

**EFFECTS OF ELECTRIC DISCHARGE PLASMA TREATMENT ON THE
POLYMER COMPOSITES****F.N. TATARDAR^{1,2}**1. *Khazar University, Mahsati Str. 41, AZ 1096, Baku, Azerbaijan*2. *Institute of Physics, Azerbaijan National Academy of Sciences,**H. Cavid Ave. 33, AZ1143 Baku, Azerbaijan**E-mail: farida.tatardar@khazar.org*

The actual problems of developing nanocomposites using gas discharge plasma in a dielectric system-dielectric-air gap -dielectric cylinder with a polymer solution are considered. In the conditions of simultaneous action of electric discharge plasma, temperature and nanoparticle ejection into the polymer solution, immobilization of nanoparticles was carried out. The effects of the electric discharge plasma process and the filler content (volume fraction) on the thermal conductivity, volt-ampere characteristics, thermally stimulated depolarization current, as well as electrical and mechanical strength were investigated. The results of the study indicate that, with increasing filler volume fraction, the thermal conductivity of the samples also increased. Furthermore, the thermal conductivity, and electrophysical and mechanical properties of the high-density polyethylene +70% *BN* composite modified using the electric discharge plasma showed improvement when compared with that without electric discharge plasma treatment.

Keywords: Thermal conductivity, polymer-composites, electric discharge plasma.**PACS:** 32.30.Rj. 33.20. Lg, 42.62.Fi.**INTRODUCTION**

Nowadays, with the increasing use of microelectronic circuits, overheating of electronic components has become an important issue. Such overheating must be distributed efficiently and quickly, therefore requiring that materials such as packaging materials, the circuit board, heat exchangers, and machinery must have good thermal conductivity, in addition to their traditional physical and mechanical properties [1–3]. As electronic systems require fast and efficient signal distribution, these materials should have high thermal conductivity, high electrical resistance, and low dielectric permittivity and loss tangent values [4]. Polymers such as high-density polyethylene (*HDPE*), polypropylene (*PP*), polyvinylidene fluoride (*PVDF*), and polyvinylchloride (*PVC*) are widely used in electronic systems, but their thermal conductivity and high thermal expansion coefficient limit their use in many applications. By addition of fillers to such plastics, their thermal behavior can be significantly improved. To produce polymers offering both thermal conductivity and electrical insulation, various thermally conductive fillers, such as diamond, boron nitride (*BN*), aluminum nitride (*AlN*), silicon carbide (*SiC*), and mica, have been used as doping materials to improve polymer-based composites [5–9]. The thermal conductivity of polymer-based composites is influenced by the filler packing density [10], particle size and size distribution, [11,12] surface treatment [13], and mixing method [14]. The degree of surface dispersion of the filler particles determines their interaction with the polymer, also determining the thermal conductivity of the system. Strong surface interaction between polymer and filler increases the thermal conductivity of the system while also reducing the interfacial thermal resistance value under a heat flux. Enhancing the

thermal conductivity coefficient through an increase of 50% in the volume content of the filler within a polymer-based composite contributes to the total thermal conductivity of the composite system. It may be possible to manufacture suitable thermally conductive dielectrics by using polymers with metal nitrides and carbides, which have unique structural, thermal, electrical, and mechanical properties. This approach relies on the structural, thermal, and electrophysical properties of the individual phases at the interface of the polymer with the metal nitride/carbide particles within such thermally conductive composites. To date, although these properties have not been fully investigated either theoretically or in terms of practical use, they have contributed to determining the thermal conductivity mechanism under an electric field. It is necessary to obtain reliable information regarding the electronic and electrical features of deep interfacial traps (localization centers of electric charge carriers) through phase interfaces in the polymer composite phase. Obtaining information about the above-mentioned phenomena could contribute to understanding of the thermal conductivity through the boundary between the polymer and the dispersant filler particles. The structure of the interphase boundary changes the thermal and dielectric properties of the polymer composite and improves the material production technology. Our aim in this work is to study the thermal, electrophysical, and mechanical properties of such polymer composites. The main goal is to obtain new information about the interfacial interactions, boundary effects, and electrical and electronic properties at the interfaces at the local level in the Quasi forbidden band of the polymer phase under electric discharge plasma treatment. One of the most important areas of investigation of the interface for both polycrystalline semiconductors and dispersed polymer

composites is the volt-ampere characteristics (VACs) obtained at different temperatures [15–17]. Analysis of resistors (thermistors) [18] and thermal activation [19] provides new opportunities to define high thermal and dielectric properties of the composite. VAC values thermally stimulated depolarization (TSD) currents, and thermistor effects allow one to identify thermal formation features that preserve the mechanical, electrophysical, and dielectric characteristics of the polymer + inorganic filler composite in a highly heterogeneous system. In this study, the heat-transfer features in the composite including a polymer with metal nitrides and carbides are defined under an electric discharge plasma, and a new thermally conductive composite with high thermal conductivity coefficient, and electrical and mechanical strength is also investigated.

MATERIAL AND METHODS

The polymer matrix was chosen based on its ability to form an interface layer with the inorganic fillers. The polarity of the polymer matrix and its preparation significantly affect the physical and chemical properties of the composite interface. Nonpolar polymers are characterized by strong covalent bonding and flexible macromolecules and have less interaction with the filler surface. Therefore, the physical structure of the polymer phase in the polymer + filler composite is not relevant. Polar and nonpolar polymers play very important roles in the thermal and electrical properties of composites. Furthermore, the polar or nonpolar nature of the polymer molecule allows the appearance of donor-acceptor bonds on the surface of the dispersed filler particles. The choice of the organic phase depends on the thermal conductivity and electronic conditions of its particle surface, which define the interfacial chemical bonding. In this study, thermally conductive composites were made with a structure containing at least two constituents. One of them is the matrix of a polymer such as *HDPE* or *PP*, while the other is the semiconductor or dielectric filler, such as aluminum nitride *AlN* (100W/mK), aluminum oxide Al_2O_3 (29W/mK), titanium carbide *TiC* (29W/m K), titanium nitride *TiN* (44 W/m K), boron nitride *BN* (300 W/m K), silicon nitride *Si3N4* (32W/mK) or titanium carbonitride *TiCN* (30W/mK). The polymers and fillers were chosen to improve the electrical, mechanical, and dielectric properties of the thermally conductive composites. The processing of the thermally conductive composites was as follows: 1. For composites whose powders were not modified by the electric discharge plasma process: Composites with 20% to 70% filler content were produced in disc and cylinder form with different dimensions by the hot-pressing method at high temperature (550K) and pressure (30MPa to 100MPa) by simultaneously mixing the polymer and filler with a pressing time of 15 min. The resulting thermally conductive composites were each polarized using the parameter values E_p 1MV/m to 6 MV/m, T_p 353K to 450K and t_p 30min. [20] 2. For composites whose powders were modified by the

electric discharge plasma process: Firstly, each powder was exposed to an electric discharge plasma process (*EDPP*) before composite formation. The electric discharge plasma process results in uniform surfaces of the polymer and filler particles. New thermally conductive composites were produced by using the resulting powder phases. Thereafter, these composites were polarized using the parameter values E_p 1MV/m to 6 MV/m, T_p 353K to 450K and t_p 30min. This resulted in two types of thermally conductive composites, i.e., those whose powders had been modified by an electric discharge plasma process and those whose powders were unmodified.

RESULTS AND DISCUSSION

The thermal conductivity of the composite results from a complex energy process occurring during heat transfer from one filler particle to another through the dielectric (polymer) interlayer between them. The interlayer thickness depends directly on the dispersion and concentration of the inorganic filler. Adhesive, adsorptive, and cohesive effects at the interface between the polymer matrix and inorganic filler can also influence the magnitude of the thermal conductivity coefficient of both the polymer + nitride and polymer + carbide composites. [24–26] The methods required to improve the production processes for polymer composites have not been fully described. It is necessary to take into consideration the electronic state, and the electrical characteristics of the interfaces between the phases [18,19,27]. Furthermore, *TSD* measurements were carried out to define the electronic interfacial characteristics of the composites. This result indicates that the polymer phase of the composite exhibits a wide spectrum of supramolecular formations. As the distribution of the generated crystalline particles throughout the phase boundary of the composite cooled with liquid nitrogen is better, this composite's thermal conductivity values are higher than for the others.

The changes in the *TSD* current of the *HDPE* +70 vol.% *BN* composite is shown in fig.1. The *HDPE*+70 vol.% *BN* composite was polarized using an electric field strength E_n of $3 \cdot 10^6$ 106V/m, temperature T_c of 370K, and polarization time t_n of 30min. Stabilizing the charge value allows one to estimate the charge and electronic state. The interfacial electric properties can then be defined according to the spectrum. Thus, the relationship between the thermal conductivity and specific features of the composites can be predicted. After application of the electric discharge plasma process, the spectrum of the *HDPE*+70-vol.% *BN* composite exhibits an increase in both the amplitude and width compared with its initial state without electric discharge plasma treatment. This indicates that the electric discharge plasma process increases the concentration of the composite charge location center. The amplitudes of both the first and second *TSD* peak currents and thermal conductivity coefficient k of the composite grow due to the increased concentration of polar (C–O–C, C=O, and OH) groups in the composite. The activation energy (E_{ac}) of the charge-trapping center obtained from the initial slope of the *TSD* current

spectra was found to depend on the polarization conditions and pretreatment applied. It was found that the E_{ac} value varied from $0.94eV$ to $1.2eV$. The maximum temperature (T_m) variation, the activation energy (E_{ac}), and the half-width of the TSD current peaks depend on both the processing conditions and the polarization of the composite. Such changes in the temperature variation of the TSD current peak and activation energy of charge relaxation verify that the EDPP pretreatment leads to changes not only in the chemical structure of the polymer but also in the formation conditions of its supramolecular structure. These experimental results indicate that there are strong relationships among the electronic state of the phase boundary, the stabilized charge value, the interfacial interaction, the formation of polar groups, and the thermal conductivity of the composite after EDPP pretreatment. In this study, the intensity of the electric discharge plasma was changed by adjusting the amplitude of the applied AC (50Hz) voltage. The discharge power was determined by the current– charge

characteristic of the electric discharge plasma system (fig. 1).

It is known that the adhesion and mechanical strength of a composite are directly defined by the interfacial interactions [29]. Electric discharge plasma processing, electrothermal polarization, macromolecule oxidation, and electric charge accumulation at the interface (fig.2) result in improvement of such interfacial interactions. Therefore, the mechanical lifetime under tension (fig.3). The longer mechanical lifetime increased interfacial charge volume, positive peak shift to the high temperature side and lower resistivity of the composite testify to an increase in the interfacial interactions and the formation of highly concentrated local levels in the quasiforbidden band of the polymer phase. The modification of the polymer phase of the composite increased the interfacial interactions. The thermal conductivity of the modified composite was considerably greater than that of the unmodified composite.

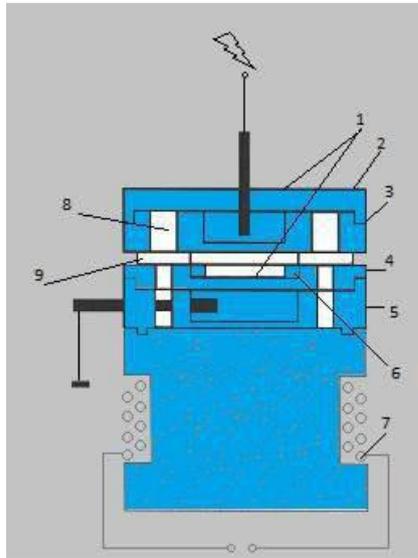


Fig. 1. A core proposed for nano structuring of polymer solution. The core consists of a metal - dielectric - gas – polymer solution - piezoelectric substrate - metal structure:
1-electrodes, 2–dielectric safety washer, 3-dielectric anode, 4-dielectric cathode, 5-insulator, 6-metallic cylinder, 7-heating element, 8-leading, 9 –limiters of dielectric distance: $T_p=383K$; $t_p=0.5$ hours.

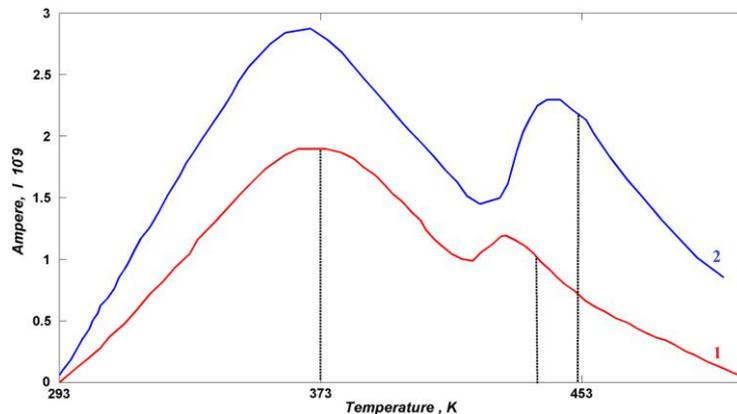


Fig. 2. TSD current spectrum for HDPE + 70% BN composite (1) without and (2) with EDPP treatment.

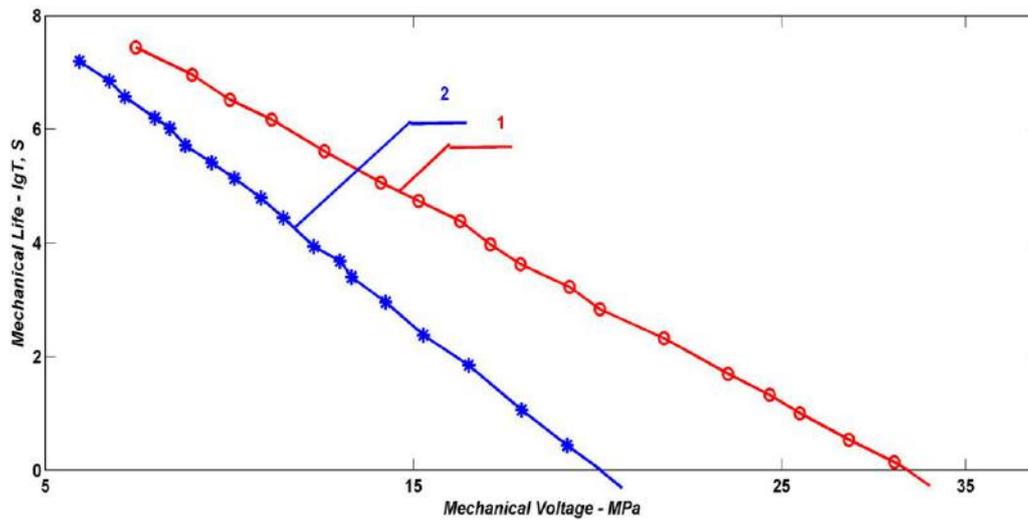


Fig. 3. Dependence of mechanical life of *HDPE* +70% *BN* composite on mechanical voltage (stress) for (1) *HDPE* +70% *BN* composite with *EDPP* (process time 1h, process voltage 8kV) and (2) *HDPE* + 70% *BN* composite without *EDPP*.

The modified composites had lower interfacial potential barriers, which define the electronic states and interfacial electric properties, compared with the unmodified composites, due to the formation of highly concentrated local levels in the quasiforbidden band during modification. *EDPP* caused macromolecule oxidation in the quasiforbidden band of the polymer phase between dispersant particles. Charge carrier creation in the direction of the temperature gradient at a certain local level concentration in the quasiforbidden band of the polymer phase contributed to transfer of thermal energy through the interface. The lower bulk resistance increased thermal conductivity and stabilized charge value at the interface (fig. 1) indicate generation of additional local levels in the quasiforbidden band of the polymer phase. The heat transfer process in the modified composites was linked to the combination of both electrons and phonons, leading to an increase in the thermal conductivity of the composites.

CONCLUSIONS

The thermal conductivity characteristics of polymer + metal nitride/carbide composites modified

by electric discharge plasma treatment were studied. Both sets of fabricated composites, i.e., *HDPE*+ - *TiC*, *HDPE*+*TiN*, *HDPE*+*AlN*, *HDPE*+*BN* and *PP*+*AlN*, with filler content ranging from 0% to 70%, were measured experimentally, and the results with and without electric discharge plasma treatment compared. Electric discharge modification of the polymer phase of the composites with metal nitrides and carbides resulted in higher thermal conductivity. The reason for this increased thermal conductivity of the composites is due to changes in the physicochemical structure of the polymer phase under the electric discharge plasma treatment. The electric discharge plasma process caused an increase in the interfacial interactions and the formation of highly concentrated local levels in the quasiforbidden band of the polymer phase. Charge carrier creation in the direction of the temperature gradient at a certain local level concentration in the quasiforbidden band of the polymer phase contributed to the transfer of thermal energy through the interface. These experimental results suggest that the fabricated *HDPE*+70% *BN* composites can find potential applications in the areas of electronics packaging, encapsulation, and printed board substrates.

- [1] R.R. Tummala. J. Am. Ceram. Soc. 1991, 74, 895.
- [2] S.Z. Yu, P. Hing and X. Hu. J. Appl. Phys. 2000, 88, 398.
- [3] Y. Zhou, H. Wang, L. Wang, K. Yu, Z. Lin, L. He and Y. Bai. Mater. Sci. Eng. 2012, B 177, 892.
- [4] S.H. Xie, B.K. Zhu, J.B. Li, X.Z. Wei and Z.K. Xu. Polym. Test. 2004, 23, 797.
- [5] P. Bujard. JP. Anserment., Proceeding Fifth IEEE SEMIT herm Symposium., 1989, pp. 126–130.
- [6] L. Li and D.L. Chung. J. Electron. Mater. 1994, 23, 557.
- [7] R.F. Hill. Proceedings of the Technical Program. National Symposium on Emerging Packing Technologies., 1996, pp. 125–131.
- [8] H. Ishida and S. Rimdst. Thermochim. Acta 1998, 320, 177.
- [9] H. Hatta, M. Taya, F.A. Kulacki and J.F. Harder. J. Compos. Mater. 1992, 26, 2.
- [10] M. Ohashi, S. Kawakami and Y. Yokogawa. J. Am. Ceram. Soc. 2005, 88, 2615.
- [11] S. Yu, P. Hing and X. Hu. Compos. Part A Appl. Sci. 2002, 33, 289.
- [12] Q. Mu, S. Feng and G. Diao. Polym. Compos. 2007, 28, 125.

- [13] *J. Gu, Q. Zhang, J. Dang, J. Zhang and Z. Yang.* Polym.Eng. Sci. 2009, 49, 1030.
- [14] *H. Zhou, S. Zhang and M. Yang.* Compos. Sci. Technol. 2007, 67,1035.
- [15] *G. Hass, M.H. Francombe and R.W. Hoffman.* Physics of Thin Films: Advances in Research and Development New York: Academic, 1975, pp. 359.
- [16] *M.H. Brodsky.* Amorphous Semiconductors, Topics in Applied Physics., New York: Springer., 1979, pp. 419.
- [17] *G. Harbeke.* Polycrystalline Semiconductors, Physical Properties and Applications., Berlin: Springer., 1985, pp. 341.
- [18] *W. Heywang.* Amorphe und Polykristalline Halbleiter., Berlin:Springer., 1984, pp. 160.
- [19] *G.M. Sessler.* Electrets., Berlin: Springer, 1980, pp. 486.
- [20] *M.K. Kerimov, M.A. Kurbanov, A.A. Bayramov, A.I. Mamedov.* Nanocomposites and Polymers with Analytical Methods, 3rd ed. (INTECH Open Access Publisher, 2011), pp. 375–404.
- [21] *B. Eliasson and U. Kogelschatz.* IEEE Trans. Plasma Sci. 1991,19, 309.
- [22] *B. Eliasson, W. Egli and U. Kogelschatz.* Pure Appl. Chem. 1994, 66, 1275.
- [23] *L. Parali.* J. Electrostat. 2015, 76, 89.
- [24] *B.S. Kolupaev.* Relaxation and Thermal Properties of Filled Polymer Systems, Lviv: Vitsa School, 1980, pp. 200.
- [25] *A.G. Milnes and D.L. Feucht.* Heterojunctions and Metal– Semiconductor Junctions, New York: Academic, 1970, pp. 432.
- [26] *E. Plyudemana.* The Interface in Polymer Composite., Peace,Moscow, 1976, pp. 299.
- [27] *E.H. Roderick.* Metal–Semiconductor Contact., Oxford:Clarendon, 1982, pp. 208.
- [28] *P.A. Tipler and G. Moscaj.* Physics for Scientists and Engineers, 6th ed. New York: Worth, 2008, pp. 434.
- [29] *A.S. Freidin, R.A. Trusov.* Properties and Calculation of Adhesive Joints., M. Chemistry, 1990, pp. 255 (in Russia).