

INFLUENCE OF ELECTROTHERMOPOLARIZATION ON STRUCTURE AND PHOTOLUMINESCENT PROPERTIES OF POLYPROPYLENE AND MnO₂-BASED NANOCOMPOSITIONS

M. A. RAMAZANOV^{a*}, A. S. HUSEYNOVA^b, F. V. HAJIYEVA^a

^a*Baku State University, Khalilov str.23, Baku city, AZ1148 Republic of Azerbaijan*

^b*Institute of Physics of Azerbaijan National Academy of Sciences, pr. H.Javid Ave, 33, Baku city, AZ1143 Republic of Azerbaijan,*

There has been investigated the influence of electrothermopolarization on the structure change and photoluminescence spectrum of nanocompositions on PP-based with MnO₂ low-molecular additions within wavelength $\lambda=250-1000\text{nm}$. It is established that photoluminescence spectra due to volume content of addition and conditions of electrothermopolarization vary strongly. Observed changes of spectra for nanocompositions depending on MnO₂ concentration are related to the change of supramolecular structure of polymers, conditions of electrothermopolarization with the change of interaction degree between polymer phases with the filler at the expense of charges accumulated at the phase boundary.

(Received November 11, 2014; Accepted January 20, 2015)

Keywords: Nanocomposition, Photoluminescence, Electrothermopolarization

1. Introduction

Compositions on polymer-nanoparticle-based under the effect of electric charge and thermal treatment change physical structure (SMS, oxidation of polymer chains and etc.) and it changes interphase interactions between composite components. As a result of polymer chain oxidation there has been increased the concentration of charge localization centers and the number of local levels in quasi-forbidden band of polymer phase which are accompanied by interphase interaction increase. As the composition is the system including two systems different from its complex electrophysical properties, so the process of interlayer polarization is quite possible. The probability of development of these above-mentioned physical processes depends on strongly the conditions of polarization, concentration and depth of trap bedding in polymer matrix and at the phase boundary of polymer and filler. Increase of accumulated charges at the phase boundary between nanocomposition components during the polarization can lead to the increase of interphase interactions, hence to the change of photoluminescent properties of nanocompositions [1-4].

It is known that during the electrothermopolarization there has been taken place the accumulation of electric charges at the phase boundary at the expence of migratory polarization can bring about the change of interphase interactions which in turn can change photoluminescent properties of nanocompositions [5-6].

In given paper we study the influence electrothermopolarization on physical structure (morphology, size of structural elements, roughness and etc.) and photoluminescent properties of nanocompositions on PP-based with MnO₂ low – molecular additions.

* Corresponding author: nanomaterials@bsu.az

2. Subjects of research and experimental method

There have been investigated photoluminescent properties of nanocompositions on PP-based with MnO_2 filler within the wavelength $\lambda=250\text{-}1000\text{nm}$. Photoluminescence spectra have been measured on spectrofluorimeter Cary Eclipse.

Production of composite sample is carried out by method of hot pressing at melting temperature of polymer and pressure 15 MPa for 3 min. with subsequent cooling under the pressure down to room temperature. Obtained samples are preliminarily under gone to the electrothermopolarization at $T_p=353\text{K}$ for $t_p=1\text{h}$.

Electric intensity in the film is $E_p=10^6\text{V/m}$. By method of atomic – force microscopy the morphology of $\text{PP}+1\%\text{MnO}_2$, $\text{PP}+0,5\% \text{MnO}_2$ nanocompositions and distribution of MnO_2 in PP polymer matrix have been studied.

3. Discussion of obtained results

Morphology of $\text{PP}+\text{MnO}_2$ nanocompositions on scanning atomic-force microscope (AFM) has been investigated [7]. In Fig.1 there have been presented AFM surface images of $\text{PP}+0,5\%\text{MnO}_2$ nanocompositions before and after electrothermopolarization. AFM study of $\text{PP}+0,5\%\text{MnO}_2$ nanocomposition sample relief shows that the relief of nanocomposition samples varies strongly after electrothermopolarization (Fig.1.2. a,b), i.e. the relief of samples becomes smoothless. It is seen that on the surface of nanocomposition samples after electrothermopolarization the communion of structural elements is taken place.

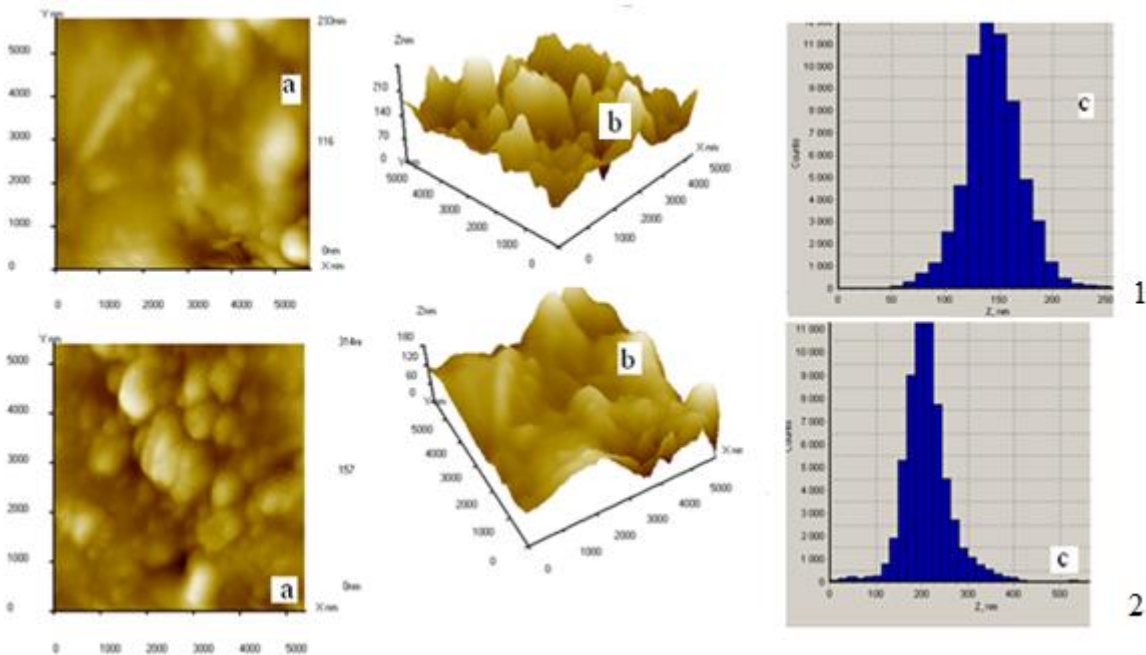


Fig.1. AFM relief image of $\text{PP}+0,5\% \text{MnO}_2$ nanocomposition before (1) and after (2) electrothermopolarization

In Fig.1c there has been shown histogram of image element values and mean – square roughness of $\text{PP}+0,5\% \text{MnO}_2$ nanocomposition surface. Histogram of surface inhomogeneity shows that after electrothermopolarization (Fig.1.2.c) under the effect of electric field the relief of nanocompositions becomes relatively smoothless. It is also shown that mean – square roughness of nanocomposition surfaces for nonpolarized samples is 100-300nm but for polarized samples is 70-200nm.

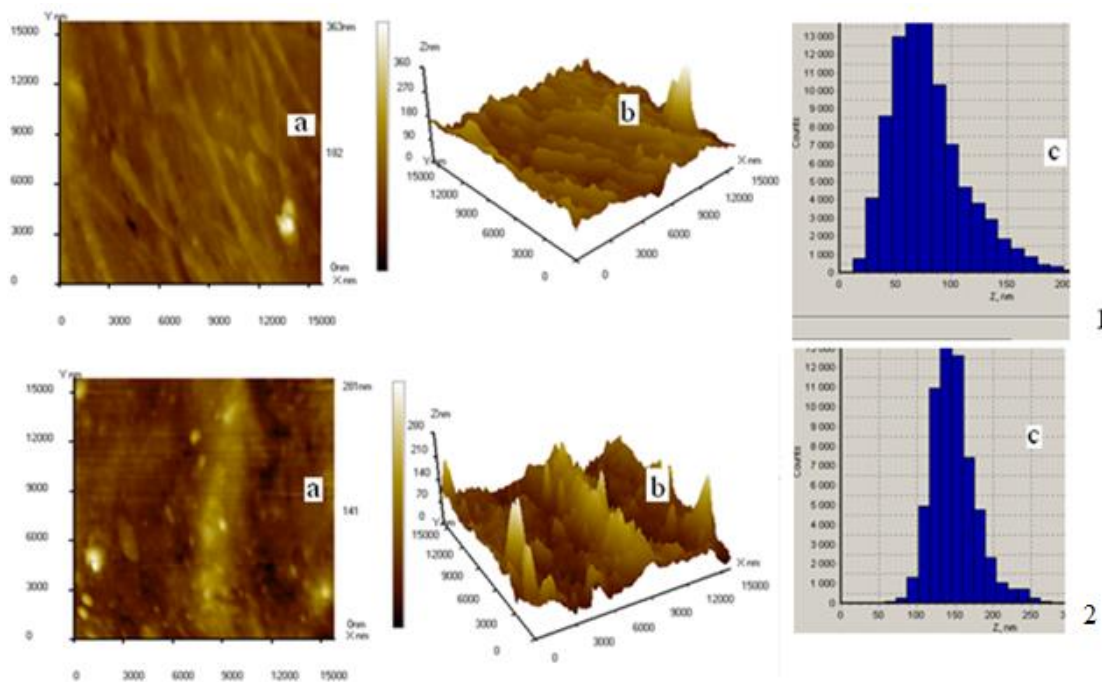


Fig.2 AFM relief image of PP+1% MnO₂ nanocomposition before (1) and after (2) electrothermopolarization

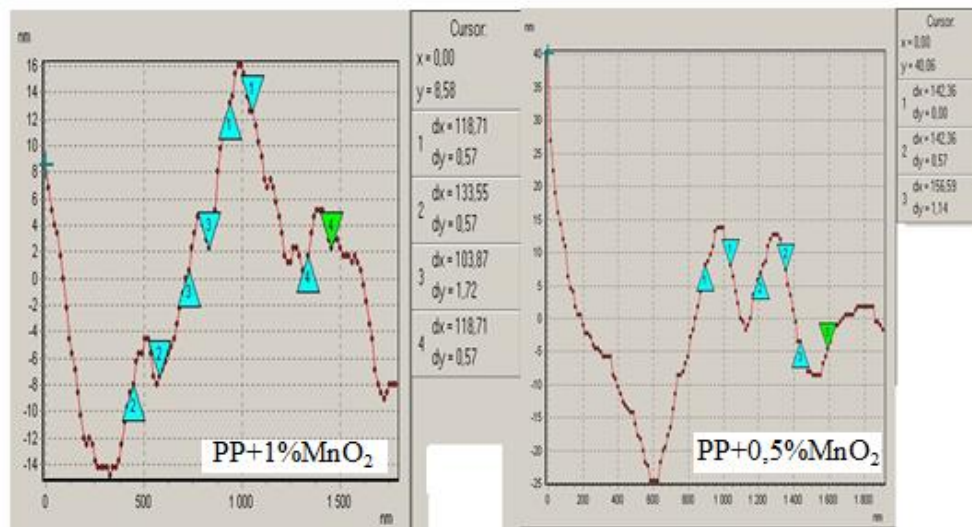


Fig.3 Sizes of structural elements of PP+MnO₂ nanocomposition surface

There has been also investigated the influence of electrothermopolarization on PP+1%MnO₂ nanocomposition morphology (Fig.2). It is established that with the increase of MnO₂ concentration the relief of nanocompositions varies. Distribution of Fourier analysis shows that structural elements of nanocomposition surface are distributed uniformly. From Fig.1, Fig.2 it is seen that due to the addition concentration and conditions of electrothermopolarization the structural element communion of surface and also the change of interphase boundaries are taken place.

From Fig.3 it is seen that on PP+MnO₂ nanocomposition sample surfaces the sizes of structural elements can be varied. It is shown that mean – square roughness of nanocomposition surface is 70–170 nm. From figures it is seen that nanoparticle sizes are 90–120nm.

There have been also investigated photoluminescent spectra of PP+MnO₂ nanocomposition before and after electrothermopolarization (ETP). In Fig.4 photoluminescence spectra of PP+0,5%MnO₂, PP+1%MnO₂ nanocomposition samples before polarization have been presented. It is seen that with the increase of MnO₂ low-molecular addition concentration the observed maximum at wavelength 420nm disappears practically. It is also seen that all maximum intensities at wavelength 320 nm, 363 nm, and 381 nm decrease. It is known that intermolecular interactions in media exhibiting photoluminescent activity can substantially affect their spectral characteristics.

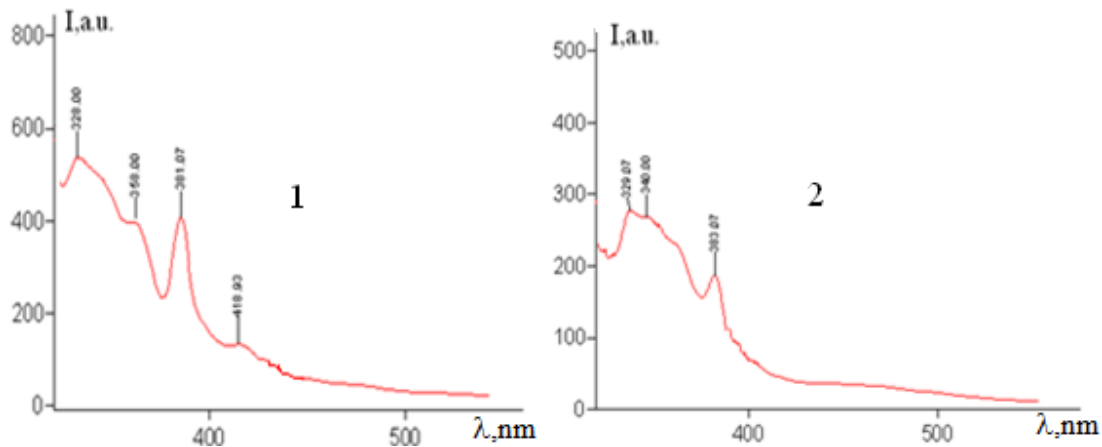


Fig.4 Photoluminescence spectra of PP+0,5%MnO₂ (1), PP+1%MnO₂ (2) nanocompositions

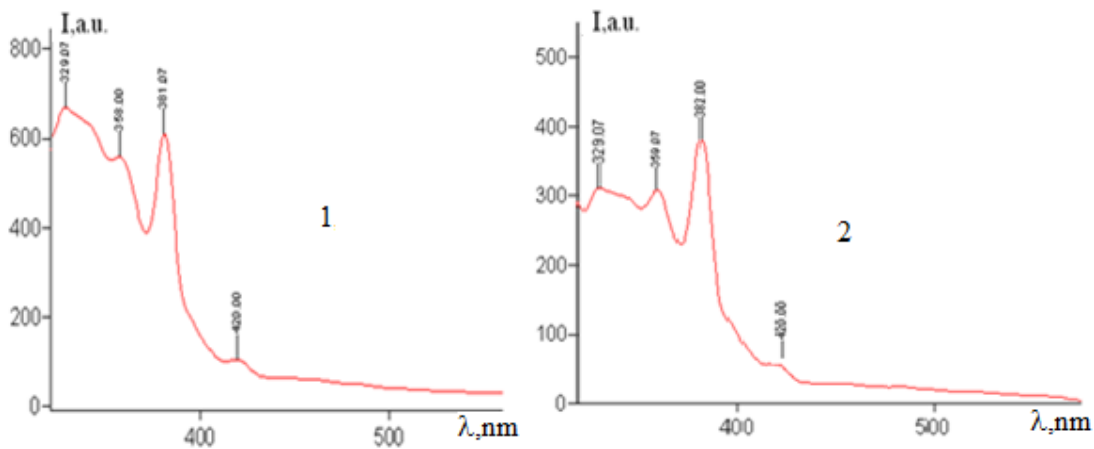


Fig.5. Photoluminescence spectra of nanocompositions after polarization1:
 1: PP+0,5%MnO₂ ($E_p = 6 \cdot 10^6$ V/m, $T=353K$, $t_p=1$ h),
 2: PP+1% MnO₂ ($E_p = 6 \cdot 10^6$ V/m, $T=353K$, $t_p=1$ h)

Interphase interactions for two-phase systems depend essentially on the structure of transition layer at the phase boundary of composition component. With the increase of MnO₂ low-molecular addition concentration in polypropylene the structural elements of nanocomposition have been decreased, i.e. there has been increased interphase interaction between nanocomposition components, as a result quenching of luminescent centers occurs at the expense of interphase interaction increase.

In Fig.5 spectra of PP+0,5%MnO₂ and PP+1%MnO₂ nanocompositions after electrothermopolarization have been presented. From Fig.5.1. it is seen that for PP+0,5%MnO₂ nanocomposition after ETP the new luminescent maxima are not observed practically, but the amplitude and half-width of maxima observed at wavelength $\lambda=320$ nm and $\lambda=381$ nm have been

increased markedly. In photoluminescence spectra of PP+1%MnO₂ Fig.5.2. before ETP three main maxima are observed, but after ETP four maxima are observed: $\lambda=329,07\text{nm}$, $\lambda=359,07\text{nm}$, $\lambda=382\text{nm}$, $\lambda=420\text{nm}$. After ETP the amplitude of all maxima increases. It is known that in mix of polymers or polymer compositions for the distinction from the dielectric constant and specific resistance after ETP there have been accumulated electric charges at the phase boundary for heterogeneity of two – phase systems at the expense of migratory polarization during ETP for nanocomposition, i.e. $\epsilon_1\rho_1 \neq \epsilon_2\rho_2$ resulting the charge accumulation at the phase boundary. The change of interaction between phases for two – phase compositions can be attended by the change of photoluminescent properties. ETP changes interphase interactions, the additional luminescent centers are activated in MnO₂ fillers and as a result the photoluminescence amplitude rises.

Thus nanocomposition photoluminescence spectra under investigation on PP–based with MnO₂ filler show that with the increase of concentration and conditions of ETP the changes of structural elements and PP+MnO₂ nanocomposition photoluminescence spectra are taken place. The observed changes of spectra for nanocompositions due to MnO₂ concentration are related to the changes of supramolecular structure of polymers, the conditions of ETP with the change of interaction degree between phases of polymer with the filler at the expense of charges accumulated at the phase boundary.

4. Conclusion

It is established that photoluminescence spectra due to volume content of addition and conditions of electrothermopolarization vary strongly. Observed changes of spectra for nanocompositions depending on MnO₂ concentration are related to the change of supramolecular structure of polymers, conditions of electrothermopolarization with the change of interaction degree between polymer phases with the filler at the expense of charges accumulated at the phase boundary.

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