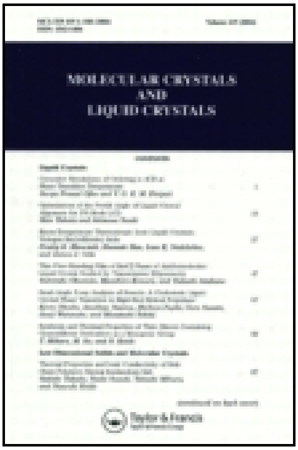

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PECULIARITIES OF SURFACE MORPHOLOGY AND COMPOSITION OF POLYMER - VANADIUM OXIDE COMPOSITE FILMS

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The surface morphology of the polymer films based on polyepoxypropylcarbazole and 3,6-di-Br-polyepoxypropylcarbazole with V_2O_5 was investigated by Atom Force Microscopy (AFM). The surface of composite has been found to be a chaotically intertwining of V_2O_5 fibres intermittent with inclusions of a corresponding polymer. Polymer inclusions are single ellipsoidal grains for PEPC composite and an aggregate of small grains for 3,6-di-Br-PEPC sample. Both V_2O_5 fibres and polymer inclusions have smaller size in 3,6-di-Br-PEPC. The mass spectra of compounds under investigation have been obtained. Both PEPC oligomer ions and those identified as complexes of M PEPC oligomers with V_2O_4 molecule and 3M PEPC oligomers with V_2O_5 molecule have been observed in mass spectrum of PEPC + V_2O_5 composite at the emitter temperature from 120°C up to 430°C. 2M, 3M and even 5M PEPC olygomers were observed in mass spectrum of 3,6-di-Br-PEPC + V_2O_5 composite at the emitter temperature from 20°C up to 600°C and 2M 3,6-di-Br-PEPC at the emitter temperature above 200°C. In this mass spectrum the ions which can be identified as PEPC oligomer complexes with V_2O_3, V_2O_4 and V_2O_5 molecules and as 3,6-di-Br-PEPC monomer complexes with V_2O_3, V_2O_4 molecules were also observed. Some observed ions can be also identified as Br-PEPC (with one atom of Bromine) monomer complexes with V_2O_4 and V_2O_5 molecules.

Keywords: polymer; poly-N-epoxypropilcarbazole; 3,6-di-bromine-poly-N-epoxypropylcarbazole; vanadium pentoxide; nanoparticle; morphology; mass spectrum; oligomer

INTRODUCTION

Recently, organic polymers have been receiving the increasing attention of researchers. Combination of good film-forming properties, simplicity of films and structures production with given spectral, electrophysical end other characteristics, regularability of these characteristics by changing of film composition or technological conditions are the indisputable advantages of these materials. Carbazole-containing polymers (such as polyvinylcarbazole, polyepoxypropylcarbazole (PEPC) and their derivatives) are widely used as registering media for optical recording of information, in electronic technology, in light emitting devices [1,2]. Doping of polymer films by oxides of transition metals is a promising way in fabrication of qualitatively new materials with specific physico-chemical properties [3]. Usage of nanoscale oxide particles allows to achieve a new level of functional application of polymer composite materials with conjugated bonds.

This work deals wih the investigation of peculiarities of surface morphology and structure of composite films based on carbazole containing organic polymers i.e. PEPC and 3,6-di-Br-PEPC with nanosize particles of vanadium pentoxide V_2O_5.

EXPERIMENTAL

Samples were prepared from poly-N-epoxypropylcarbazole (PEPC) or 3,6-di-Br-poly-N-epoxypropylcarbazole (PEPC) solution in acetone and water sol of vanadium pentoxide (V_2O_5 sol was prepared by Bilts technique). The composite was synthesized by the following way: a) V_2O_5 sol was added to PEPC solution in acetone at 1:1 ratio that corresponded to the V_2O_5 contents in the composite film of 33.82 mass %; b) V_2O_5 sol was added to 3,6-di-Br-PEPC solution in acetone at 1:1 ratio that corresponded to the V_2O_5 content in the composite film of 24.80 mass %. The films were formed as "sandwich"-structures by casting of the PEPC + V_2O_5 or 3,6-di-Br-PEPC + V_2O_5 composites on a glass substrate coated with ITO layer width of $\sim 0.15\,\mu m$ of the thickness and resistance of about 100 Ohm/□. As a result of solution desiccation on air at room temperature the films with thickness between 5 to 10 μm were obtained.

The morphology of the film surface was investigated by the Atomic Force Microscopy (AFM), NanoScope IIIa of a Digital Instruments Corporation. Resolution in horizontal plane is about 10 A, and that in vertical one is about 1 A. The Field Mass Analyser designed and made by L. Pisarzhevski Institute of Physical Chemistry of the National Academy of Sciences of Ukraine was used for mass-spectrometer analysis of composites under investigation. For analysis was performed by a combined ion source with two ways of ionisation: thermo evaporation and desorption by a strong electrical field.

The surface morphology (a) and contrast enhancement (b) of investigated composites are given in Figures 1, 2 . The values of point altitudes for the surface are transferred by tints of grey. The white colour corresponds to the top value of altitude of film surface. The sizes of V_2O_5 fibres and

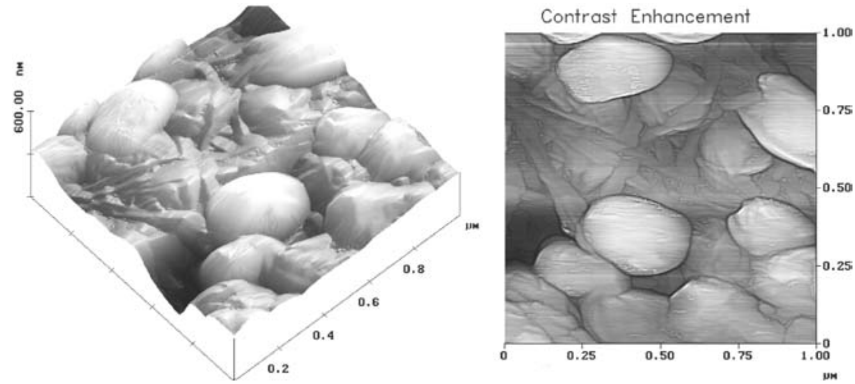

FIGURE 1 AFM image of surface of PEPC+V_2O_5 (V_2O_5 contain is 33.82 mass %) composite films: a) surface morphology; b) contrast enhancement of the same region of surface.

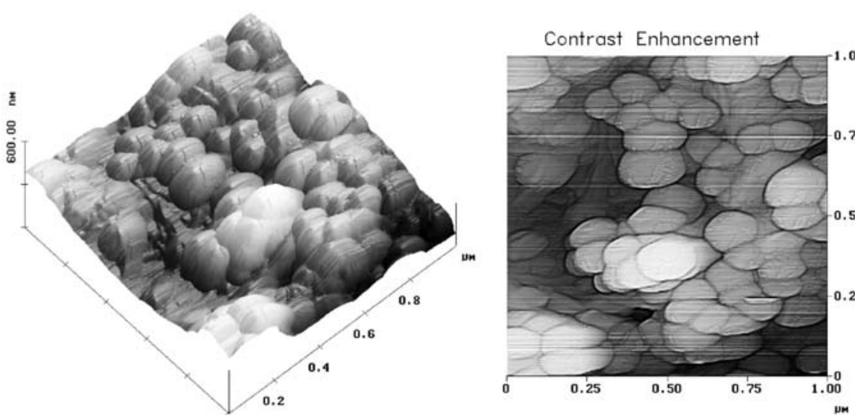

FIGURE 2 AFM image of surface of and 3,6-di-Br-PEPC + V_2O_5 (V_2O_5 contain is 24.80 mass %) composite films: a) surface morphology; b) contrast enhancement of the same region of surface.

TABLE I The Size of V_2O_5 Fibres and Polymers Grains in Composites of PEPC + V_2O_5 (33.82 mass %) and 3,6-di-Br-PEPC + V_2O_5 (24.80 mass %)

Film	Diameter of V_2O_5 fibres, nm	Length of V_2O_5 fibres, nm	Size of polymer grain, nm	The most typical size of polymer grain, nm
PEPC + V_2O_5 composite (33.82 mass % of V_2O_5)	30–50	300–400	250 × 350	250
3,6-di-Br-PEPC + V_2O_5 composite (24.80 mass % of V_2O_5)	20–30	200–300	70 × 150	125

polymer grains in composites are summarized in Table I. The results of the mass-spectroscopy analysis of respective composites (ion observed and their identification) are listed in Table II.

From Figures 1, 2 we can see in both composite films contrary to the V_2O_5 one the V_2O_5 fibres lose ordering and have the considerably less size. The surface of the PEPC + V_2O_5 composite film (Fig. 1) is a chaotically arranged intertwining of vanadium pentoxide fibres of 30–50 nm in diameter and 300–400 nm in length, braiding the polymer inclusions as the single ellipsoidal grains with size of about 250 × 350 nm.

Surface of a film of an aggregate 3,6-di-Br-PEPC + V_2O_5 (Fig. 2) is also chaotically intertwining of V_2O_5 fibres with 20–30 nm in diameter and 200–300 nm in length which surround the polymer inclusions as the clusters of ellipsoidal grains with the size of about 70 × 150 nm.

RESULTS AND DISCUSSION

One can see the clear differences in surface morphology of composite films. Both the size of V_2O_5 fibres and this of polymer inclusions (see Table I) are less in the case of brominated PEPC. The nature of polymer inclusions in composite is also different: in the PEPC composite the inclusions are the relatively large grains, and in the brominated PEPC composite they are the aggregates of small-sized ones. Probably it is due to both differences of polymers, and their interaction with V_2O_5.

In mass spectra of PEPC + V_2O_5 composites (see Table II) only 2M (m/z = 447) dimer ions are observed at the temperature of emitter heating of about 120°C. While increasing emitter temperature up to 200°C 2M (m/z = 446), 3M (m/z = 669), 4M (m/z = 892), 5M (m/z = 1115) oligomers in a mass spectrum are observed, i.e. more massive molecules start to be evaporated.

TABLE II Desorption Mass Spectra of Composites under Investigation

Emitter temperature, °C	Ion mass, a.u.m.	Gross weight – formula of ion
	$PEPC + V_2O_5$ composite (33.82 mass % of V_2O_5)	
120	447	$2M_{PEPC}$
200	446, 669, 862, 1115	$2M_{PEPC}$, $3M_{PEPC}$, $4M_{PEPC}$, $5M_{PEPC}$
290	669, 855, 892. 1115	$3M_{PEPC}$, $3M_{PEPC} + V_2O_5$, $4M_{PEPC}$, $5M_{PEPC}$
350	389	$M_{PEPC} + V_2O_5$
430	854	$3M_{PEPC} + V_2O_5$
	3,6-di-Br-PEPC + V_2O_5 composite (24.80 mass % of V_2O_5)	
20	449, 533, 550, 561, 610	$2M_{PEPC}$, $M + V_2O_3$, $M + V_2O_4$, $M + V_2O_5$, $2M_{PEPC} + V_2O_4$
30	390, 409, 464, 533, 561, 596, 628	$M_{PEPC} + V_2O_4$, $M_{PEPC} + V_2O_5$, M-Br + V_2O_4, $M + V_2O_3$, $M + V_2O_5$, $2M_{PEPC} + V_2O_3$, $2M_{PEPC} + V_2O_5$
50	(389, 390), 446, 534	$M_{PEPC} + V_2O_4$, $2M_{PEPC}$, $M + V_2O_3$
90	449, 490, 533, 669	$2M_{PEPC}$, M-Br + V_2O_5, $M + V_2O_3$, $3M_{PEPC}$
140	450, 479, 533, 548, 561	$2M_{PEPC}$, M-Br + V_2O_5, $M + V_2O_3$, $M + V_2O_4$, $M + V_2O_5$
200	410, 534, 561, 615, 631, 762	$M_{PEPC} + V_2O_5$, $M + V_2O_3$, $M + V_2O_5$, $2M_{PEPC} + V_2O_4$, $2M_{PEPC} + V_2O_5$, 2M
250	534, 762	$M + V_2O_3$, 2M
310	388, 534, 549, 762	$M_{PEPC} + V_2O_4$, $M + V_2O_3$, $M + V_2O_4$, 2M
370	762, 1147	2M, 3M
470	761, 1045	2M, 3M $4M_{PEPC} + V_2O_4$
> 550	762	2M
> 600	450, 762, 892, 1074, 1117	$2M_{PEPC}$, 2M, $4M_{PEPC}$, $4M_{PEPC} + V_2O_5$, $5M_{PEPC}$

Note: nM_{PEPC} – PEPC olygomers, nM – 3,6-di-Br-PEPC olygomers.

While further increasing of emitter temperature (290°C) the ions with m/z = 854, 855 mass numbers appear also in the mass spectrum in addition to 3M, 4M and 5M oligomers. Most likely they correspond to the complex formed by $3M_{PEPC}$ oligomer with V_2O_5 (m/z = 182) and 3M oligomers with added carbazole fraction CH_2-$NC_{12}H_8$ (m/z = 180). Finally, the emitter temperature increasing up to 510°C leads to absence of the oligomers in the mass spectrum. We can see only the ions with m/z = 389, which probably correspond to the complexes formed by M PEPC oligomers with V_2O_4 (m/z = 166), which in this case can be assigned to M oligomers M with added carbazole fraction $NC_{12}H_8$ (m/z = 166).

To ascertain of the nature of ions with mass numbers of m/z = 337, 546, 572, 590, 591, 868, the additional investigations are to be made.

In mass spectra of 3,6-di-Br-PEPC + V_2O_5 composite the ions with mass numbers of m/z = 449 and 669 are observed at the heating temperature of emitters from 20°C up to 600°C. They can be identified as ions of PEPC dimer and trimer. At higher temperatures (above 600°C) the ions with mass numbers m/z = 892, 1117 are observed, which can be PEPC oligomers ions $4M_{PEPC}$, $5M_{PEPC}$ composition.

The ions with mass numbers m/z = 762, 1147, which can be attributed to M or 2M 3,6-di-Br-PEPC dimers and trimers (m/z = 381) and (m/z = 762), respectively, become available in mass spectrums of the corresponding composite only at high temperatures from 200°C to 600°C. In the mass spectrum of above mentioned composite there are ions with mass numbers m/z = 390, 409, 596, 610, 628, which can be assigned to complexes formed by PEPC monomers with V_2O_4 and V_2O_5, PEPC dimers with V_2O_3, V_2O_4, and V_2O_5. The ions with mass numbers m/z = 534, 549, 561 are also recognized in mass spectrum of this composite. They can be assigned to 3,6-di-Br-PEPC monomer complexes with V_2O_3, V_2O_4 and V_2O_5. One can see the peaks of ions with mass numbers m/z = 464, 479, 490 at temperatures 30°C–140°C. They can be attributed to complexes of one Bromine atom PEPC monomer with V_2O_4 and V_2O_5.

To ascertain of the nature of ions with mass numbers m/z = 337, 397, 419, 422, 435–436, 478, 492, 503, 506–508, 521, 577, 580, 588, 644, 772, 780–781, 806–808, 857–858, 881, 975, 1033, 1092, 1134, 1162, 1164–1167, 1191–1193, 1196, 1216, 1218, 1221, 1223, 1304, 1409, 1412 the further investigations are to be made.

Analyses of mass spectra show, that there are oligomers of polymers yourself and also their complexes with molecules of vanadium oxide of variable valence V_2O_3, V_2O_4 and V_2O_5.

The recognized facts: (i) presence of dimmers and trimers in 3,6-di-Br-PEPC + V_2O_5 composite; (ii) complexes of monomers of 3,6-di-Br-PEPC + V_2O_5 composite and V_2O_3, V_2O_4, V_2O_5 are available; (iii) presence of dimmers, trimers and even 5-mers of PEPC at high temperatures of emitter; (iv) complexes of V_2O_3, V_2O_4, V_2O_5 and PEPC monomers, dimers and 4-mers, say that during bromination not all PEPC molecules are changed into 3,6- di-Br-PEPC and there are PEPC oligomers in brominated polymer. This is supported by a fact that the complexes of Br-PEPC (with one Br atom) with V_2O_4 and V_2O_5 are recognized in mass spectra of 3,6-di-Br-PEPC + V_2O_5 composite. So, at a bromination there was a replacement of one atom of hydrogen with atom of bromine.

The correlation between the structure of films and their optical and electrical properties has been established as well. The increase in the 3,6-di-Br-PEPC conductivity under V_2O_5 doping was found to be considerably higher than in case of PEPC. It increases by 3–6 orders of significance in the first case as compared with pure polymer and only by 1–5 orders in the second one. It can be connected with the size and distribution of polymer grain and V_2O_5 fibers in composites. Thus, the more specific size for polymer grain in PEPC + V_2O_5 composite exceeds the one for 3,6-di-Br-PEPC + V_2O_5 composite two times and fiber size one and half times, respectively. The character of polymer grain distribution in composite is different as it was above stated.

We recognized also that the photoluminescence intensity of PEPC + V_2O_5 composite is much more than this of 3,6-di-Br-PEPC + V_2O_5. Probably, the bigger polymer grain size (single) appears to be more preferable for better luminescence properties. It should be noted, that heavy atoms of bromine can quench the luminescence.

CONCLUSIONS

The surface morphology for composites of PEPC + V_2O_5 and 3,6-di-Br-PEPC + V_2O_5 was found to have the differences. The cause of difference in composites lies in the different structure of PEPC + V_2O_5 and 3,6-di-Br-PEPC + V_2O_5 polymers and their interaction with vanadium oxide.

The analysis of mass spectra of composites has exhibited the presence of oligomers of the corresponding polymers and complexes of oligomers with V_2O_3, V_2O_4 and V_2O_5 molecules.

In the 3,6-di-Br-PEPC + V_2O_5 composite there are oligomers of this polymer, complexes of its monomers with V_2O_3, V_2O_4 and V_2O_5. It is possible to suppose that in brominated polymer there are PEPC oligomers. This endorses the presence of V_2O_5 complexes formed by Br-PEPC (with one bromine atom) with V_2O_4 and V_2O_5.

Probably, in both composites there are the complexes with charge transfer formed by oligomers of corresponding polymers with derivated by oligomers of the corresponding polymer with vanadium oxide molecules of variable valence.

On the basis the of experimental data obtained, one might make a conclusion that to obtain the material with good conductivity 3,6-di-Br-PEPC+V_2O_5 composite should be used. At the same time to obtain the material with good luminescence the PEPC composite is preferable.

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