

Influence of temperature and time regimes of crystallization and electrothermopolarization on the physical structures of polypropylene and M_nO_2 -based composition

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This paper deals with the influence of temperature and time regime of crystallization and electrothermopolarization on the physical structure and electret properties of the composition on the base of polypropylene (PP) and MnO_2 .

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1. Introduction

It is experimentally established that temperature and time regime of crystallization and conditions of PP+ MnO_2 composition polarization change supramolecular structure of polymer and as a result surface electret charge density and lifetime have been changed.

It is known that structurization behavior in polymers and composites on their base depends on the macromolecules and external conditions where formation of supramolecular structures have been taken place. Small amounts of fillers incorporated in the polymer play a part of artificial nuclei of crystallization that leads to the improvement of their properties. [1-3].

When incorporated considerable amount of fillers the properties of polymer material are determined by both structural changes in polymer matrix and changes in near-surface layer of filler.

The fillers influence on the rate of crystallization or cure, temperature of relaxation transitions, electric, stress-strain, thermal and other properties.

The main cause of supramolecular formation is the superiority of intermolecular interaction forces between groups of atoms appearing in polymer macromolecular over the intermolecular interaction forces and rather high flexibility of macromolecules. By the change of isothermal regime of pressing and temperature and time conditions of crystallization one can vary supramolecular structure in polymers and composite systems that is very important for creation of high-effective composite materials for various transducers. [4-5].

This paper deals with the influence of temperature and time regime of crystallization and electrothermopolarization on the physical structure and electret properties of the composition on the base of PP and MnO_2 . MnO_2 concentration varies from 0 up to 2% cub. content. Additions can create in polypropylene new

artificial crystallization nuclei and new centers-traps for electric charge which can favour increase of value of surface electret charge density and lifetime. PP+ MnO_2 composition has been obtained from PP solution by mixing PP and MnO_2 with subsequent removal of solvent. Compositions have been produced by method of hot pressing at PP melting temperature and pressure 15 MPa with subsequent cooling under pressure at different rates up to room temperature.

To obtain composition samples with different temperature and time crystallization regimes, i.e. supramolecular structures, film production process from compositions have been taken place in 3 regimes: in the first case samples obtained by hot pressing have been cooled at high rate-2000 deg/min by submerging samples in the liquid nitrogen, i.e. samples have been undergone nitrogen quenching. In the second case compositions are obtained in the regime when the melt between two foils is submerged in the mixture ice-water and by the given method of quenching rate of cooling is 20-30deg/ sec, so obtained samples are called "quick-cooled" (QC).

In the third case melt is cooled slowly up to the room temperature with the rate 2 deg/min, obtained samples are called "slow-cooled"(SC).

Polymer compositions have been subjected electrothermopolarization at $T_n=353-393$ K and by intensity of electric field $E=(3-10)\cdot 10^6$ V/ m for 1h with the subsequent cooling under the effect of electric field up to the room temperature. Surface electret change density (Q_{el}) due to the storage time have been studied by induction method [6].

Microstructures of PP+ MnO_2 compositions have been investigated by scanning atomic power microscope (APM) [7].

By IR spectroscopy growth of destructive processes in PP+ MnO_2 has been estimated.

In Fig. 1 there have been given images of PP+MnO₂ relief before and after electrothermopolarization. APM relief investigation of PP+MnO₂ composition samples shows that relief of composition samples changes highly

after electrothermopolarization, i.e. sample relief turns smoothless. It is seen that on the surface of composition samples after electrothermopolarization some structural changes have been take place.

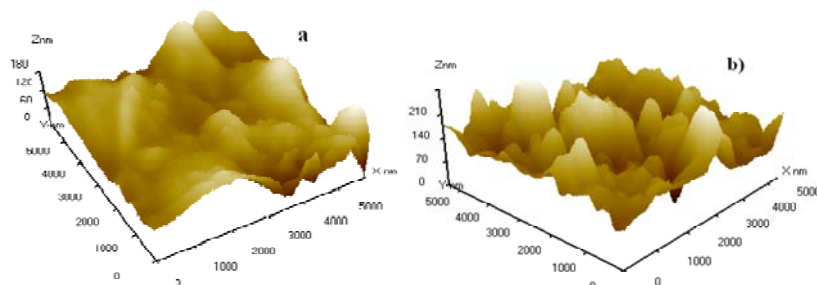


Fig. 1. APM images of PP+0.5% cub.content. MnO₂-based: (a) unpolarized and (b) polarized.

In Fig. 2 there has been shown histogram of values of image elements and root-mean-cube surface roughness of composition PP+0.5% cub content MnO₂. Histogram of surface heterogeneity shows that after polarization under the effect of electric field composition relief turns

comparatively smoothless. It is also shown that root-mean-cube surface roughness of composition for unpolarized samples is 100-200nm but for polarized samples is 150-250 nm.

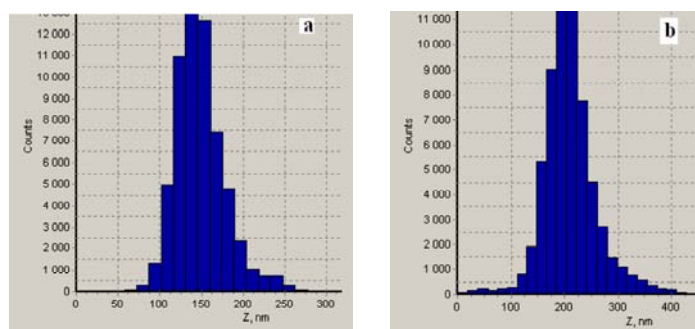


Fig. 2. Histogram of PP+0,5% cub content. MnO₂-based composition roughness: (a) unpolarized and (b) polarized.

In Fig. 3 there have been represented APM 3D images of PP+MnO₂ composition relief obtained at different temperature and time regimes of polypropylene crystallization. From the figure it is seen that relief of

PP+MnO₂ composition due to temperature and time regimes of crystallization changes highly, i.e. supranolecular structure of polymer in composition has been changed.

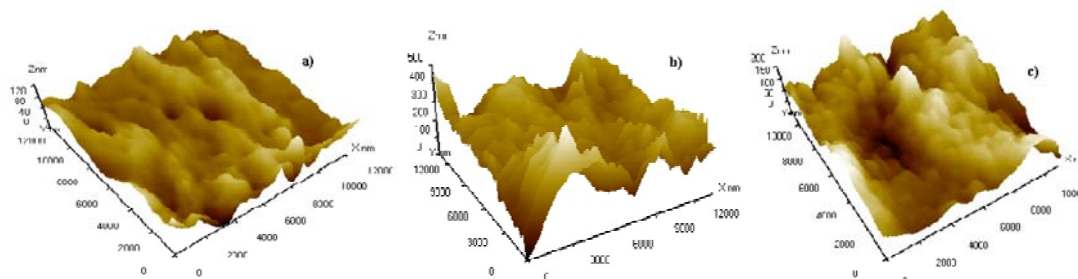


Fig. 3. APM image of PP+0,5% cub content MnO₂ – based composition: (a) nitrogen quenching; (b) water quenching and (c) slow cooling.

In Fig. 4 there has been shown histogram of values of image elements and root-cube-mean surface roughness of PP+0.5% cub.content MnO₂ – based composition obtained at different temperature and time regimes of

crystallization. Aystogram of surface heterogeneity shows that composition relief due to temperature and time regimes of crystallation has been changea highly, i.e. samples obtained in “nitrogen quenching” regime are

smoother than composition samples obtained in “water quenching” and “slow cooling” regimes.

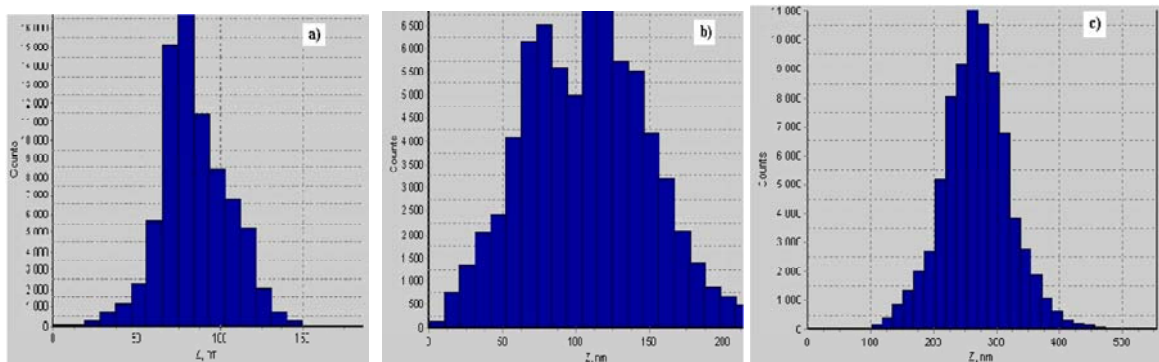


Fig. 4. Histogram of PP+0,5% cub.content MnO₂-based composition roughness: (a) nitrogen quenching; (b) slow cooling and (c) water quenching.

It is also shown that root-mean-cube surface roughness of composition for samples “nitrogen quenching” is 70-130 nm, for samples “slow cooling” is 70-170 nm, for samples “water quenching” is 200-350 nm.

Experiments show that by electrohermopolarization the value of stabilized charge Q in PP+0.5 % cub. content MnO₂-based composites also depends on temperature and time regimes of matrix crystallization. In Fig. 5 there has been given change of value of surface electret charge density of composites obtained under different conditions of polymer matrix crystallization due to electric intensity of polarization.

Samples are polarized at $T_p=373K$, $E_p=5 \times 10^6$ V/m, $t_p=1h$.

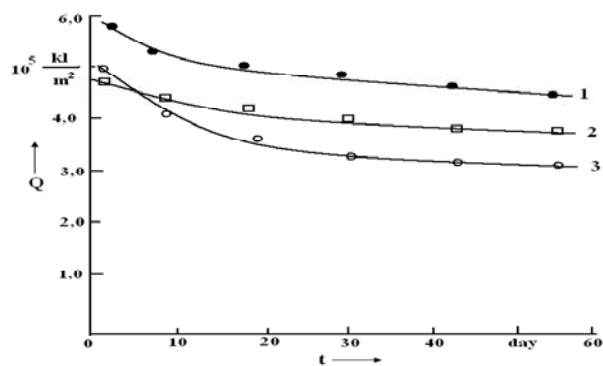


Fig. 5. Dependence of surface density of electret charges Q on storage time (t_s) of PP+0.5% cub. content MnO₂ obtained at different temperature and time regimes of crystallization: (1) nitrogen quenching; (2) water quenching and (3) slow cooling.

Experiment results show that charge stabilization in composites is determined by supramolecular structure of polymer matrix controlled by the change of crystallization conditions. Space and surface charges creating high local electric field favouring effective composite polarization

are responsible for formation of high surface density of electret charges being characterized by value Q .

Thus above-mentioned experimental results show that temperature and time regimes of crystallization and conditions of PP+MnO₂ composition polarization change supramolecular structure of polymer, as a result surface electret charge density and lifetime have been changed.

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