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INVESTIGATION OF STRUCTURE AND ELECTROPHYSICAL PROPERTIES OF NANOCOMPOSITE MATERIALS ON THE BASIS OF ZIRCONIUM DIOXIDE IN ISOTACTIC POLYPROPYLENE MATRIX.

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In this paper is presented the study of structure and morphology of nanocomposite materials on the basis of zirconium dioxide nanopartcles (ZrO_2) and isotactic polypropylene (PP) by IR-spectroscopy and AFM microscopy and investigated the electrophysical properties (ε, tgδ, ρ) of nanocomposites depending on the temperature. Has been shown that introduction of nano-sized fillers in polymeric matrix does not impact the chemical structure, but changes the supramolecular structure of polymer. The AFM study reveals that increasing the volume content of zirconium dioxide particles influence on supramolecular structure of polymer and rising of particle size in polymeric matrix. Has been found the increasing of volume content of ZrO_2 up to 3% lead to rising of dielectric permeability where as the further increasing of ZrO_2 concentration bring to decreasing of dielectric permeability. The dependence of dielectric permeability, tgδ and nanocomposition resistivity from temperature, ZrO_2 concentration and frequency shows that introduction of 21 nm sized ZrO_2 nanoparticles up to 3% into polymeric matrix leads to attainment of optimal structure.

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1. Introduction

During last decade the rapid development of synthesis methods in science of polymeric materials led to optimization of composite polymeric materials preparation, containing nanosized structures and study of its properties. In nanoscale, due to considerable increasing of surface atoms and surface effect, such fundamental properties as structure of electronic levels and transmissions, electron affinity, conductivity, temperature of phase crossing and esc. are in dependence of size, shape and chemical surrounding of nanophase [1]. Introduction of inorganic nanoparticles in organic polymer with taking into consideration the above mentioned peculiarities bring to appearance at forming nanocomposite (hybrid composite) new properties, for example fluorescent, optical, catalitical, magnetic and other properties. These new materials successfully found the application in biotechnology and medicine, energetics, producing of packing materials, microelectronics, optics and optoelectronics, catalysis, sensor devises and other areas.

The nanoparticles participate in formation of supramolecular structure and it evidently has positive impact on properties of forming material. Zirconium dioxide has got good mechanical, heat-insulated and dielectric properties in wide temperature interval, which makes possible to consider it as perspective material for preparation of constructive material as well as its application in microelectronics.

The variety of application areas of nanopowder materials on the basis of zirconium dioxide assume the preparation of materials with definite functional properties including for application in disperse phase: polymer fillers, catalysts and its carriers.The purpose of presented work is the study of filler influence on supramolecular structure of polymer and its electro physical properties.

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2. Experimental part

As the investigation object was chosen the powder of isotactic polypropylene with grain size 0,5-1,0 micron, as filler – zirconium dioxide nanoparticles with sizes 21 nm, stabilized by 3% Y_2O_3 [5, 6]. Nanocomposite polymer+ZrO_2 was prepared as follows: the powder of izotactic propilene was dissolved in toluene at 120^0 C. Then at solution of polymer was added the nanopowder of ZrO_2 – 3mol.%Y_2O_3. By hot pressing method at melting point of PP and pressure 10 MPa the samples of nanocomposites films were prepared. By this method were synthesized the nanocomposites with filler ZrO_2 0.1; 0.5; 1; 2; 5; 7; 10 mass %.

IR spectra were recorded on spectrometer FT-IR Varian-3600 Excalibur Series at 4000-400 cm^{-1} intervals.

The morphology of samples was studied by atomic force microscope Integra-Prima (NT-MDT, Zelenograd). For scanning was used special silicon cantilever, prepared by plasma chemical method of etching with radius of curvature of needle 20 nm and resonance frequency 1-5 Hz. The size of scanning area is 1x1 micron. The measurement was implemented at mode semi contact microscopy in air, where was fixed the vibration of cantilever needle, that determine the surface topography. The scanning rate and scanning lines number on the image are 1.969 Hz and 256 Hz correspondingly.

The measurement of dielectric permeability, dielectric loss angle tgδ and resistivity ρ of nanocomposites was carried out by measuring device Immittance MNIPI E7-20. With application of broadband immittance E7-20 was carried out the measurement of frequency dependence of dielectric permeability, dielectric loss and resistivity at temperature interval T=293-453K and frequency interval f= 25-10 Hz.

3. Results and discussion

The IR spectra of pure isotactic polypropylene (PP) and nanocomposites on the basis of PP and ZrO_2 nanoparticles (PP+ZrO_2) are presented on picture 1 (a,b,c). Has been found that introduction of ZrO_2 nanoparticles in PP matrix bring to change of physical structure of polymer. The IR study of nanocomposites show that 1% ZrO_2 content in polymer brings to increasing of intensity of absorption band at 2906 cm^{-1}, 2839 cm^{-1}, 1376 cm^{-1} and 1459 cm^{-1}. The 1376 cm^{-1} band corresponds to symmetrical deformational vibration of CH_3 group, the absorption band at 1459 cm^{-1} – ansymmetrical deformational of CH_3 group, 2839 cm^{-1} corresponds to valence vibration of CH_2 group. When the content of filler ZrO_2 concentration is more than 1% the intensity of absorption band at 2839 cm^{-1}, 1459 cm^{-1} and 1376 cm^{-1} sharply decline. IR studies show that introduction of nanosized fillers in PP matrix not influence the chemical structure, but change the physical structure of polymer, i.e. the increasing the intensity of absorption band of polymer.

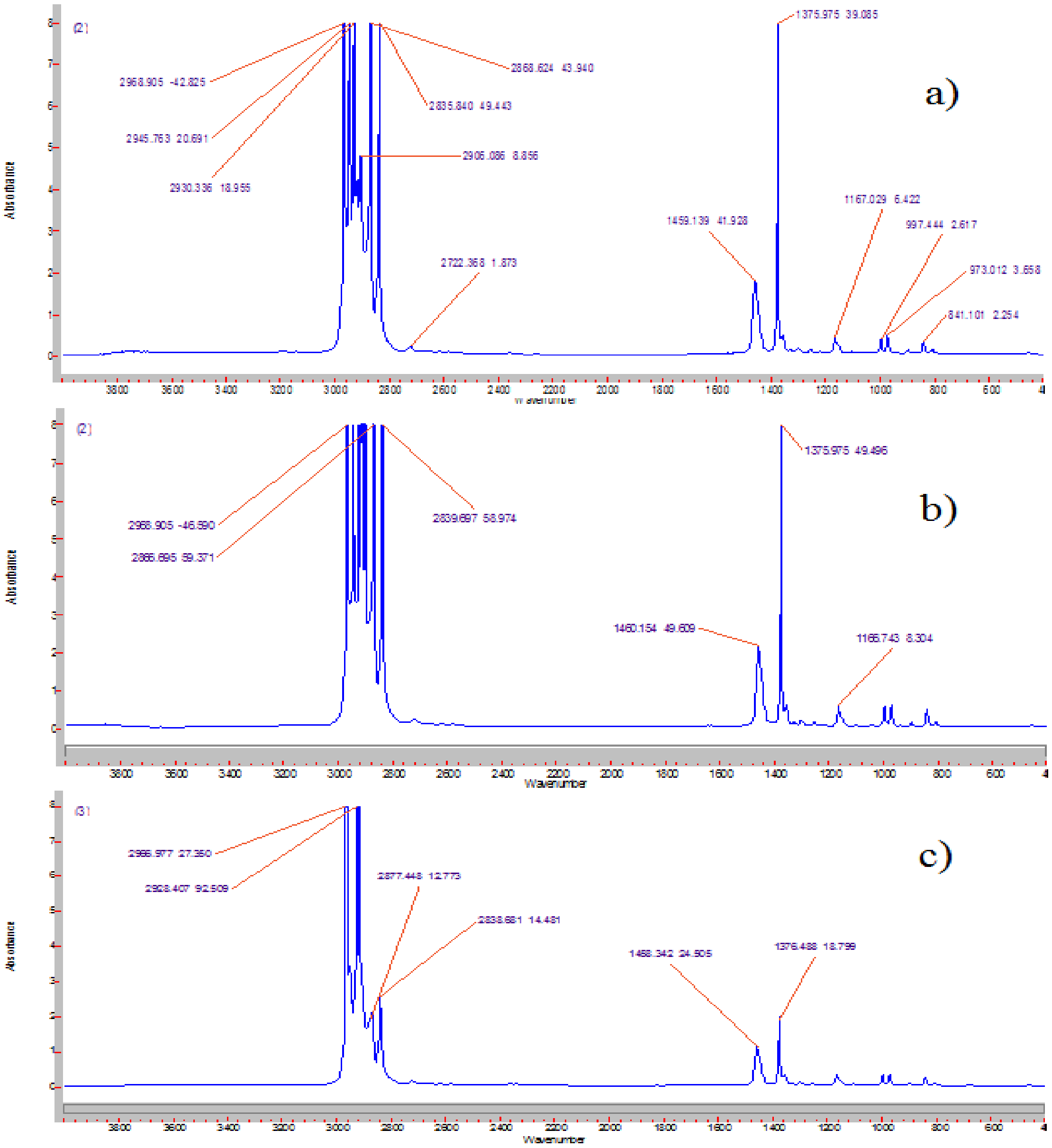

Fig. 1. IR spectra of pure izotactic polypropilen (a) and nanocomposites PP+0,1%ZrO$_2$ (b) and PP+1%ZrO$_2$ (c)

The 2D and 3D AFM images of surface topography of pure PP and nanocomposites PP+ZrO$_2$ are presented on Figs.2 and 3 As it shown the introduction of nanosized powder into polymeric matrix lead to change of supramolecular structure of PP. AFM images reveal that introduction of 0.1% concentrated nanopowder the zirconium dioxide nanoparticles have filamentary form.

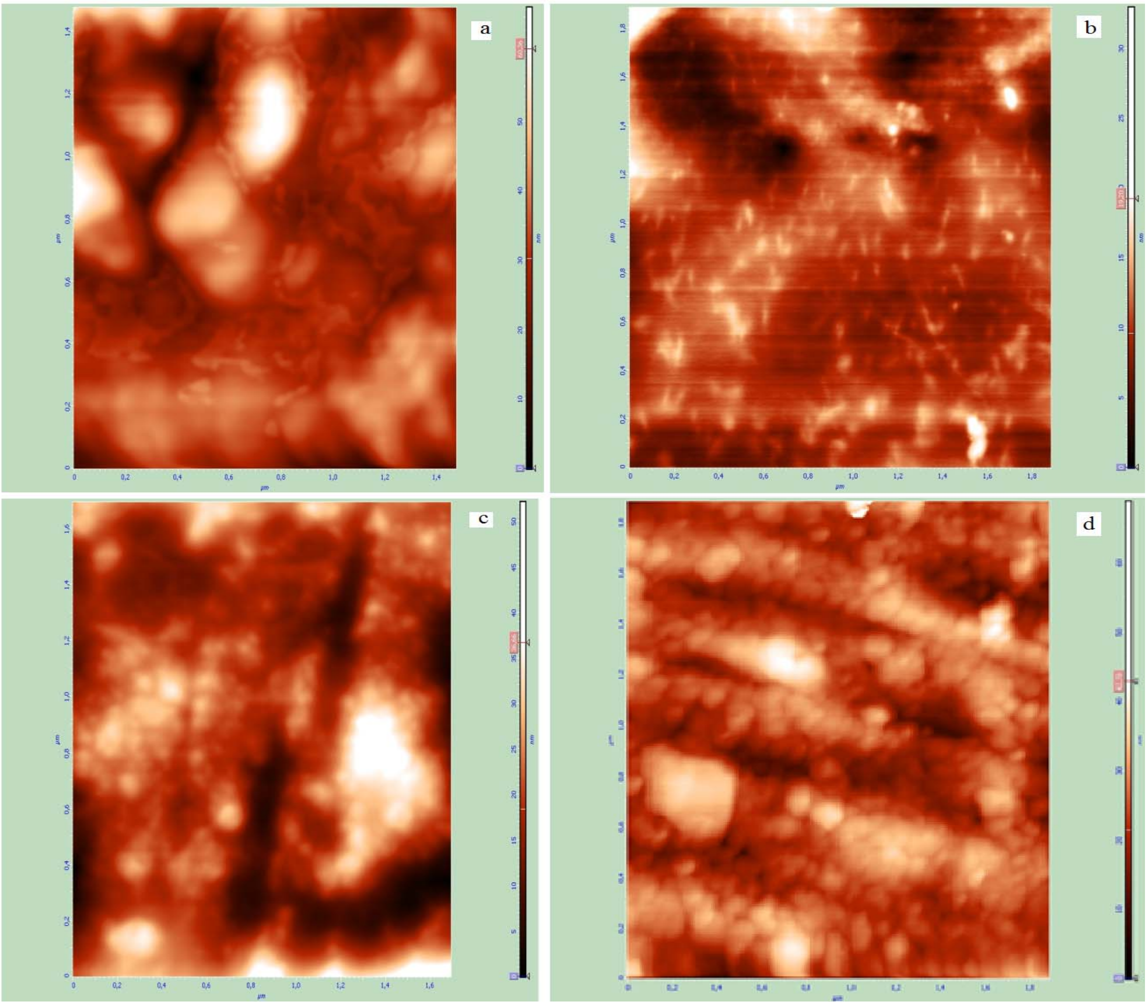

Fig.2 Two dimentional image (2D) of PP (a) and nanocomposite PP+ZrO_2 *(0,1%(b); 1%(c) and 3%(d))*

When the volume content of ZrO_2 in polymeric matrix is 0,1% the size of forming nanoparticles vary in the interval 20-30 nm. With increasing of volume content of zirconium dioxide in polymer occurs the rising of nanoparticles size. So, when the volume content of ZrO_2 in polymeric matrix is 1% the sizes of forming nanoparticles vary in interval 40-60 nm and when it is 3% the size vary 70-100 nm. With further increasing of ZrO_2 concentration the surface elements got the spherulitic shape.

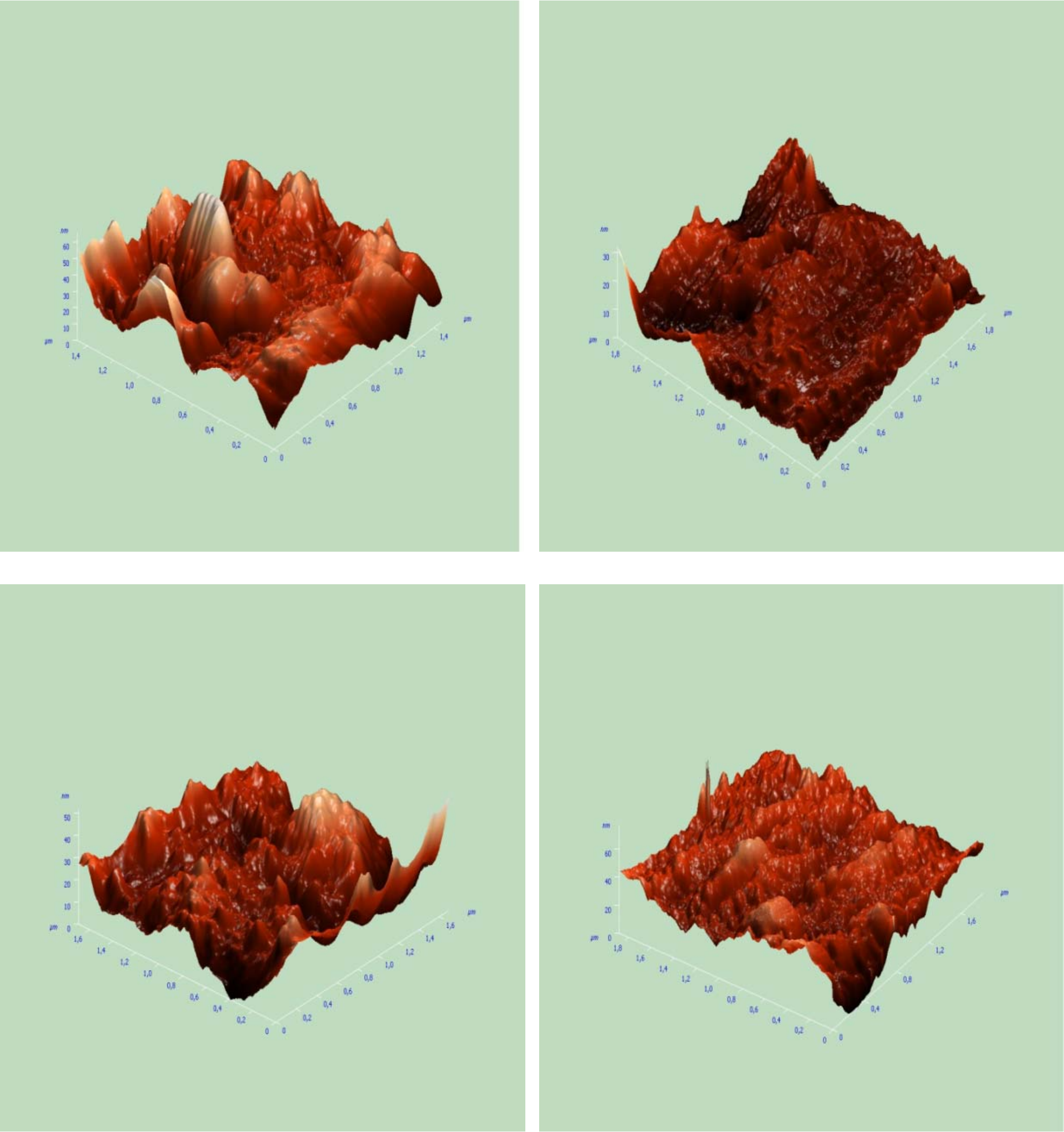

Fig.3 Three dimentional image (3D) of PP and nanocomposite PP+ZrO_2 0,1%; 1% and 3%

The structural surface elements of nanocomposite PP+ ZrO_2 is shown on picture 4. As it is seen from picture the increasing of volume content of ZrO_2 in polymeric matrix lead to change of supramolecular structure of polymer. So the average roughness of surface for nanocomposite PP+0,1%ZrO_2 makes 10 nm, for PP+1%ZrO_2-19 nm, for PP+3%ZrO_2 - 31 nm. Consequently has been found that the increasing of ZrO_2 concentration bring to change of physical structure of polymer.

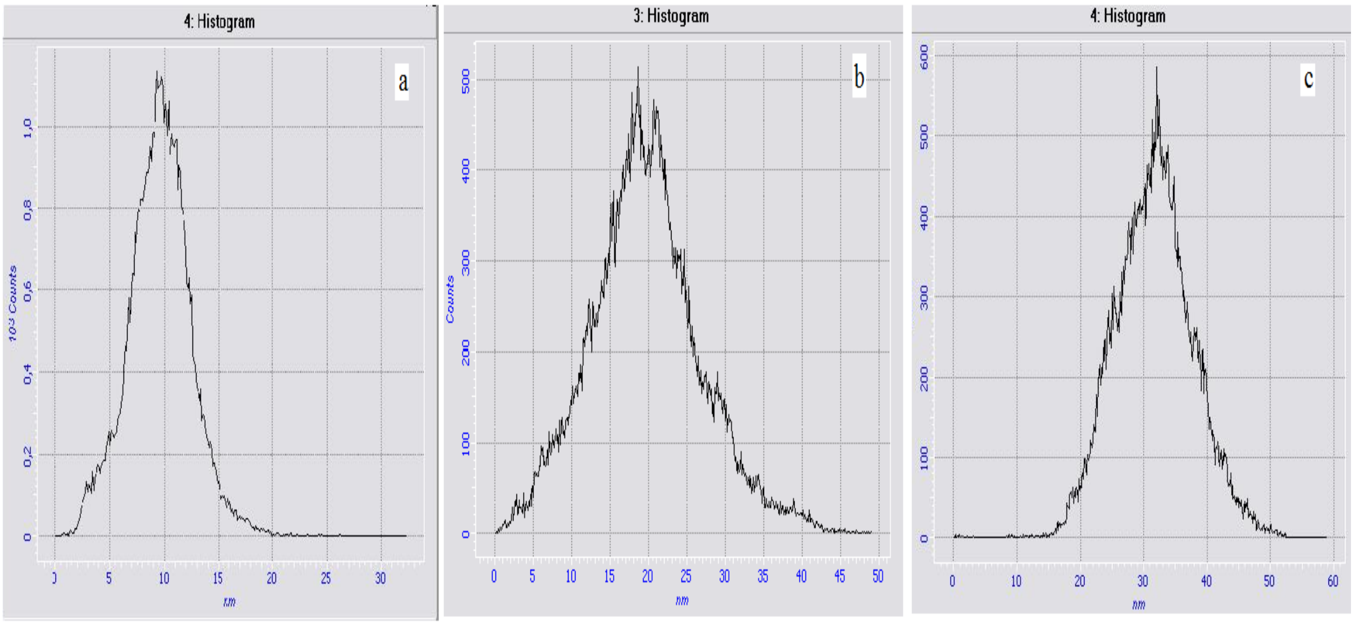

Fig.4 Histograms of average surface roughness of nanocomposite PP + ZrO_2 (0,1%; 1% и 3%)

Has been studied the dependence of dielectric properties (ε, tgδ и ρ_v) of nanocomposite PP+ZrO_2 from temperature. The dependence of dielectric permeability (ε) of nanocomposite PP+ZrO_2 from temperature is shown on picture 5. As it is shown on pic.5 the increasing of temperature the value ε does not change up to 413K, and then decrease at 423K. The declining of dielectric permeability of nanocomposite at 413 K is explained by decomposition of polypropylene crystalline phase, i.e. with decomposition of polypropylene crystalline phase the spacing between nanoparticles rise and, as result the dielectric permeability of nanocomposite diminish. Experimentally have been found the increasing of volume content of ZrO_2 up to 3% lead to rising of dielectric permeability where as the further increasing of ZrO_2 concentration bring to decreasing of dielectric permeability (pic.6). It is also found that the value tgδ change with extremum in dependence of ZrO_2 concentration, i.e. the increasing of ZrO_2 nanoparticles content led to diminish of tgδ and at 3% ZrO_2, the value of tgδ is minimal whereas the further increasing of ZrO_2 concentration led to rising of tδ (pic.7). The increasing of dielectric loss means the increasing of relaxation process, i.e. due to increasing tgδ the conductivity at 3% ZrO_2 content is minimal. This result correlates very well with increasing of dielectric permeability [3,7].

The declining of dielectric permeability of nanocomposite at ZrO_2 content more than 3% is explained by decomposition of phisical structure of polimeric matrix of nanocomposites.

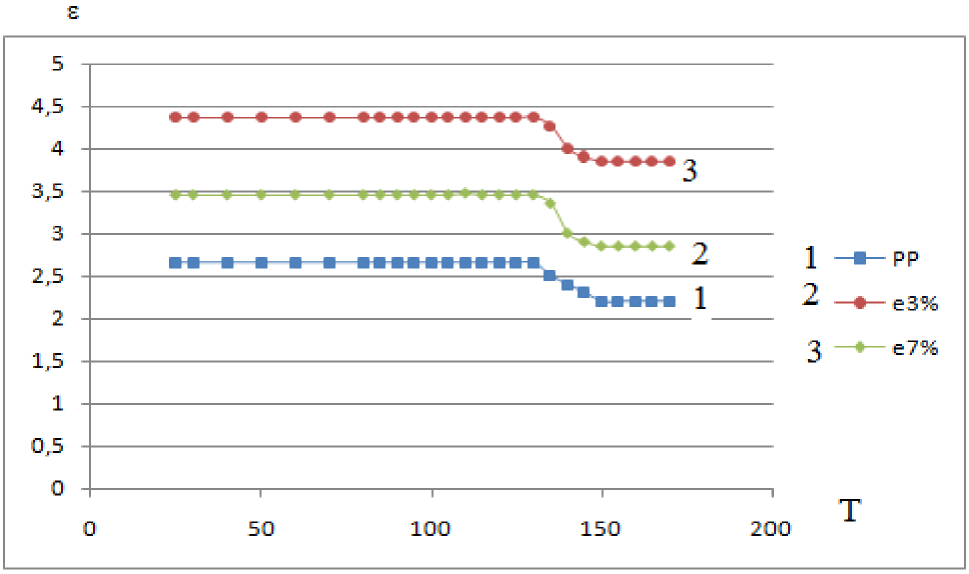

Fig.5 The dependence of dielectric permeability of PP and PP+ZrO_2 from temperature.

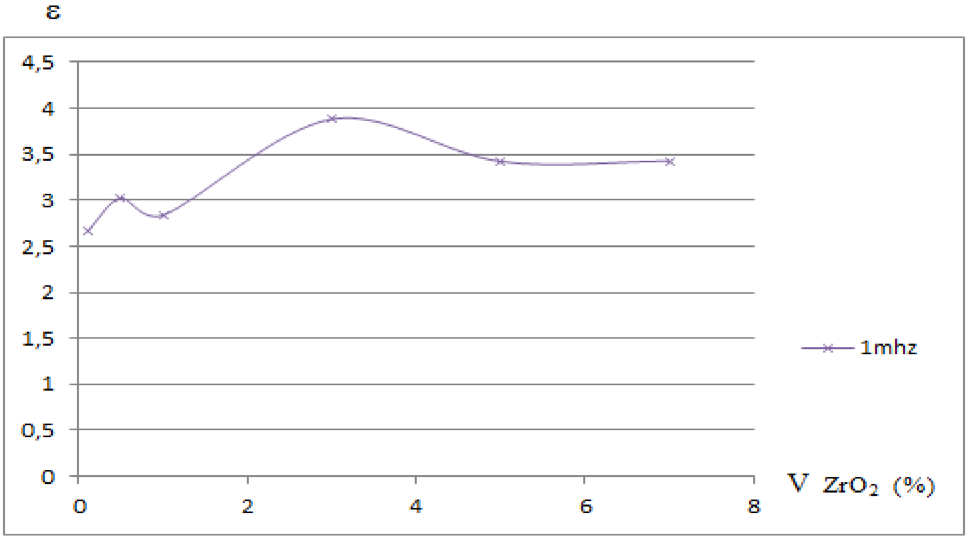

Fig.6 The dependence of dilectric permeability of nanocomposites (PP+ZrO_2) from volume content of ZrO_2

The further increasing of ZrO_2 nanoparticles concentration led to rise of nanocomposite conductivity and this correlate with change of dielectric permeability depending on concentration. The dependence of resistivity from temperature shows before the decomposition temperature of crystalline phase the resistivity does not change. At decomposition temperature of polymer crystalline phase the resistivity discontinuously rise and then diminish.

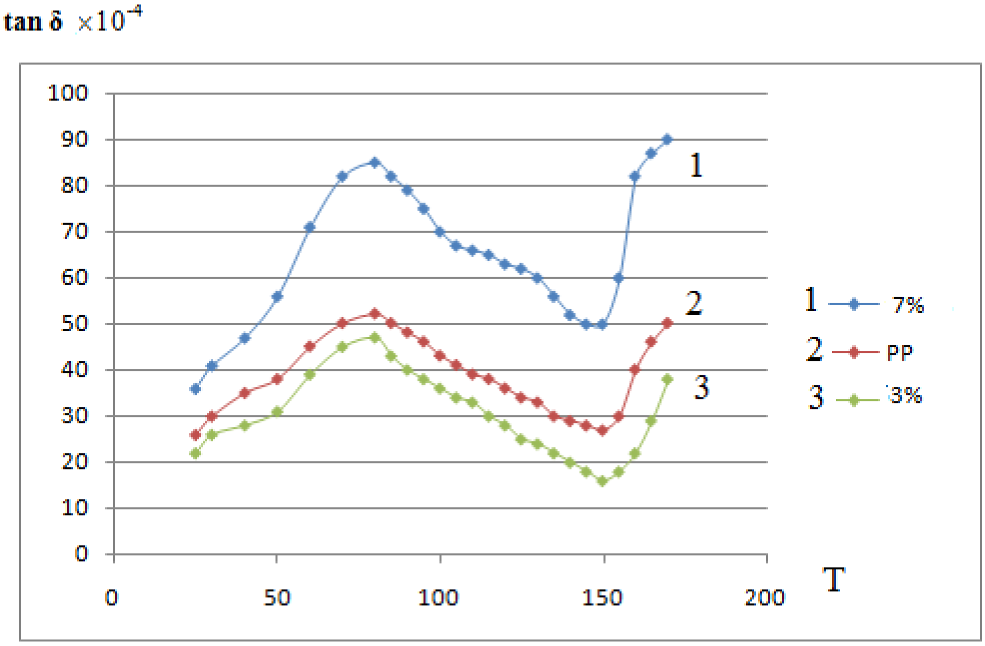

Fig. 7 The dependence of tg δ of PP and PP+ZrO$_2$ nanocomposites from temperature.

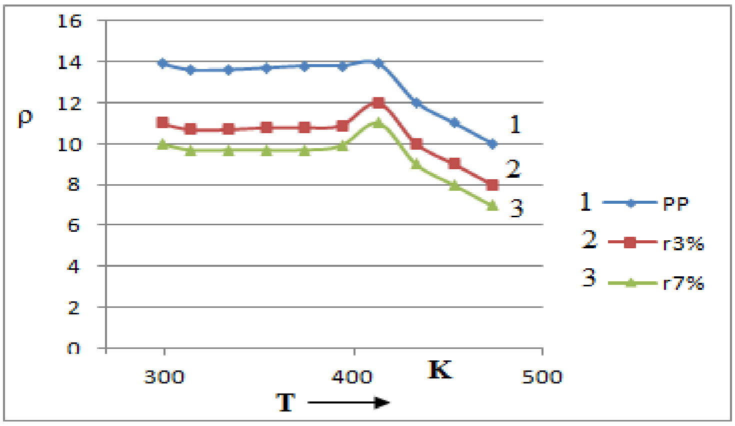

Fig. 8 The dependence of resisitivity of PP and PP+ZrO$_2$ nanocomposite from temperature.

Here is observed the PTCR effect in nanocomposites, i.e. at decomposition temperature of polymer crystalline phase the spacing between nanoparticles increase and this led to increasing of resistivity (pic.8)

Consequently dependence of dielectric permeability, tgδ and nanocomposite resistivity from temperature, ZrO$_2$ concentration and frequency shows that introduction of 21 nm sized ZrO$_2$ nanoparticles up to 3% into polymeric matrix leads to attainment of optimal structure. At decomposition temperature of polymer crystalline phase the resistivity discontinuously rise and then diminish, i.e. the posistor effect is observed.

Acknowledgments

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