs, S. Van Vlierberghe, P. Dubruel, C. Leys, E. Schacht.* Plasma-polymerization of HMDSO using an atmospheric Pressure dielectric barrier discharge plasma process Polym. 6 (1), 537, 2009.

[13] *M.A. Kurbanov, V.A. Gol'dade, S.V. Zotov, I. S. Ramazanova, A.F. Nuraliev, F.F. Yakhyaev, U.V. Yusifova, B.G. Khudayarov*. Generation of craze-formation centers in polymer films under the action of electric discharge plasma. Technical Physics 63(7), 965 (2018).

[14] *M.A. Kurbanov, I.S. Sultanakhmedova, É.A. Kerimov, Kh.S. Aliev, G.G. Aliev, G.M. Geidarov.* Plasma crystallization of polymer–ferroelectric/piezoelectric ceramic composites and their piezoelectric properties. Physics of the Solid State 51(6), 1223, 2009.

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