DIELECTRIC PROPERTIES OF HDPE-CdS/ZnS COMPOSITES

E.G. HAJIEVA, A.M. MAHARRAMOV, M.M. GULIYEV, R.S. ISMAYILOVA

Institute of Radiation Problems of Azerbaijan NAS
Str. B.Vagabzade 9, Baku, Azerbaijan

Ternary high density polyethylene/cadmium sulphide /zincsulphide (HDPE- CdS/ZnS) were fabricated using hot pressing the powder mixture technique. The dielectric behavior of such composites over a wide temperature (from 25 to 130^0C) and frequency (from 25 to $1\cdot10^6$Hz) ranges was studied using broadband dielectric spectroscopy.

1. INTRODUCTION

Semiconductor/polymer composites have been extensively investigated during the last four decade due to their improved performance and potential applications. Potential areas of application of composite materials include micro-and nanoelectronics, low voltage flat panel, sensors, photovoltaic devices, light emitting devices etc.[1-3]. Micro- and nanocomposite materials have attracted attention in both fundamental studies as well as technical applications. The polymers are widely used in the technology of preparation of composite materials in the quality of matrix that serves for assembling the micro-and nanoparticles into clusters and for avoiding the agglomeration, as a matrix in self-assembling materials that induce ordering and anisotropic orientation, as well as acting as a functional element [4]. The field of dispersing semiconducting micro-and nanoparticles within a polymer matrix is of sufficient interest because of the possibility of producing polymer composite based devices which can be processed in required geometries, morphologies and composition with consequent control over the different electro-optical properties.

Studies on synthesis and physical properties of different polymer based composite have been reported by many researchers such as polyvinylchloride (PVC)/CdS [5], LDPE/CdS [6], PVC/ZnO [7], copolymer of vinylidene fluoride and tetrafluoroethylene F42/CdS/ZnS and polyvinyldene floride F2/CdS/ZnS [8], polyamine (PANI)/CdS/ZnS [9,10], polyvinyl-alcohol (PVA)/CdS [11], poly(methyl methacrylate) PMMA/CdS [12], ect. It has been observed that the incorporation of micro-and nanoparticles into polymer improves the thermal stability, glass transition temperature, specific heat and mechanical properties. Several researches have shown that along with thermal stability electrical conductivity of the polymers plays important role to modify the polymer properties to be used for advanced applications [1].

Among the polymers, high density polyethylene (HDPE) is one of the most common and popular thermoplastic polymers having the characteristic like low price, excellent electric insulation and good reproducibility.

The quantum confinement of electrons and photons inorganic semiconductor particles used in the composites exhibit physical and chemical properties which are different from the properties of corresponding bulk materials. Among various inorganic semiconductors CdS/Zn Shave received great attention because of their attractive properties and potential for application in photonics and optoelectronics. Further investigation of the polymer-based composites are equally important for understanding the mechanism of transport and photoluminescence in the materials, developing of materials with advanced characteristics, as well as for possible minimizing the toxicity of Cd-based materials.

A.F.Gochuyeva et al. [8] was found a possible mexanism of photoelectret effect to be formed at the same time under the impact of strong electric field and lights is offered in the composites based on polar (fluoride-containing) and non-polar (polyolefins) polymers and inorganic semiconductors CdS/ZnS. It was found that the polarity of the polymer matrix is mainly dependent on the potential difference of photoelectret inorganic phase at predetermined volumetric content.

Studies on PANI-CdS and PANI-ZnS nanocomposites have been reported in [9,10]. In [9] authors report about details of comparative studies on electrical properties of PANI/ZnS nanocomposite at different weight % of ZnS. The increase conductivity in 25% nanocomposite is attributed to polymer chain mobility and activation of dopant. S.D.Bompilwar et al. [10] shows that as the weight percentage of CdS/ZnS nanoparticles increases in the polyanilene (PANI) matrix, half decomposition temperature increases gradually and activation energy also increases. These results indicate that the polymer composites are thermally more stable as compared to that of pure PANI. In [13] A.Shik et al. considers photoelectric phenomena in a composite medium in which inclusions from o type –II heterojunction with a host matrix. The model describes, in particular, polymer-based photosensitive structures with different types of semiconducting or inclusions. It was shown that the separation on no equilibrium carriers due to interface electric fields increases the hole component of photoconductivity, decreases the electron component, and results in a substantial increase of the total photoconductivity. In this work authors considered the theory of this effect in detail, elucidate its general features, and determine its influence on the properties of composite based photoconductors and photodiodes.

In this paper we report the study of a HDPE - CdS/ZnS composite system, were distributed at random in the continuous polymer phase to form a 0-3 type of connectivity.

2. EXPERIMENTAL
1. Materials.

The matrix polymer used in this work is a commercial white powder high density polyethylene (HDPE) with particle sizes in the range of 150-200μm. The various physical parameters of HDPE are as follows: density 958kg/m^3, melting temperature =150^{0}C, dielectric constant at 1 kHz = 2.4, dissipation factor at 1kHz =0.0066 and volume resistivity = 5·10^{13}Ohm·sm. As the filler binary CdS/ZnS (50/50) with average particle size ranging from 50 to 63μm was used without treatment.

2. Composite sample preparation.

In the former case, CdS/ZnS powder in the desired amount was mixed thoroughly with the HDPE powder in an agate pestle mortar for 1h.This process coated the CdS/ZnS powder on the surface of the HDPE particles, so it is referred to as prelocalization of the conductive phase. Prolonged mixing improved the homogeneity of the spatial distribution of the conductive particles and their uniform coating thickness on the HDPE particles. The tumble mixed prelocalized powders was prepared for different graphite contents of 0-50vol.%. The resultant powder was further dried at 100^{0}C for 6h prior to compression molding. Then, the CdS/ZnS composites were prepared by hot - pressing the powder mixture technique of. The dried powder was filled in a tool steel die having diameter 26mm. The ponder was heated at an average heating rate of 6^{0}C/min under pressure of 15MPa to a maximum temperature of 150^{0}C. After soaking period of 10 minutes, the dick samples of 26mm diameter and thickness 12Om were punched from the plates and cooled down to 0^{0}C in a water-ice mixture (quenching mode) at atmospheric pressure to eliminate porosity, bubbles or blisters. This procedure improves the electrical properties, minimizes the after – shrinkage and enhances the quality and appearance of the samples. Thus, composites containing 0-50vol.% CdS/ZnS in the HDPE matrix were prepared. The specimens were sealed in air free polyethylene bags prior to measurements to avoid atmospheric and humidity effects that may induce same changes in the conductivity of the specimens.

The preparation mode of the composite makes it possible to obtain reproducible electrophysical parameters (electric resistance, capacitance, dielectric losses, Q quality) for most of some concentration. Some samples that had parameters differing from the parameters of the main group were not considered in the analysis (the number of these samples was not high).

3. Measurements.

To provide better contact with measuring probe surface, the disk specimens for the dielectric and resistivity measurements were coated with conducting silver paste at both sides as two electrodes. Samples were tested by two electrode scheme using a specially constructed sample holder shielded and grounded heated measuring cell of "sandwich" type, used for heating the samples, having system of measuring and potential electrodes with diameters of 15 and 20 mm, respectively. For measurement the samples were clamped firmly between the clamping stainless steel electrodes at a constant applied pressure of 5kq·sm^{-2}. The centering of the electrodes was provided by a special mandrel.

For studying the dielectric properties, the capacitance (C) and dissipation factor $(tan\delta)$ of the samples were measured using a broadband precision immitanse meter (model E7-20, Belarus) from frequency 25 t0 10^{6}Hz at room temperature. The dielectric constant (ε') evaluated by the relation $\varepsilon'=CL/\varepsilon_0$ S where ε_0 is the permittivity of the free space (8,854x10^{-12}F/m). The dissipation factor was obtained directly from the instrument.

The properties of composites i.e. ε' and $tan\delta$ were estimated also at a constant frequency (1kHz) with varying temperature (from 20 to 150^{0}C). The heating rate of the samples was maintained at 3^{0}C/min. A calibrated copper –constantan thermocouple was used to measure the temperature of the specimen.

The samples were short circuited for one hour before taking any measurements to avoid any stray capacitance effects.

3. RESULT AND DISCUASION

The complex dielectric constant is usually defined as $\varepsilon=\varepsilon'- i\varepsilon''$, where ε' is known as real part of permittivity. It is a measure of how much energy from an electric field is stored in a material. The ε'' is the imaginary part of permittivity and is also called as loss factor. It is a measure of how dissipative or lossy a material is to an external electric field. The ratio of imaginary to the real parts ($\varepsilon''/\varepsilon'$) is tanδ.
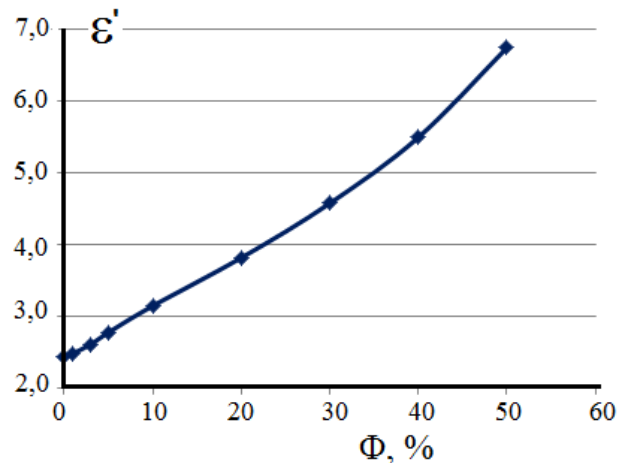

Fig. 1. Dielectric constant (ε′ at 10^{13}Hz) of HDPE – CdS/ZnS composites as a function of volume fraction of CdS/ZnS filler.

Fig. 1. shows the variation of ε′ with CdS/ZnS content at the room temperature for the HDPE- CdS/ZnS microcomposites tested at a frequency of 1kHz. It can be seen that the ε′ increases with increasing filler content. At 50vol.% CdS/ZnS, ε′ value reaches to 6,75, being ~2,8 times higher than that of neat HDPE (the measured at room temperature value of real part of complex dielectric

permittivity at frequency 10^3Hz for a pure HDPE sample is equal to 2.4). Then increment in ε' of composite with addition of CdS/ZnS content could be mainly ascribed to following two reasons [14]. One reason is Maxwell-Wagner (MW) interfacial polarization originating in the insulator filler (HDPE- CdS/ZnS) interfaces. MW effect arises when filler particles is dispersed within a non-conducting phase. The charge carries will be trapped at the boundaries of the fillers particles and matrix forming space charges. And when the electric field is applied these space charges will orient themselves along the applied field. Another reason is due to the formation of mini-capacitor networks in the HDPE- CdS/ZnS composites with increasing CdS/ZnS content. The minicapacitors consist of various CdS/ZnS microplatelets separated by a thin insulating polymer matrics. Such behavior of the ε' of the composite material with a semiconductor filler mainly depends on the MW polarization, the surface energy of the dielectric and the filler, the conductance of the system, and its proximity to the percolation threshold [15]. At a low concentration of the filler in the composite material, ε' increases due to the VM polarization. However, as the concentration increases due to the difference in the surface energy of the components, the structure of the composite material becomes unstable, and CdS/ZnS particles form clusters whose surface is smaller than the total surface of the particles that form it. An increase in the number of clusters with an increase in the filler concentration is accompanied by a decrease in the dielectric layer between the particles and yields an increase in the capacity (and, as a result, in ε'). The lower magnitude of the experimental values for a higher CdS/ZnS content in comparison with the predicted result based on the Lichtenecker rule [16], may be due to the presence of isolated pores. Similar to ε', ε'' and $tan\delta$ values of the composites are also increases with CdS/ZnS content.

Fig. 2a shows the dielectric constant ε' behavior for the HDPE and the composites with temperature measured at 1 kHz. As can be seen, the dielectric constant all composites first negligibly decrease up to 70^0C. A sharp decrease in dielectric constant for all the specimens is found when temperature reaches 70^0C and when the temperature approaches 100^0C ε' tends to be independent of the temperature for pure HDPE. Figure 2a shows that the temperature dependence of ε' does not depend on the CdS/ZnS content.

Fig. 2b shows the temperature dependence of loss tangent for neat HDPE and the HDPE-CdS/ZnS composites, respectively. It can be seen that an increase in the CdS/ZnS concentration in the matrix to 10vol% also yields a substantial increase in tanδ for all composites. The dielectric losses at the unital temperature of 20^0C was 0,0066±0,0009 for HDPE; for the composite materials with the filler particle concentration of 50vol.%, in increases to 0,069±0,0005. Large dielectric losses are related to the higher electric conductance as compared to pure HDPE. The electrical conductivity these specimens was monitored with respect to composition, i.e., CdS/ZnS concentration at the frequency of 1kHz showed that the introduction of about 50vol.% of CdS/ZnS into HDPE

results in the electric conductance increase from for pure HDPE to for composite materials. This is over orders of magnitude higher than that of pure HDPE. The increase of conductivity with increasing of concentration of CdS/ZnS due to increases the charge carries which increasing filler contact where the CdS/ZnS particles at a low concentrations are represented by small darker regions and become large when the CdS/ZnS content increases and the network will be connected to each other containing the overlapping paths to allow the charge carries to pass through, where the charge carriers with routes through which the electrical resistance be less [17].

From the Figure 2b, it can be noted that the the dielectric losses becomes temperature dependent when the CdS/ZnS content approaches a value 10vol.%. The variation of tanδ with temperature becomes significant in the range of 50-130^{0}C. At low temperatures (up to 50^{0}C) tanδ attains rather constant values, while at temperatures higher than 50^{0}C increases rapidly with temperature and composition showing a maximum at 70^{0}C and then vanished. Pure HDPE and the composite system with 3 and 5vol.% filler content do not exhibit a peak.

In Figure 3 dielectric permittivity (ε') and loss tangent (*tanδ*) as a function of frequency, at room temperature, for all the examined systems is presented. As expected, the dielectric constant of HDPE-CdS/ZnS micrrocomposites increases with the increase in CdS/ZnS content. From Fig. 3a, it can be seen that the dielectric constants of neat HDPE and its microcomposites with 3vol.% filler content are nearly independent of frequency. For the HDPE-10vol% CdS/ZnS microcomposite the dielectric constant decreases markedly with increasing frequency. The room temperature value of permittivity for HDPE-10vol% CdS/ZnS at frequency 25Hz is about 3,31, which decrease to about 2,90 at $5\cdot10^5$Hz. The frequency dependence of dielectric study indicates that introduction of CdS/ZnS increases the dielectric constant of the HDPE from about 2,5 to 3,31 at 10vol% of CdS/ZnS content. The ε' values for 10vol% filler content are higher than both unfilled and with 3 and 5vol% filler content, probably due to a more important contribution of the interfacial polarization.

The variation of *tanδ* with the frequency for all tested filler concentrations at room temperature is shown in Figure 3b. The *tanδ* values of pure HDPE increases with increasing frequency from about 0,0027 to 0,0257 when the frequency reaches to $1\cdot10^6$Hz. A significant drop in tgδ occurs when the frequency reaches $5\cdot10^4$Hz. Pure HDPE do not exhibit a peak. Two relaxation processes are observed in both magnitudes in the frequency ranged studied. The peak located at around $1\cdot10^5$Hz is labeled as α - relaxation. It is then caused in the HDPE main chains by cooperative micro-Brownian motions within their amorphous regions [18]. The process at about 50Hz is ascribed to the molecular motions within the crystalline fraction of the HDPE material and it is named as α_c relaxation [19]. As seen in tgδ dependence, the location of α_c relaxation peak is shifted slightly toward higher frequencies (shorter times) with increasing filler content.
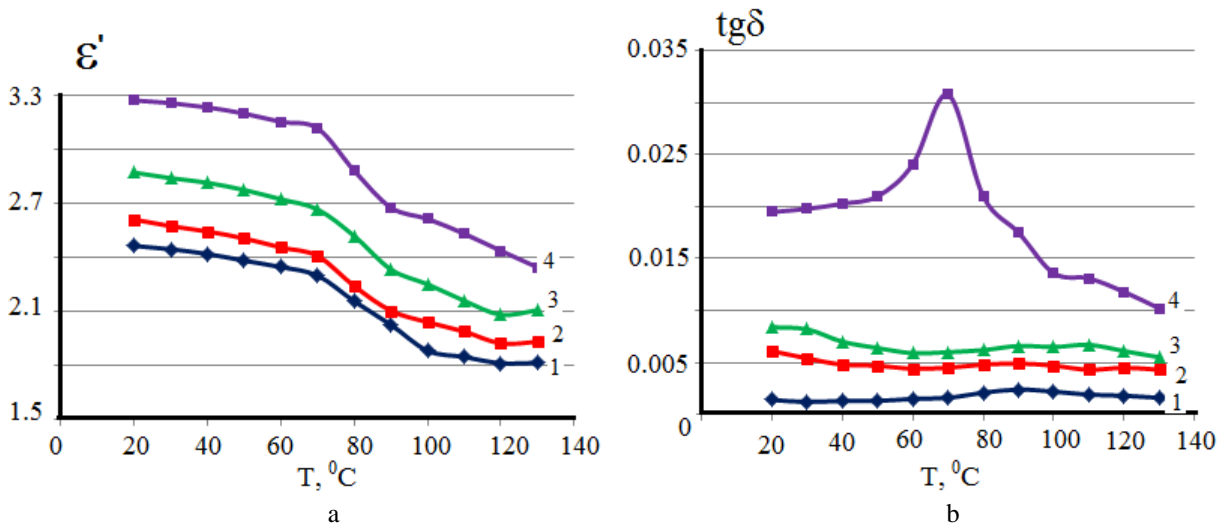
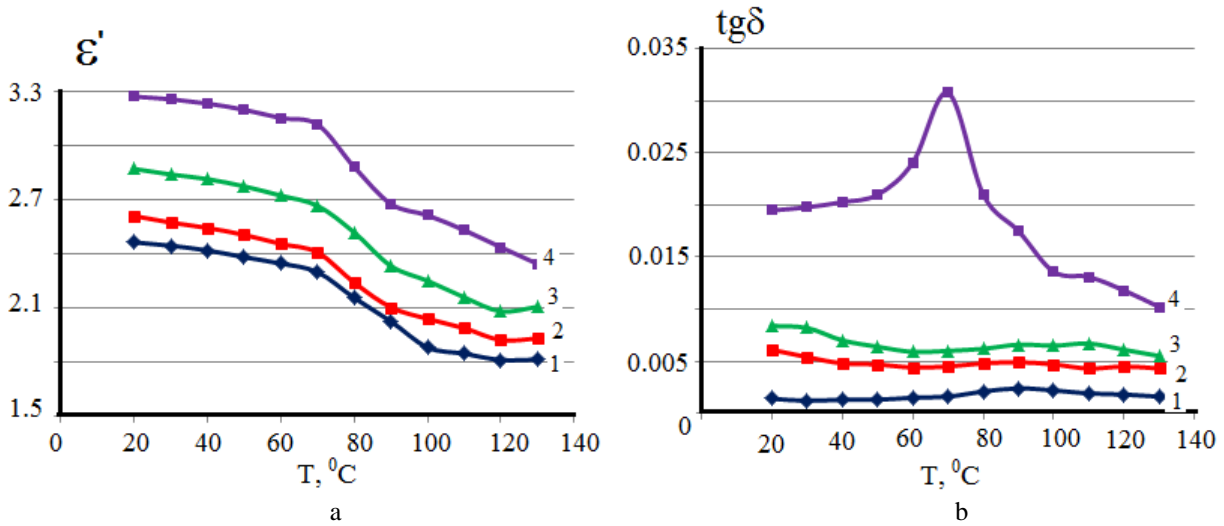*Fig. 2.* Dielectric constant (ε') (a) and loss ($tan\delta$) (b) as a function of temperature.

Fig. 3. Dielectric constant (ε') (a) and loss ($tan\delta$) (b) as a function of frequency.

CONCLUSIONS

In summary, ternary HDPE- CdS/ZnS microcomposites were fabricated using hot-pressing the powder mixture technique. Electrical measurements showed that the real part of permittivity of ternary HDPE/CdS/ZnS microcomposites increases with increasing CdS/ZnS content. The room temperature dielectric spectra show two relaxations process which is attributed to the MW relaxation. The peak shift to higher frequencies as the filler content is increased. In addition, both dielectric permittivity (ε') and dielectric loss ($tg\delta$) of the composites were found to be frequency and temperature dependent.

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