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Preparation and Investigation of Structural and Dielectric Properties of PEO–PVA–Fe₂O₃ Nanocomposites for Electronic Nanodevices

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The PEO–PVA–Fe₂O₃ nanocomposites are prepared from mixing PVA and PEO with different concentrations of Fe₂O₃ nanoparticles (0, 1.5, 3, 4.5 and 6 wt.%) by using the casting method. The structural and dielectric properties of PEO–PVA–Fe₂O₃ nanocomposites are studied. Optical microscopy images show that the iron-oxide nanoparticles form a continuous network inside the polymer blend at concentration of 4.5 and 6 wt.%. FTIR spectra show shift in some peak position and change in the intensities of others comparing with PEO–PVA blend. The dielectric properties of nanocomposites demonstrate that the dielectric constant, dielectric loss and A.C. electrical conductivity of PEO–PVA blend increase with increasing of Fe₂O₃ nanoparticles' concentration. The dielectric constant and dielectric loss of PEO–PVA–Fe₂O₃ nanocomposites decrease, while the A.C. electrical conductivity increases with increasing frequency. These results indicate that the PEO–PVA–Fe₂O₃ nanocomposites may be considered as promising materials for electronics and electrical nanodevices.

Наноккомпозити поліетиленоксид (ПЕО)полівініловий спирт (ПВС)–Fe₂O₃ виготовлено змішуванням ПВС і ПЕО з наночастинками Fe₂O₃ в різних концентраціях (0, 1,5, 3, 4,5 та 6 мас.%) методом лиття. Досліджено структурні та діелектричні властивості наноккомпозитів ПЕО–ПВС–Fe₂O₃. Зображення оптичної мікроскопії показують, що наночастинки оксиду Феруму утворюють безперервну мережу всередині полімерної суміші за концентрацій у 4,5 і 6 мас.%. Спектри інфрачервоної спектроскопії на основі Фур'є-перетвору показують зсув в позиції одного піка та зміну інтенсивності інших у порівнянні із сумішшю ПЕО–

ПВС. Діелектричні властивості наноккомпозитів демонструють, що діелектрична проникність, діелектричні втрати й електропровідність змінного струму суміші ПЕО–ПВС зростають із збільшенням концентрації наночастинок Fe_2O_3 . Діелектрична проникність і діелектричні втрати наноккомпозитів ПЕО–ПВС– Fe_2O_3 зменшуються, тоді як електропровідність змінного струму зростає зі збільшенням частоти. Ці результати вказують на те, що наноккомпозити ПЕО–ПВС– Fe_2O_3 можна розглядати як перспективні матеріали для електроніки й електричних нанопристроїв.

Key words: polyethylene oxide, polyvinyl alcohol, Fe_2O_3 nanoparticles, nanocomposites, structural properties, dielectric properties.

Ключові слова: поліоксиетилен, полівініловий спирт, наночастинок Fe_2O_3 , наноккомпозити, структурні властивості, діелектричні властивості.

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1. INTRODUCTION

Nanoparticles (NPs) are the easiest type of 1–100 nm size constructions. Any collection of atoms bonded together with a structural radius of less than 100 nm can be considered as a nanoparticle in theory. They are a connection between bulk materials and molecular or atomic structures. Nanoparticles have distinct chemical and physical characteristics compared to bulk products such as reduced melting points, greater surface area, mechanical strength, particular optical characteristics and particular magnetizations [1, 2]. The interfacial and surface characteristics can be changed in the presence of chemical agents. Indirectly, such agents can stabilise against coagulation and aggregation by maintaining particle charge and by modifying the outermost layer of the particle. In the past decade, the synthesis of iron oxide nanoparticles has been intensively developed not only for its fundamental scientific interest but also for many technological and biomedical applications [2, 4].

There is an important aspect of nanotechnology, which is the miniaturization of current and new instruments, sensors and machines that will greatly influence the world. Examples of possible miniaturization are: computers with infinitely great power that compute algorithms to mimic human brains, biosensors that warn us at the early stage of the onset of disease and preferably at the molecular level and target specific drugs that automatically attack the diseased cells on site, nanorobots, which can repair internal damage and remove chemical toxins in human bodies, and nanoscale electronics that constantly monitor our local environment [5, 6].

Nanotechnology has an extremely broad range of potential appli-

cations from nanoscale electronics and optics, to nanobiological systems and nanomedicine, to new materials, and, therefore, it requires the formation and contribution from multidisciplinary teams of physicists, chemists, materials scientists, engineers, molecular biologists, pharmacologists and others to work together on: (i) synthesis and processing of nanomaterials and nanostructures, (ii) understanding the physical properties related to the nanometer scale, (iii) design and construction of novel tools for characterization of nanostructures and nanomaterials, (iv) design and fabrication of nanodevices or devices with nanomaterials as building blocks [7, 8]. Work on the fabrication and the processing of nanomaterials and nanostructures started long time ago, far earlier than nanotechnology emerged as a new scientific field. Such research has been drastically intensified in the last decade, resulting in overwhelming literatures in many journals across different disciplines. The research on nanotechnology is evolving and expanding very rapidly [9, 10].

Polyethylene oxide is the most interesting base material because of its high chemical and thermal stability. PEO is a semi-crystalline polymer, possessing both amorphous and crystalline phases at room temperature. It can solvate a wide variety of salts even at very high salt concentrations. The solvation of salts occurs through the association of the metallic cations with oxygen atoms in the backbone [11, 12]. Polyvinyl alcohol (PVA) is an important water-soluble transparent polymer and is extensively used in industries due to the excellent chemical and physical properties, non-toxicity, good chemical resistance, good film formation capacity, biodegradability and high crystal modulus. PVA is used here in hydrolyzed form with the degree of 85% hydrolysis. It is a polymer with many technological, pharmaceutical and biomedical applications [13, 14]. Iron oxides are interesting due to their catalytic, magnetic, and semiconducting properties, and because they are produced during corrosion. Their applications include, *e.g.*, usage as pigments, catalysts in styrene synthesis, and as a material for high-density magnetic storage. At room temperature, the normal stoichiometric forms of iron oxides Fe₂O₃ [15].

This paper aims to synthesis and characterization of PEO-PVA-Fe₂O₃ nanocomposites for employ in optoelectronics fields.

2. EXPERIMENTAL PART

The PEO-PVA-Fe₂O₃ nanocomposites were prepared from mixing the PVA and PEO with different concentrations of the Fe₂O₃ nanoparticles by using the casting method. These samples were added as PVA 50 wt.% with PEO 50 wt.%; the mixtures were stirred continuously for 40 minutes at temperature of 70°C until homogeneous

solutions were obtained, after casting in different Petri dishes, the solutions were left to dry at room temperature for films to form. The films were transferred into a desiccator for continuous drying.

The structural properties of PEO-PVA-Fe₂O₃ NCs examined by the optical microscope (OM) provided by Olympus (Top View, type Nikon-73346) and the Fourier transformation infrared (FTIR) spectroscopy (Bruker company type vertex-70, German origin) with variety wave number 500–4000 cm⁻¹.

The dielectric properties of PEO-PVA-Fe₂O₃ nanocomposites were measured by using LCR meters in the frequency range (100 Hz to 5 MHz).

The dielectric constant (ϵ') of nanocomposites is defined by the equation [16, 17]

$$\epsilon' = C_p/C_0, \quad (1)$$

where C_p is parallel capacitance and C_0 is vacuum capacitor.

The dielectric loss (ϵ'') is given by the equation [18]

$$\epsilon'' = \epsilon' D, \quad (2)$$

where D is displacement.

The A.C. electrical conductivity is determined by the following equation [19, 20]:

$$\sigma_{A.C.} = \omega \epsilon'' \epsilon_0, \quad (3)$$

where ω is the angular frequency.

3. RESULTS AND DISSCUSION

3.1. Structural Properties

3.1.1. Optical Microscopy

Figure 1 shows the images of PEO-PVA-Fe₂O₃ nanocomposites films were taken for samples of different concentrations at magnification power $\times 10$. However, they show a clear difference to the samples as shown in images *a*, *b*, *c*, *d* and *e*.

When the concentrations of Fe₂O₃ increase in PEO-PVA blend, the nanoparticles form actuators inside the polymer blend. When the concentration of nanoparticles reaches to 4.5 wt.%, the nanoparticles form a continuous network. Charge carriers can move through the nanocomposites due to the network of channels that runs through them [21–23].

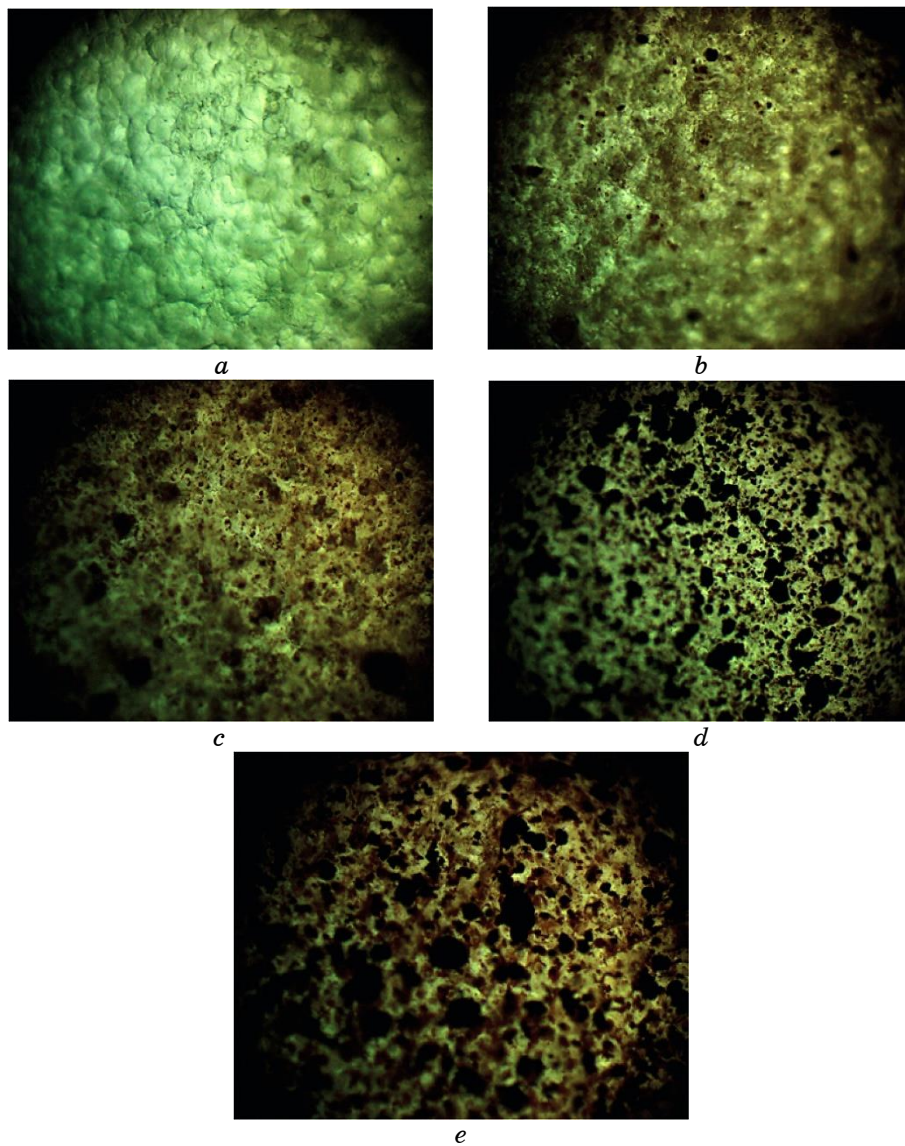


Fig. 1. Photomicrographs for PEO-PVA-Fe₂O₃ nanocomposites: *a*—for PEO-PVA blend; *b*—for 1.5 wt.% Fe₂O₃ NPs; *c*—for 3 wt.% Fe₂O₃ NPs; *d*—for 4.5 wt.% Fe₂O₃ NPs; *e*—for 6 wt.% Fe₂O₃ NPs.

3.1.2. FTIR Spectroscopy of PEO-PVA-Fe₂O₃ Nanocomposites

The FTIR spectroscopy can be used to analyze a wide range of materials such thin films, powders, and other forms.

Information is provided for both blends composition and polymer-

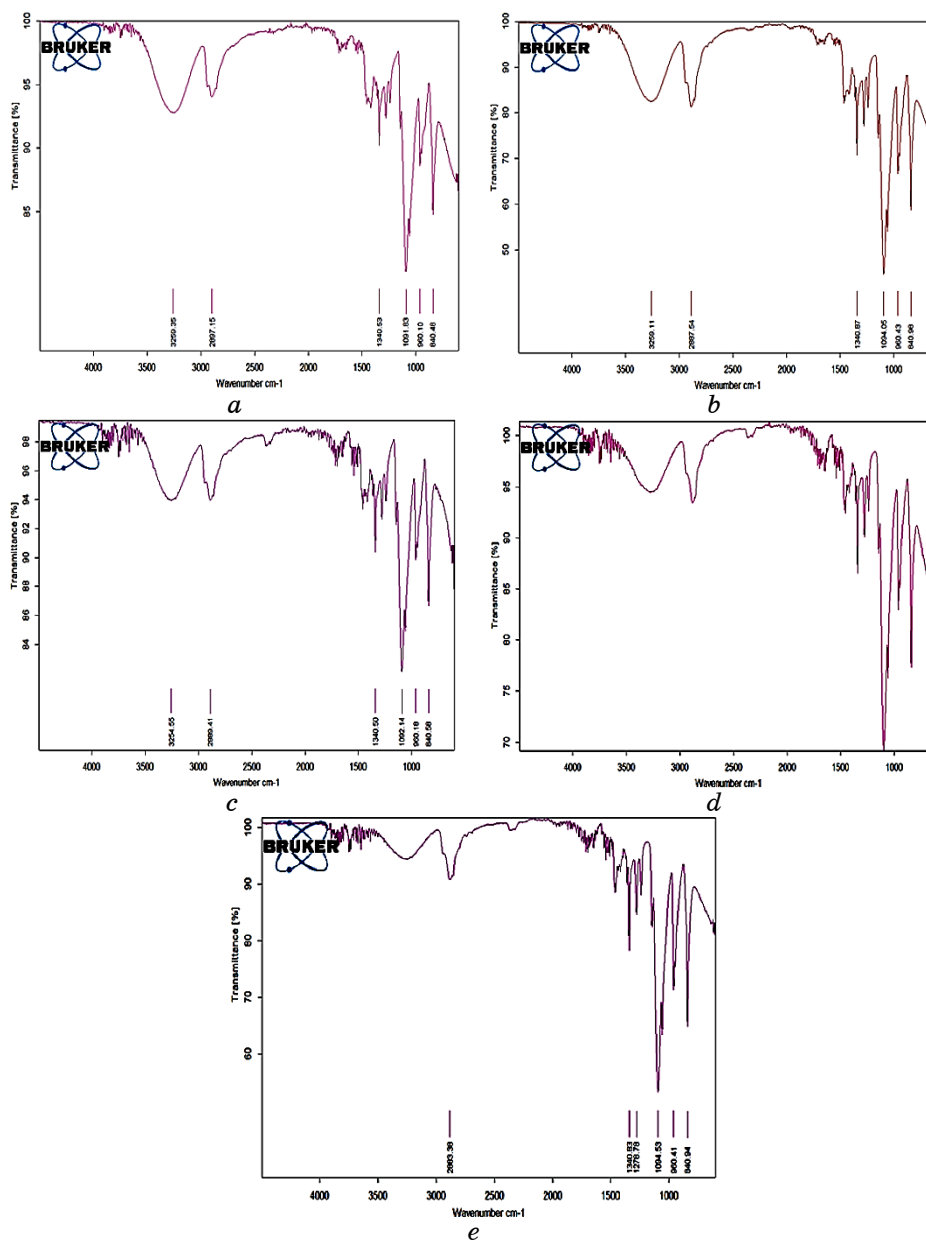


Fig. 2. FTIR spectra for PEO-PVA-Fe₂O₃ nanocomposites: *a*—for PEO-PVA blend; *b*—for 1.5 wt.% Fe₂O₃ NPs; *c*—for 3 wt.% Fe₂O₃ NPs; *d*—for 4.5wt% Fe₂O₃ NPs; *e*—for 6 wt.% Fe₂O₃ NPs.

polymer interactions using those vibrational modes attributed to free and hydrogen bonded of hydroxyl and carbonyl groups.

Figure 2 shows the FTIR radiation spectra of PVA-PEO-Fe₂O₃ nanocomposites. For all samples of nanocomposites, broadband at around 3259.36–3655 cm⁻¹ is observed because of OH groups in the polymers matrix chain. The other bonds as C–O–C group can be noted in the bands at 1094 cm⁻¹ where attributed to the PVA film, which was not so transparent. Peaks at 2897–2900 cm⁻¹ were due to the presence of C–H groups. The C=C stretching mode appears in the bands at 1550–1620 cm⁻¹. The peak at 1091–1098 cm⁻¹ of the band is strong for all samples of nanocomposites; this is due to the stretching mode of C–O group. The two strong bands observed at around 1340–840 cm⁻¹ are due to the stretching and bending modes of CH₂ group [24–27]. Finally, with the addition of Fe₂O₃ nanoparticles to the polymer blend, two significant changes are observed: slight changes in intensities of absorption bands and in vibrational bands; this indicates decoupling between the corresponding vibrations due to interaction between Fe₂O₃ nanoparticles and the two polymers [28].

3.2. The A.C. Electrical Properties of PEO-PVA-Fe₂O₃ Nanocomposites

Figure 3 shows the effect of adding the Fe₂O₃ nanoparticles on the dielectric constant of PEO-PVA blend. The dielectric constant increases with increasing of the concentration of Fe₂O₃ nanoparticles. The reason for this increase is formation of clusters of Fe₂O₃ nanoparticles inside the nanocomposites at low concentrations of Fe₂O₃

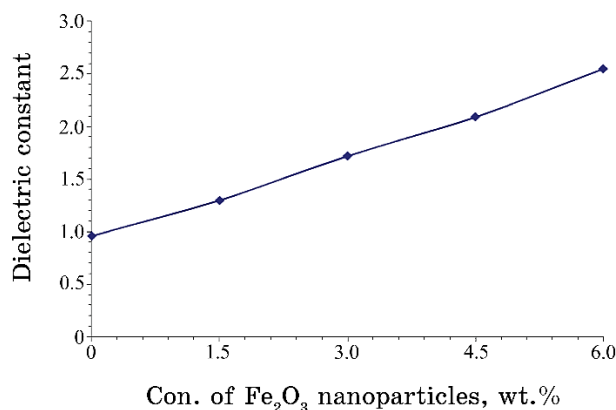


Fig. 3. Effect of Fe₂O₃ nanoparticles' concentration on dielectric constant for PEO-PVA blend.

nanoparticles; hence, the dielectric constant becomes low, and at high concentrations of Fe_2O_3 nanoparticles, they form a continuous network inside the nanocomposites [29, 30], and so, the value of dielectric constant increases with increases of the Fe_2O_3 nanoparticles' concentration. This is similar to the results reached by other researchers [31, 32].

The variation of dielectric constant of PEO-PVA- Fe_2O_3 nanocomposites with frequency is shown in Fig. 4. This figure show that the dielectric constant of all nanocomposite samples decreases as the frequency of applied field increases. It can be due to the tendency

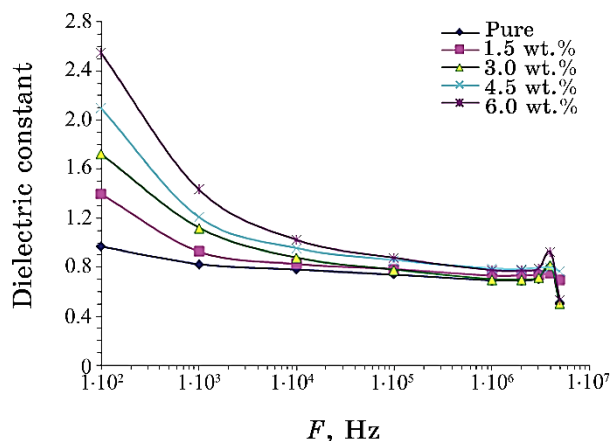


Fig. 4. Variation of dielectric constant for PEO-PVA- Fe_2O_3 nanocomposites with frequency.

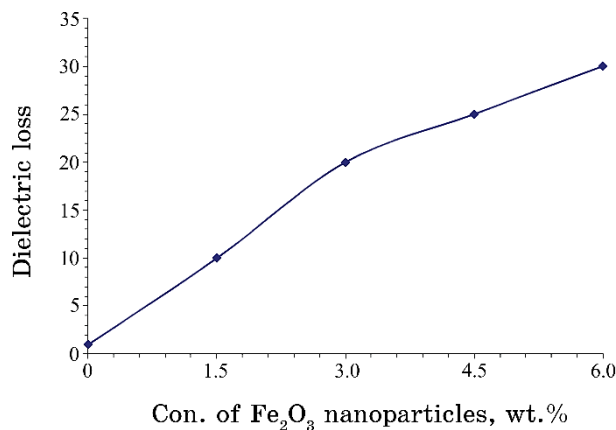


Fig. 5. Effect of Fe_2O_3 nanoparticles' concentration on dielectric loss for PEO-PVA blend.

of dipole in nanocomposite samples in order to orient themselves in the directions of the electrical fields applied and to decrease the polarization of the space charge to absolute polarisation [33, 34]. These ones are similar to the researchers' findings [35, 36].

Figure 5 shows the dielectric loss as a function of frequency of PEO-PVA-Fe₂O₃ nanocomposites. This figure indicates that the dielectric loss of nanocomposites decreases with a rise in the frequency of the applied electric field; this behaviour is due to a decrease in the contribution of the space charge polarization [37, 38], as well as the high value of the dielectric loss for PEO-PVA-Fe₂O₃ nanocomposites at low frequencies.

The dielectric loss of PEO-PVA-Fe₂O₃ nanocomposites increases as the concentration of Fe₂O₃ nanoparticles increases (Fig. 6); this is related to the increase in the number of carriers of charge [39]. When the concentration of nanoparticles exceeds a high ratio, the nanoparticles form a continuous network in the nanocomposites [40]. These results are similar to the other researchers' results [41].

Figure 7 shows the variation of A.C. electrical conductivity of PEO-PVA-Fe₂O₃ nanocomposites. The A.C. conductivity slightly increases at low concentrations of the Fe₂O₃ nanoparticles. The conductivity increases with increasing of the concentration of Fe₂O₃ nanoparticles, because of the increase of the charge carriers and the formation of a continuous network of Fe₂O₃ nanoparticles inside the nanocomposites [42–45]. Consequently, the conductivity is increasing with the increasing of Fe₂O₃ nanoparticles' concentration for PEO-PVA-Fe₂O₃ nanocomposites.

Figure 8 shows the plot of the variation of A.C. electrical conductivity of PEO-PVA-Fe₂O₃ nanocomposites with frequency at

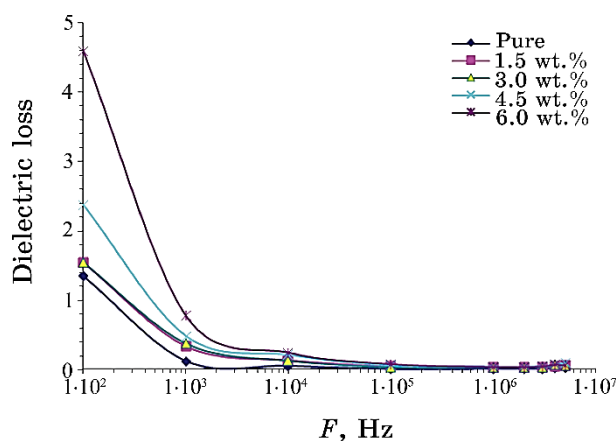


Fig. 6. Variation of dielectric loss for PEO-PVA-Fe₂O₃ nanocomposites with frequency.

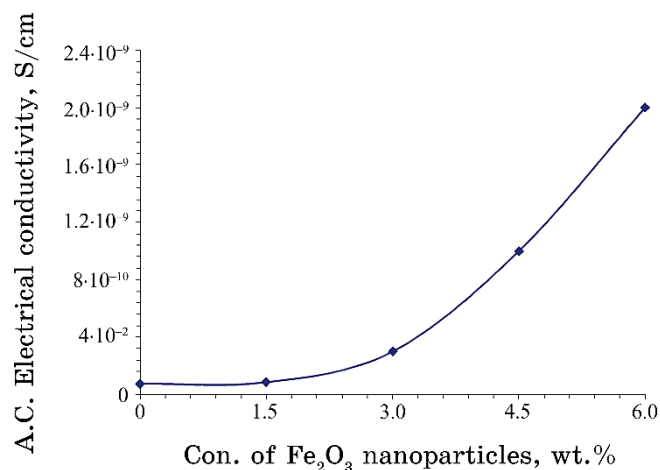


Fig. 7. Effect of Fe₂O₃ nanoparticles' concentration on A.C. electrical conductivity for PEO-PVA blend.

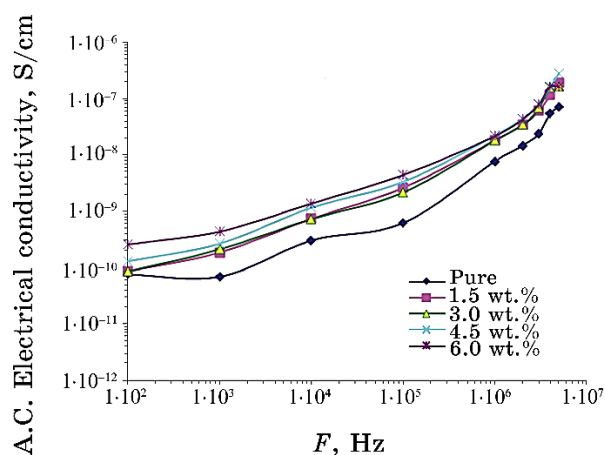


Fig. 8. Variation of dielectric constant for PEO-PVA-Fe₂O₃ nanocomposites with frequency.

room temperature. The A.C. electrical conductivity increases with increasing of the frequency of electric field for all samples of nanocomposites, where the frequency acts as a pumping force, pushing the charge carriers between the different conduction states [46, 47].

4. CONCLUSIONS

The optical microscopy images show that the Fe₂O₃ nanoparticles

form a continuous network inside the polymer blend at concentrations of 4.5 and 6 wt.%.

FTIR spectra show shift in some bands and change in the intensities of other bands. In addition, there are no chemical interaction between Fe₂O₃ nanoparticles and PEO-PVA blend.

The dielectric constant, dielectric loss and A.C. electrical conductivity of PEO-PVA blend increase with increasing of Fe₂O₃ nanoparticles' concentration. The dielectric constant and dielectric loss of nanocomposites are decreased with increasing the frequency, while A.C. electrical conductivity is increased with increasing of the frequency.

Finally, such behaviour makes PEO-PVA-Fe₂O₃ nanocomposites to be considered as excellent electronics materials for electrical applications.

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