Polymer Nanocomposites: Synthesis and Physical Properties

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1. Introduction

Development of the science of metal-containing nanoparticles, including those stabilized in polymer matrices, is stimulated by the steady growth of interest paid to this problem in many areas of chemistry, physics, and materials science (Pomogailo et al., 2004; Gubin et al., 2005, a; Gubin et al., 2005, b; Scomski, 2003; Hy eon, 2003; Lin & Samia, 2006; Gubin et al., 2002; Ushakov et al., 2005).

As is well known, materials based on metal-containing nanoparticles are thermodynamically unstable (Gubin, 2000). Isolation within a matrix is a prospective method for stabilization of nanoparticles. Various polymers can be used for this purpose, e.g. polyethylene (Gubin et al., 2005, b; Zanetti & Costa, 2004), polypropylene (Gubin et al., 2005, b; Zanetti et al., 2001), polytetrafluoroethylene (Korobov et al., 2004; Yurkov et al., 2006), etc. These polymers have relatively high thermal stability, unique rheologic properties, high dielectric strength, they are chemically inert and processable, which provides means for fabrication of objects of desired form and dimensions. Methods for syntheses of these polymers are well elaborated.

Most polymer materials are good dielectrics with stable physical and chemical properties (Xia et al., 2006). Chemical stability of polymers allows using them in severe conditions (Hong et al., 2003). Modification of polymers with various inorganic fillers is used for altering their mechanical, electric, and other operational properties (Brosseau et al., 2001). The intensity of these properties’ change depends on the nature, composition, morphology, and concentration of filler, as well as parameters of the flow process of filler’s introduction into the matrix.

Nanoscaled fillers are especially interesting for creation of composite materials based on polymer matrices, as the first have a number of properties which are not specific for bulk materials (Kawasumi et al., 1997; Wang & Herron, 1991; Siegel, 1993; Gleiter et al., 2001; Gubin et al., 2003). Supposedly, introduction of metal-containing nanoparticles into polymers and variation of their composition, concentration, and sizes would provide means
for controlling mechanical, electrical, magnetic, and other properties of composite nanomaterials produced this way (Gangopadhyay & De, 2000). Herein we present results of a few years of studies concerned with development, creation, and investigation of composite nanomaterials based on metal-containing nanoparticles embedded in the low density polyethylene (LDPE) matrix. The selection of LDPE as the stabilizing matrix was made due to the material’s low cost and well-developed production technology. Besides that, LDPE can be readily mixed with both organic and inorganic fillers (Pomogailo et al., 2004; Gubin et al., 2005, b; Yurkov et al., 2006; Xia et al., 2006; Hong et al., 2003; Hong et al., 2005). LDPE is a thermoplastic polymer, which allows using it for making objects of desired form and dimensions in mild conditions. Due to the abovementioned properties, LDPE is widely used in electrical engineering and radio engineering industries. Nanoparticles containing iron, cobalt, copper, cerium oxide and semiconductor CdS were used as the fillers in the course of this work.

2. Experimental

The general protocol for synthesizing nanoparticles embedded in a polymer matrix is as follows. A metal-containing precursor solution is added to the rapidly stirred LDPE-oil solution-melt at 270-300°C (Gubin et al., 2005, b; Gubin et al., 2003). Argon is supplied to the reactor during all the synthesis for removing air and gaseous reaction products (fig. 1).

![Fig. 1. Schematics of the laboratory setup for synthesis of composite materials based on metal nanoparticles and organic polymer matrices: 1 – glass reactor (3- or 4-necked flask); 2 – bath; 3 – thermometer; 4 – high-speed electric stirrer; 5 – dropping funnel with backpressure; 6 – bubbler with pyrogallol; 7 – condenser; 8 – electric heating mantle; 9 – lab jack; 10 – argon source; 11 – waste accumulation](image_url)

Formates, acetates, oxalates, and carbonyls of iron and cobalt were used as the metal-containing precursors. Copper acetate, zinc and cadmium thioacetate complexes were used for syntheses of semiconductor nanoparticles; cerium nitrate and complex compounds of
cerium were used for syntheses of ceria nanoparticles. The synthesis of CdS nanoparticles was performed in two stages. First, CdCl₂ nanoparticles were prepared in LDPE-oil solution melt via dropwise addition of an acidified cadmium chloride solution. The second stage was chemical modification of the formed cadmium chloride nanoparticles via their interaction with hydrogen sulphide. The latter was bubbled through the LDPE-oil solution-melt with cadmium-containing nanoparticles (CdCl₂) using argon as the carrier gas.

Reactions of thermal decomposition of the precursors used are listed below:

\[
\begin{align*}
\text{Fe(CO)₅} & \rightarrow \text{Fe} + 5\text{CO} \text{ (the main reaction)}, \\
\text{Fe(CO)₅} & \rightarrow \text{FeO} + \text{CO} + \text{C}, \\
\text{Fe(CO)₅} & \rightarrow \text{FeC} + \text{CO} + \text{CO₂}, \\
\text{Fe(HCOO)₃} & \rightarrow \text{Fe} + \text{CO₂}↑ + 2\text{CO}↑ + \text{H₂O}. \\
\text{Fe(CH₃COO)₃} & \rightarrow \text{FeO} + \text{CO₂}↑ + 2\text{CO}↑ + \text{H₂O}; \\
\text{Co(HCOO)₂} & \rightarrow \text{Co} + \text{CO₂}↑ + 2\text{CO}↑ + \text{H₂O}. \\
\text{Co(CH₃COO)₂} & \rightarrow \text{CoO} + \text{CO₂}↑ + 2\text{CO}↑ + \text{H₂O}. \\
\text{Cu(CH₃COO)₂} & \rightarrow \text{Cu} + 2\text{CO} + \text{H₂} + 2\text{CH₃O} \\
\text{CdCl₂} + \text{H₂S} & \rightarrow \text{CdS} + 2\text{HCl}↑ \\
\text{Ce(NO₃)₃} \cdot 6\text{H₂O} & \rightarrow \text{CeO₂} + \text{H₂O} + \text{NO₂}↑; \\
\text{(Et₄N)₂Ce(NO₃)₆} & \rightarrow \text{CeO₂} + \text{H₂O} + \text{N₂O}↑ + \text{CO₂}↑; \\
\text{(NH₄)₂Ce(NO₃)₆} & \rightarrow \text{CeO₂} + \text{H₂O} + \text{N₂O}↑ + \text{O₂}↑; \\
\text{[Me(CH₃COO)₂} \cdot \text{(NH₂)₂CS} \cdot \text{H₂O}] & \rightarrow \text{MeS} + \text{thiocarbamide decomposition products}
\end{align*}
\]

It is worthwhile to say that side reactions can take place during a synthesis, which will have effect on chemical composition of resulting nanoparticles. Besides that, nanoparticles of like composition can be prepared using different precursors.

The samples produced were separated from oil with benzene using a Soxhlet extractor and were dried in vacuum afterwards. All the samples were stored in air. The materials produced were coloured powders, with colours dependant on nanoparticles’ sizes and composition.

Samples in the form of tablets were produced via hot pressing in a steel die using a hand screw press (6 kN). The pressing temperature was selected in such a way as to transform all the powder to a plastic mass avoiding its thermal destruction. Tablets 12...25 mm in diameter and 0.25...3 mm thick were prepared this way.

The protocol described was used for preparation of nanocomposites based on LDPE containing nanoparticles (Kosobudsky & Yurkov, 2000; Yurkov et al., 2001; Yurkov et al., 2002; Yurkov et al., 2007; Fionov et al., 2008, b; Taratanov et al., 2009, a; Popkov et al., 2009;...
3. Electrophysical properties of nanocomposites

3.1 Electrophysical properties of composites containing magnetic nanoparticles

Five samples have been synthesized for conducting these studies. Samples 1 and 2 were prepared from Fe(CO)$_5$ and contain different amounts of iron-containing nanoparticles embedded in low density polyethylene. The nanoparticles are comprised of three phases: metallic iron, iron oxide and carbide. Sample 3 was prepared from iron (III) formate Fe(HCOO)$_3$ and contains nanoparticles which are mainly comprised of Fe$_3$O$_4$. Sample 4 was synthesized using iron (II) oxalate FeC$_2$O$_4$·2H$_2$O; nanoparticles in it are comprised of iron oxide Fe$_3$O$_4$ and ε-Fe. Sample 5 was prepared via thermal destruction of cobalt (II) acetate and contains nanoparticles with complex structure; the nanoparticles are comprised of CoO, Co, and Co$_3$O$_4$ (Gudoshnikov et al., 2003; Yurkov et al., 2007, b).

Volume resistance, $\rho_V$, and permittivity, $\varepsilon$, values of the abovementioned samples are listed in tables 1 and 2. Figures 2, 3 depict dependencies of $\rho_V$ and $\varepsilon$ of the samples with Fe-containing nanoparticles as functions of concentration, C. The sample with C = 0 is low density polyethylene with no filler which was subject to all operations involved in preparation of the abovementioned samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C, wt. %</th>
<th>$\rho_V$, $\Omega \cdot m$ at voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 V</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Sample 1</td>
<td>5</td>
<td>1.4·10$^{14}$ ±50%</td>
</tr>
<tr>
<td>Sample 2</td>
<td>10</td>
<td>5.5·10$^{13}$ ±25%</td>
</tr>
<tr>
<td>Sample 3</td>
<td>20</td>
<td>4.5·10$^{12}$ ±25%</td>
</tr>
<tr>
<td>Sample 4</td>
<td>20</td>
<td>9.5·10$^{13}$ ±25%</td>
</tr>
<tr>
<td>Sample 5</td>
<td>20</td>
<td>2.8·10$^{13}$ ±25%</td>
</tr>
</tbody>
</table>

Table 1. Volume resistance of composite nanomaterials

<table>
<thead>
<tr>
<th>Sample</th>
<th>C, wt. %</th>
<th>$\varepsilon$ (1 kHz)</th>
<th>$\varepsilon$ (1 MHz)</th>
<th>$d$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>0</td>
<td>2.94</td>
<td>2.70</td>
<td>-</td>
</tr>
<tr>
<td>Sample 1</td>
<td>5</td>
<td>2.98</td>
<td>2.69</td>
<td>4.9</td>
</tr>
<tr>
<td>Sample 2</td>
<td>10</td>
<td>3.63</td>
<td>3.32</td>
<td>5.1</td>
</tr>
<tr>
<td>Sample 3</td>
<td>20</td>
<td>4.52</td>
<td>3.56</td>
<td>11.5</td>
</tr>
<tr>
<td>Sample 4</td>
<td>20</td>
<td>3.67</td>
<td>3.37</td>
<td>2.4</td>
</tr>
<tr>
<td>Sample 5</td>
<td>20</td>
<td>3.96</td>
<td>3.01</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 2. Permittivity of composite nanomaterials
DC volume resistance of the samples ($10^{11} - 10^{15} \, \Omega \cdot m$) steadily lowers as the filler concentration $C$ grows; the values are in the range typical for dielectrics. The lower volume resistance of the materials compared to that of the “empty” LDPE it is a result of polyethylene structure change towards higher amorphism and porosity which results in higher molecular mobility and lower ion dissociation energy in the polymer. This is also the reason for the steady growth of permittivity which occurs as the filler concentration increases.

The difference between volume resistance and permittivity values of the processed unfilled LDPE and the “normal” LDPE ($10^{16} - 10^{18} \, \Omega \cdot m$, 2.2-2.3) can be attributed to a higher amount of admixtures as a result of the treatment.

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Fig. 2. Volume resistance of samples 1, 2, 3 as a function of nanoparticles weight concentration at different voltage: 1 – 100 V; 2 – 1000 V

Fig. 3. Permittivity of samples 1, 2, 3 as a function of nanoparticles weight concentration at low frequencies: 1 – 1 kHz; 2 – 1 MHz
Volume resistance of samples with 5% and 10% wt. nanoparticles (samples 1 and 2), as well as that of the “empty” polyethylene, weakly depends on the field applied and linearly decreases as concentration of nanoparticles increases within all the operating field strength range.

As concentration of nanoparticles reaches 20% wt., dependence of volume resistance as a function of applied voltage becomes more pronounced. Samples 4 and 5 have 3 times less volume resistance at 1000 V than at 100 V, whereas the resistance drop of sample 3 is more than 10 times at the same voltages.

Additional contribution to admittance current can be made by polarization phenomena caused by nanoparticles’ polarization: macro-shift polarization (within a sample) and micro-shift polarization (within some sites), as well as slowly developing dipole polarization.

Conductivity of filled LDPE depends on both composition and size of nanoparticles it contains. It is well illustrated by the lower volume resistance of sample 3 compared to that of samples 4 and 5 at 1000 V.

The steady growth of permittivity is caused by the contribution of metal-containing nanoparticles’ polarization. The nanoparticles have more loose electron shells and hence higher polarizability compared to those of the polymer matrix, which results in the growth of permittivity $\varepsilon$ as the filler concentration increases.

The difference between permittivity values of samples 3 and 4 which have equal nanoparticles concentrations is due to the higher susceptibility of larger particles.

Results of permittivity and electromagnetic radiation absorption measurements performed at microwave frequencies for samples with different filler concentrations are given in figs. 4 and 5.

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**Fig. 4.** Permittivity as a function of microwave radiation frequency: 1 –sample 1; 2 – sample 2; 3 – sample 3
Fig. 5. Microwave absorption as a function of radiation frequency: 1 – sample 1; 2 – sample 2; 3 – sample 3

The data on permittivity and absorption in the microwave range can be used for estimating proportion of amplitude and time characteristics of relaxation processes. The decrease of permittivity and almost constant dielectric losses of samples 1 and 2 can be explained by decrease of relaxation processes’ intensity with the relaxation rate unchanged. The increase of nanoparticles’ concentration to 20% wt. (sample 3) results in decrease of relaxation time, but relaxation intensity doesn’t change. There is a tendency towards increase of both dipole relaxation process intensity and rate as concentration of nanoparticles in the polymer grows. Just as in case of low frequencies, the dependencies mentioned above can be attributed to polarization of metal-containing nanoparticles whose susceptibility increases along with their size. The results of microwave measurements indicate that the samples produced have steady permittivity and absorption in a wide frequency range within the band studied. Samples containing 30% wt. iron- or cobalt-containing nanoparticles have low volume resistance ($\approx 10^2$ $\Omega \cdot m$). Nanoparticles in these samples are relatively large ($d_{av} \approx 8$ nm) and have well-formed metallic core. Electromagnetic radiation power reflection and extinction coefficients at 30 GHz are given in table 3 (Fionov et al., 2008, a).

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>$C$, % wt.</th>
<th>$K_{ref}$</th>
<th>$K_{ext}$, dB/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE+Co$_3$O$_4$</td>
<td>30</td>
<td>0.10</td>
<td>77</td>
</tr>
<tr>
<td>LDPE+Fe$_3$O$_4$</td>
<td>30</td>
<td>0.53</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 3.

Application of such composite materials in microwave equipment as nonlinear distribution elements (fillers of waveguide ducts and resonators, thin-film coats, electromagnetic screens, etc.) would lead to creation of a number of new devices for electromagnetic signal transformation and elements of active stealth technology.
3.2 Study of complex magnetic and dielectric permittivity at microwave frequencies

Samples prepared for measuring complex magnetic and dielectric permittivity at microwave frequencies using the cavity method were in the form of powders (granule size less than 300 μm) put in capillary vessels.

Among the materials with no more than 20% wt. nanoparticles, the one with 20% wt. Co-containing nanoparticles has the highest values of $\varepsilon' \approx 6.5$, $\varepsilon'' \approx 0.11$, $\mu' \approx 1.6$, and $\mu'' \approx 4.9 \cdot 10^{-3}$ at 6.5 GHz.

Results of measurements performed for powders containing Fe$_3$O$_4$ are given in fig. 6. Dielectric and magnetic permittivities, as well as dielectric and magnetic losses, grow as concentration of Fe$_3$O$_4$ increases. The highest values of $\varepsilon'$ and $\mu'$ are observed for nanocomposites with 63% wt. Fe$_3$O$_4$ at the long-wave part of the studied frequency range (25.0 and 4.5, respectively); the highest dielectric and magnetic losses are detected at 5-12 GHz ($\varepsilon''_{\text{max}} \approx 10$) and 3-6 GHz ($\mu''_{\text{max}} \approx 2.7$), respectively.

As magnetic properties ($\mu'$ and $\mu''$) of the nanocomposites are mainly determined by magnetic properties of nanoparticles, whereas dielectric properties are affected by concentrations of free and bound charges in the whole system, the unsteady behaviour of $\varepsilon'$ and $\varepsilon''$ in case of different concentrations of metal-containing nanoparticles at different frequencies can be attributed to uncontrolled changes of composite structure.

![Fig. 6. Effect of Fe$_3$O$_4$ weight concentration of $\varepsilon^*$ and $\mu^*$ of a composite as functions of frequency:](image)

For this reason, the influence of synthesis conditions on phase composition of metal-containing nanoparticles and electrophysical properties of composites has been investigated. Three types of materials have been studied: the initial one, annealed in inert atmosphere, and annealed in air.

Basing on Mössbauer spectra, nanoparticles in the initial sample with 63% wt. Fe$_3$O$_4$ were found to contain 11% wt. $\alpha$-Fe with Fe$_3$O$_4$ being the rest. Concentration of $\alpha$-Fe has dropped to 4% wt. after annealing in inert atmosphere. Nanoparticles in samples prepared by annealing in air were entirely comprised of $\gamma$-Fe$_2$O$_3$. 

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XRD data revealed some ordering of nanoparticles structure after annealing, perhaps as a result of their recrystallization. The influence of the additional thermal treatment and oxidation of the initial composite which contained 63% wt. Fe₃O₄ can be seen in fig. 7. The treatment in inert atmosphere leads to increase of dielectric permittivity and both magnetic and dielectric losses in the composite. The most prominent result of the additional oxidation of Fe₃O₄ nanoparticles to Fe₂O₃ is the decrease of dielectric losses and $\varepsilon'$. Magnetic losses also decreased a bit at 3 - 7 GHz.

According to the percolation theory, dependencies of conductivity and dielectric permittivity of composites with disperse phase as functions of filler concentration can be described as (Efros & Shklovskii, 1976):

$$\sigma \sim \sigma_m (v_f - v_f^*)^{-q}$$

$$\varepsilon' \sim \varepsilon_m (v_f - v_f^*)^{-q}, \quad v_f < v_f^*,$$

where $\sigma_m$ is the specific conductivity of the polymer matrix; $\varepsilon_m$ is the dielectric permittivity of the polymer matrix; $v_f$ is the volume concentration of the filler; $v_f^*$ is the percolation threshold. Therefore, conductivity and dielectric permittivity of a composite with a conducting filler are exponential functions, which provides means for explanation of $\varepsilon'$ and $\varepsilon''$ dependencies as functions of nanoparticles concentration.
As it follows from the results of studies of the influence of thermal treatment on $\varepsilon'$ and $\varepsilon''$, these values are mainly determined by the inner structure of nanoparticles or ratio of phases they are comprised of, which can have a significant effect on concentrations of free and bound charges in them. Contribution of charge states on both the surface of nanoparticles and metal-polymer interface can be another important factor. Magnetic losses in these materials as a function of frequency can be attributed to the resonance of domain borders in single-domain particles and natural ferromagnetic resonance.

### 3.3 Electrophysical properties of composites containing CdS nanoparticles

Nanocomposites based on semiconductor nanoparticles stabilized in LDPE matrix are of special practical interest (Ushakov et al., 2006; Ponomareva et al., 2007, a; Kul’batskii et al., 2009; Radchenko et al., 2009). Electrophysical properties of a series of such materials containing 20% wt. CdS nanoparticles have been studied. The samples differed in average sizes of nanoparticles which were in the range from 4.9 to 19.5 nm.

Electric conductivity values ($\sigma$) of the samples measured at 300…420 K were in the range of 0.01÷0.54 $\mu$S. A dependence of $\sigma$ as a function of reciprocal temperature during heating and cooling of a nanocomposite with CdS nanoparticles 4.9 nm in size is depicted in fig. 8 (the arrows indicate the process direction). A small hysteresis of $\sigma$ is observed during cooling, which is obviously connected to reorganization of the dielectric matrix material. The temperature hysteresis of electric conductivity is a new property of the nanocomposite medium. Also, two dramatic changes of conductivity are observed during heating at ca. 75 and 95°C. They can be probably attributed to a change of energy of charge carriers, which enables the latter to overcome potential barriers in the nanocomposite material.

Fig. 9 depicts a dependence of the real part of dielectric permittivity $\varepsilon$ as a function of temperature during heating and cooling (curve 1). The permittivity value increases during heating. Interestingly, this process continues during cooling after the temperature maximum has been reached. As a result, the value of $\varepsilon$ changes after the heating-cooling loop and doesn’t change for some time (for at least 7 days). If the heating-cooling cycle is repeated, capacitance of the nanocomposite medium will increase, but this time the change will only be 10-20% of that after the first loop. The hysteresis becomes hardly observable starting from the 3rd or 4th loop. This behaviour of the composite material is obviously connected to the thermally stimulated process of the dielectric matrix structure rearrangement and, as a result, emerging of metastable states of the medium. The same dependence for the “empty” LDPE is depicted by curve 2 in fig. 9. In general, the behaviour of the dependence is almost the same as in case of the metal-polymer nanocomposite; the only prominent difference is the much smaller (at least, 2 times smaller) temperature susceptibility of dielectric permittivity of LDPE. Therefore, impregnation of nanoparticles into a polymer matrix makes dielectric permittivity of the resulting material more susceptible to temperature changes, retaining the nature of its dependence as a function of temperature, in general. Permittivity $\varepsilon$ of nanocomposites based on LDPE with 20% wt. CdS nanoparticles is 5.60±0.32 at 35°C.

Fig. 10 depicts temperature dependencies of the relative value of dielectric permittivity of nanocomposite samples with 20% wt. CdS which differ in average sizes of the nanoparticles. Curves 1, 2, and 3 in fig. 10 correspond to the average sizes of 4.9, 5.6, and 6.2 nm, respectively. As it follows from the dependencies acquired, size of nanoparticles has little effect on dependencies of relative permittivity as a function of temperature during cooling.
However, a prominent effect is observed during heating. These dependencies are congruent for all the studied materials up to 50°C. As temperature rises further, the growth rate of susceptibility to temperature becomes higher in case of smaller particles. It’s worthwhile to note that size of nanoparticles has almost no effect on the relative change of dielectric permittivity during heating and cooling.

![Graph showing conductivity](image1)

**Fig. 8.** Conductivity of a nanocomposite with 20% wt. CdS in LDPE as a function of reciprocal temperature

![Graph showing dielectric permittivity](image2)

**Fig. 9.** The real part of dielectric permittivity as a function of temperature measured for: 1. nanocomposite comprised of LDPE and 20% wt. CdS nanoparticles; 2. - LDPE
Fig. 10. Relative dielectric permittivity values as functions of temperature measured for nanocomposites with 20% wt. CdS nanoparticles in LDPE with the average size of nanoparticles equal to: 1) 4.9 nm; 2) 5.6 nm; 3) 6.2 nm

Changes of dielectric loss factor induced by heating and cooling have been estimated. The relative change of dielectric loss factor after the whole cycle was found to be 1.79. The value of dielectric loss factor of the samples studied was 0.0088 at 35°C (which was the initial temperature).

Fig. 11 depicts dependences of dielectric relaxation time as functions of temperature measured during the heating-cooling process. Heating leads to a monotonous growth of dielectric relaxation time. Also, a small temperature hysteresis of the relaxation time values is observed.

Fig. 11. Dielectric relaxation times of samples comprised of 20% wt. CdS in LDPE as functions of temperature
Dielectric relaxation times did not exceed 20 ns.

Fig. 12 depicts relative activation energy of relaxation processes as a function of temperature during heating and cooling of the sample containing 20% wt. Co. A common feature of the dependences measured is the growth of activation energy during heating and its decrease during cooling, which corresponds to a change of charge carrier energy with temperature changing and, therefore, a shift of Fermi level within the band gap of the material. It may result in release of trapped charges, therefore changing dielectric properties of a medium. It’s worthwhile to note that this dependence is almost linear. The range of dielectric relaxation activation energy change was found to be $10 - 30 \text{kJ/(K} \cdot \text{mol)}$.

![Fig. 12. Relative activation energy of dielectric relaxation processes in samples comprised of 20% wt. CdS nanoparticles in LDPE as a function of temperature](image)

Therefore, the measured kinetic and energy parameters of temperature dependences in composite nanomaterials based on LDPE containing 20% wt. CdS nanoparticles allow qualitatively describe energy spectra of such materials. In our assumption, they are a set of mini-zones in the band gap near the top of the valent zone. In this case, the behaviour of dependencies of the parameters of the composites studied as functions of temperature can be attributed to charge carrier transitions between those mini-zones (Ul’zutuev et al., 2009). Further investigations revealed that such hysteresis behaviour of dielectric permittivity, dielectric losses, and time of dielectric relaxation as functions of temperature are also inherent to composite nanomaterials comprised of ceria nanoparticles in LDPE.

### 3.4 Electrophysical properties of composites containing Cu@Cu$_2$O nanoparticles

Fig. 13 depicts dependences of relative values of specific conductivity ($G_x/G_0$, curve 1), permittivity ($\varepsilon_x/\varepsilon_0$, curve 2), and dielectric loss coefficient (curve 3) as functions of nanoparticle concentration recorded at 1 MHz and $T = 300 \text{K}$ for samples comprised of Cu@Cu$_2$O nanoparticles in LDPE which have different concentrations of nanoparticles. The initial values of conductivity, permittivity, and dielectric loss coefficient of the Cu@Cu$_2$O/LDPE sample with low nanoparticles concentration ($x < 10\% \text{ wt.}$) were $G_0 = 1.1 \mu\text{S/m}$, $\varepsilon_0 = 2.5$, and $\tan\delta_0 = 0.015$, respectively. As concentration of nanoparticles
grows, dielectric permittivity increases up to 6 times, dielectric losses at 1 MHz increase up to 3 times, and specific conductivity becomes almost up to 1.5 times higher at 30 mass.% nanoparticles. However, conductivity decreases as concentration of nanoparticles rises from 10% to 20% wt.

Fig. 13. Relative values of specific conductivity \( \frac{G_x}{G_0} \) (curve 1), dielectric permittivity \( \frac{\varepsilon_x}{\varepsilon_0} \) (curve 2), and dielectric loss coefficient \( \tan \delta_x/\tan \delta_0 \) (curve 3) as functions of nanoparticles concentration \( x, \text{wt.\%} \) in composites comprised of Cu@Cu$_2$O nanoparticles in LDPE.

Studies of applications of Cu-containing nanocomposites in waveguide and resonator SHF devices as dielectric insertions revealed that such materials are prospective for controlling resonance frequencies of induced waves and field structure in such systems.

Logarithmic dependencies of current at 1 MHz as functions of reciprocal temperature measured for samples with 20, 25, and 30% wt. Cu@Cu$_2$O in LDPE are given in fig. 14 (curves 1, 2, and 3, respectively).

Logarithmic dependencies of current as functions of reciprocal temperature measured at 1 MHz for nanocomposites with different concentrations of copper-containing nanoparticles are depicted in fig. 14.

The current maximum (point A) shifts to higher temperatures as nanoparticles concentration grows. Different signs of derivatives of these functions are obviously due to different mechanisms of charge carrier dissipation in the nanocomposites.
Fig. 14. Logarithmic dependences of current as functions of reciprocal temperature measured at 1 MHz for nanocomposites with different concentrations of copper-containing nanoparticles. Point A corresponds to a current maximum.

3.5 Optical properties of the CeO$_2$ nanocomposites

The main measured values were the coefficient of reflection $R=I_r/I_o$ and coefficient of transmission $T = I_{out}/I_o$, where $I_r$, $I_{out}$, and $I_o$ are the intensities of the reflected, transmitted and initial optical signals, respectively. Calculations of all the main spectral and optical properties of the samples were based on the measured dependencies $R(\lambda)$ and $T(\lambda)$. The “Kubelk-Munk” two-stream model was used as the experimental model; it has been successfully applied for optical investigations of biological environments.

The spectral dependencies of the optical absorption coefficient of the composite nanomaterials with the nanoparticle sizes ranging from 3.3 nm to 4.9 nm are shown in Figure 15. The measured dependences have absorption maxima shifted 15 nm far from each other. The maximum absorption corresponding to the larger nanoparticles is shifted towards the short wavelength region. It should be noted that the edge of the fundamental optical absorption of the low density polyethylene matrix is located in the short wavelength region (nm). It is known that the optical properties of composite materials mainly depend on the properties of excitons and polaritons. Excitons and polaritons are induced within the nanoparticles and at the nanoparticle-matrix boundaries (the Maxwell Wagner effect).

New aspects of exciton-radiation interaction are discussed from the viewpoint of microscopic nonlocal optical sponse developed for the study of nano-structures materials are reviewed in (Gorobinskii et al., 2007; Ushakov et al., 2008). Localization of excitons within the nanoparticles dramatically increases the binding energy (up to 20-30 meV) and the exciton oscillator strength. The increase of the binding energy is due to the decrease of the distance between electrons and holes which leads to intensification of the Coulomb interaction. Applying a matrix with small permittivity may increase the binding energy by an order of magnitude (up to 0.2-0.3 eV). The dielectric amplification caused by the
Coulomb energy concentration showed a large difference in the dielectric constants of nanoparticles in this matrix system. The measurement of the dielectric constant of the 10% wt. CeO$_2$-PE composite material showed its effective value to be 3.8±0.1 at a frequency of 1 MHz. The dielectric constant of LDPE is equal to 2.2±0.1. The collected optical absorption spectra (Figure 15) correspond to the exciton spectra of nanoparticles of different sizes. The coefficient of optical absorption $K$ for the exciton transitions is determined by the following equitation [27]:

$$K = A \frac{8}{\pi^2} \left( \frac{\bar{a}}{a_{ex}} \right)^3 \left( \frac{\hbar^2 \pi^2}{M \bar{a}^2} \right)^{-1} \sum_n \frac{1}{n^2} \delta \left( \Delta + E_{ex} - \frac{\hbar^2 \pi^2 n^2}{2M \bar{a}^2} \right)$$

where $A$ is the variable proportional to the square of the modulus of the matrix dipole moment calculated based on the Blokhov functions; $\bar{a}$ is the average size of nanoparticles; $a_{ex}$ is the exciton radius; $M = m_e + m_h$ is the total mass of an exciton ($m_e$ is the mass of an electron, $m_h$ is the mass of a hole); $\hbar$ is the reduced Planck constant; $n$ is the number of electron levels ($n = 1$ is the lowest level); $E_{ex}$ is the exciton energy; $\Delta = h\omega - E_g$; $h\omega$ is the photon energy; $E_g$ is the band-gap energy.

According to Equation (1), the shift of the absorption maximum for the highest oscillation strength ($n = 1$) depends on the value of $M\bar{a}^2$; i.e., it depends on the mass and average radius of an exciton. In the case of ensembles of nanoparticles with the same average size, a decrease in their size without changing their mass shifts the absorption maximum towards the short-wave region of the spectrum (the so-called “blue shift”). In our case, the inverse situation occurred: the absorption maximum for the CeO$_2$ nanoparticles obtained from (Et$_4$N)$_2$Ce(NO$_3$)$_6$ with the size of 4.9 nm is shifted by 15 nm towards higher frequencies compared to the CeO$_2$ nanoparticles with the size of 3.3 nm obtained from (NH$_4$)$_2$Ce(NO$_3$)$_6$. Apparently, the shift can be explained by the fact that the mass of an exciton is noticeably lower for larger nanoparticles than for smaller ones. Hence, the multiplication product of the mass of an exciton by its radius gives a lower value for larger particles and results in a longer shift than for small nanoparticles. The widening of the optical absorption spectra at wavelengths longer than 550 nm observed for the nanoparticles with different average sizes (curves 1 and 2; Figure 15) is caused by the statistical size distribution of the particles.

The dispersion characteristics of the 10% wt. CeO$_2$-LDPE composite are shown in Figure 16. The index of refraction is noticeably higher for the smaller nanoparticles than for the larger ones. The exception is the point “a” ($\lambda = 623$ nm). The dispersion curve is very steep in the 400 – 500 nm region for the smaller nanoparticles, and this steepness is not observed for the larger nanoparticles.

The mean values of the index of refraction $<n_0>$ and the index of absorption $<k>$ in the complex index of refraction $(n = n_0 - jk)$ of the composite medium were calculated based on spectral data. For the pure polyethylene, these values are $<n_0> = 1.5$, and $<k> = 1.166 \times 10^{-5}$. The dependencies of the index of refraction as subject to the nanoparticle size are shown in Figure 17 (a). As mentioned previously, composite nanomaterials are the media with the complex index of refraction $n = n_0 - jk$; where $n_0$ is the index of refraction, and $k$ is the index of absorption.

The increase in the index of refraction with the decrease of the nanoparticle size can be explained by the growth of the polarization of the electric dipoles at the nanoparticle matrix boundary (the Maxwell-Wagner effect) (see Figure 17).
The optical absorption, which is determined by the absorbing volume and the size of nanoparticles, increased along with an increase in concentration, in which case, the average value of the optical absorption coefficient should grow along with the size of the nanoparticles. Such behavior of both the optical refraction and absorption indexes is depicted in Figures 17 (b, c).

Fig. 15. Optical absorption in the 10% wt. CeO₂-LDPE composite nanomaterial: line 1 corresponds to the CeO₂ nanoparticles with the size of 3.3 nm; line 2 corresponds to the CeO₂ nanoparticles with the size of 4.9 nm. The points “a” and “b” are the maxima of the curves at 492 and 477 nm, respectively.

Fig. 16. The dispersion characteristics of the CeO₂-LDPE nanocomposite containing 10% wt. CeO₂ nanoparticles with different sizes. Curve 1: the average size of nanoparticles is 3.3 nm; curve 2: the average size of nanoparticles is 4.9 nm.
Fig. 17. Dependencies of the index of refraction (a), index of optical absorption (b), and absorption coefficient of the materials with nanoparticles having different average sizes (c).

Interesting optical properties of composites based on ZnO, CdS, and CuO nanoparticles were described elsewhere (Ushakov et al., 2006; Ponomareva et al., 2007, b; Yurkov et al., 2009; Kul’batskii et al., 2009).
4. Conclusion

1. Electrophysical properties of metal-polymer nanocomposites comprised of iron-, cobalt-, copper-containing or CdS nanoparticles embedded in low density polyethylene have been studied.
2. Measurements revealed that dielectric permittivity and electromagnetic radiation absorption of a nanostructured material grow as concentration of nanoparticles in the material increases.
3. Variation of size and concentration of nanoparticles has been found to change electrophysical properties of composite materials, namely: dielectric permittivity, volume resistance.
4. Microwave measurements characterize the samples studied as materials with steady absorption and permittivity in a wide band within the frequency range studied.
5. Dependences of dielectric permittivity, dielectric losses, and dielectric relaxation times of composite materials comprised of CeO$_2$ or CdS nanoparticles impregnated in LDPE have a hysteresis nature as functions of temperature.
6. Composites undergo additional polarization after cooling, and their dielectric permittivity increases by $\Delta \varepsilon$ (this value depends on nanoparticles size). $\Delta \varepsilon$ equals 1.3-1.4 for small nanoparticles (~5 nm) and lowers as nanoparticles size grows.

The composite medium changes its state stepwise during heating. The transition occurs at lower temperatures in case of smaller nanoparticles and longer times of dielectric relaxation, which is obvious because smaller nanoparticles are more chemically active. The higher the activation energy, the more rapid are the processes of dipole orientation in external magnetic field.

5. References


Due to their good mechanical characteristics in terms of stiffness and strength coupled with mass-saving advantage and other attractive physico-chemical properties, composite materials are successfully used in medicine and nanotechnology fields. To this end, the chapters composing the book have been divided into the following sections: medicine, dental and pharmaceutical applications; nanocomposites for energy efficiency; characterization and fabrication, all of which provide an invaluable overview of this fascinating subject area. The book presents, in addition, some studies carried out in orthopedic and stomatological applications and others aiming to design and produce new devices using the latest advances in nanotechnology. This wide variety of theoretical, numerical and experimental results can help specialists involved in these disciplines to enhance competitiveness and innovation.

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