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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Specific Features of Formation and Molecular Structure of Polyaniline-Based Composite Coatings Deposited from Active Gas Phase

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Abstract—Regular trends in formation of composite polymeric coatings based on polyaniline (emeraldine base) and thermoplastic polymers (polytetrafluoroethylene, polyurethane) from the gas phase generated by electron-beam dispersion were determined. The dependence of the molecular structure and adsorption activity of the deposited coating on its composition at various modes of support treatment was examined.

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Conducting polymers attract researchers' attention owing to wide possibilities of developing on their basis new promising materials for various applications. In particular, conducting materials based on polyconjugated polymers are efficiently used as coatings for protection of electronic circuit components, absorption of electromagnetic radiation, scattering of electrostatic charges, and also in shutter and filtering optical devices and in fabrication of color displays, chemotron devices, and sensors [1–3].

Preparation of thin conducting polymeric coatings involves certain problems associated primarily with their poor chemical resistance and unsatisfactory mechanical properties. It should be noted that the majority of conducting polymers are synthesized as powders. With the aim to enhance the physicomechanical and protective properties, powders and fibers of conducting polymers are introduced into an inert polymeric matrix (polyvinyl chloride, polycarbonate, etc.) [2]. Another problem is that, to attain good electrophysical properties, it is necessary to increase the structural ordering of the polymeric phase. In this connection, the procedure based on deposition of coatings from an active gas phase generated by electron-beam dispersion of the starting materials shows much promise from the viewpoint of the possibility of depositing layers of complex composition and preset design and preparing thin-film systems with controllable molecular structure [4].

The goal of this study is elucidation of specific features of electron-beam dispersion of a polyconjugated polymer [emeraldine (polyaniline, PANI) base] and its mixtures with thermoplastics [polytetrafluoroethylene (PTFE), polyurethane (PU)], determination of the molecular structure of the coatings deposited form volatile dispersion products, and assessment of the efficiency of using these coatings as adsorption-active elements of sensors.

EXPERIMENTAL

Coatings were prepared from an active gas phase formed by the action on a uniform powder or mechanical mixture of powders of electron beam with an electron energy of 800–1600 eV and density of 0.01–0.03 A cm^{-2}, using a device schematically shown in [5]. The deposition rate and effective coating thickness were determined with a quartz thickness meter (QTM). The temperature of the target surface in the zone of the action of the electron beam was measured directly in the course of dispersion with an IPE 140 radiation pyrometer. The radiation passed from the vacuum chamber through a window made of KRS-5 crystal. The lower limit of temperature

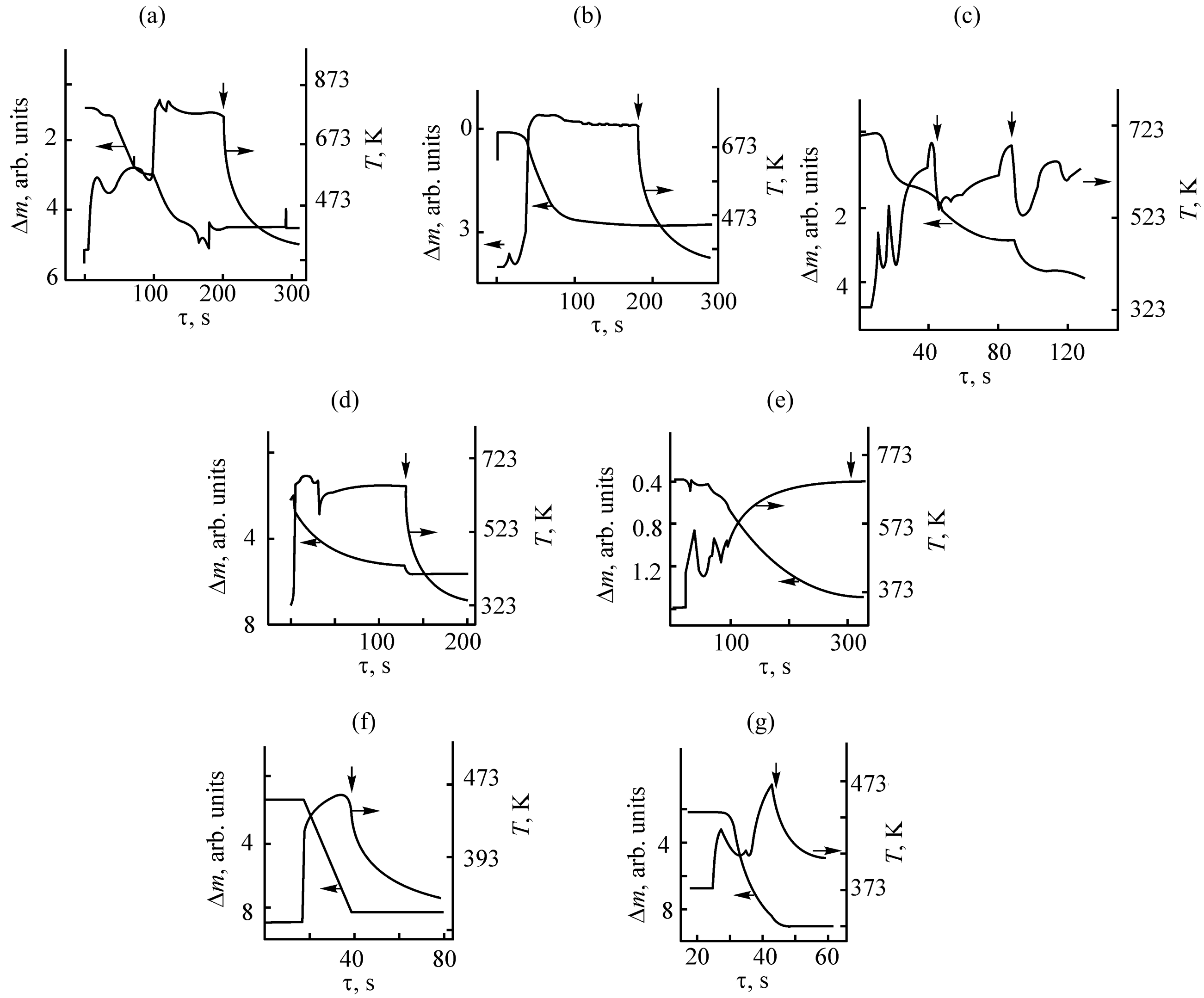

Fig. 1. Variation with time of the target surface temperature *T* and of the coating thickness in electron-beam dispersion of (a) PANI, (b) PANI–PTFE (2 : 1), (c) PANI–PTFE (3 : 1), (d) PANI–PTFE (1 : 2), (e) PANI–PU (1 : 1), (f) PTFE, and (g) PU. (Δm) Weight change and (τ) time.

measurement was 322 K. The pressure in the vacuum chamber was determined with an ionization manometer. The distance from the electron gun to the target was 150 mm, and from the target to the support, 120 mm. The coatings were deposited at the initial pressure of residual gases in the vacuum chamber of about 10^2 Pa.

As a target material to be dispersed we used powders of PANI base (M_w = 5500000) and its mixtures with PTFE [GOST (State Standard) 10007–80] or with polyurethane (Desmopan 385), and also with sulfamic acid and aluminum chloride. The choice of PANI base instead of the salt was based on the results of experiments on thermal deposition of polyaniline [6], which showed that vacuum evaporation of PANI salt under continuous heating is accompanied by formation of films with a very defective structure. Yet there is no fundamental difference in the choice of the base or salt in the electron-beam dispersion process. In particular, the thermal component of the electron-beam action on PANI salt would be accompanied by complex chemical reactions affecting the conducting properties of the starting powder [7, 8]. The radiation component of the electron-beam action will apparently exert a similar effect.

As supports in the deposition of coatings we used quartz plates (in spectroscopic measurements in the visible range), films of metal-coated Lavsan (analog of

Mylar, in recording IR spectra), and silver-coated single crystals of quartz (in evaluation of adsorption properties).

To examine the effect of support on the structure and properties of coatings, in some experiments we deposited 0.1-μm sublayers of PTFE characterized by relatively low surface energy (3–8 mJ m^{-2}) [4] and pretreated the support surface with argon ions (Ar^+) generated with a Radikal ion source. The parameters of ion bombardment were as follows: ion current 0.2 A, accelerating voltage U_a = 1 kV, current density j = 1.2 A m^{-2}, and treatment time 10 min.

To examine the effect of the support temperature on the structure of the forming coatings, the deposition was performed onto supports heated to 180°C. For comparison, in the vicinity of the heated support we arranged a support that was not specially heated.

Spectroscopic studies were performed with a Specord M-40 UV–Vis spectrophotometer and a Vertex-70 IR Fourier spectrophotometer (Bruker) using a standard MATIR attachment. As reflecting prism we used a KRS-5 crystal (base angle 45°). The conductivity of the formed coatings was studied with an HP4156B precision analyzer (Hewlett–Packard, USA) by the standard two-probe procedure. Quartz plates were used as supports. In conductivity measurements, onto supports with the deposited coating we applied bands of Kontaktol paste (BMK resin with Ni powder, R = 0.01 Ω cm) 1.52 mm long at a distance of 18–20 mm from each other. The coating thickness required for calculating the conductivity was determined by two independent procedures: scanning electron microscopy and with a profilometer.

Adsorption properties of coatings were studied using a multichannel device of the electronic nose type [9]. Its operation principle consists in measurement of frequency shifts of an 8-channel array of sensor elements with thin sensitive layers. Coatings were deposited onto standard (6 MHz) radiotechnical AT-cut quartz resonators which served as sensor elements. The distance between the adjacent resonators was 0.5 cm, so that their high-frequency mutual effect was minimal. Sensors were placed in a chamber which was filled with saturated ammonia vapor. After each measurement the chamber was purged with dry air.

Electron-beam dispersion of polymers is accompanied by the occurrence of complex physicochemical processes determining the structure and properties of the forming coating [10]. One of major factors affecting these processes is thermal effect of the electron beam on a substance. In electron-beam dispersion of PANI powder, the crucible temperature can exceed 773 K, which is higher than the temperature of the polymer degradation [6] (Fig. 1a). The initial period of the electron-beam treatment of the target is characterized by the highest rate of the coating deposition. The target surface temperature in this period does not exceed 623 K. In the subsequent period, the target temperature increases, but the coating deposition rate drastically decreases, virtually to zero.

In electron-beam dispersion of a PANI–PTFE powder mixture, an increase in the weight fraction of the fluorinated component leads to a significant monotonic decrease in the temperature in the dispersion zone (Figs. 1b–1d). For example, an increase in the PTFE content in the target from 0 to 66% causes a decrease in the maximal temperature in the dispersion zone by more than 200 K.

It should be noted that electron-beam treatment is accompanied by ejection of PTFE powder particles from the crucible, apparently due to the polymer charging. Specifically the polymer charging largely determines the kinetics of the dispersion and coating growth: After the lapse of 30–40 s from the start of dispersion, braking electric field arises and the electron energy decreases. As a result, the deposition rate decreases considerably. It is restored only after switching the electron source off and then switching it on again (Fig. 1c).

Electron-beam dispersion of a mixture of PANI and PU powders occurs in the more stable mode compared to dispersion of the PANI–PTFE mixture (Fig. 1). As in electron-beam dispersion of a PANI–PTFE mixture, the character of variation with time of the temperature in the dispersion zone and of the coating growth rate is preserved. It should also be noted that the target temperature in the process is considerably lower than the temperature recorded in the course of dispersion of PANI powder.

Thus, the target composition considerably affects the temperature conditions of the electron-beam dispersion. The kinetic dependences shown in Fig. 1 suggest predominantly nonthermal mechanism of the PANI dispersion. A decrease in the dispersion rate in late steps of the process, with a considerable increase in the temperature in the zone exposed to electron beam, may be due to a decrease in the electron energy

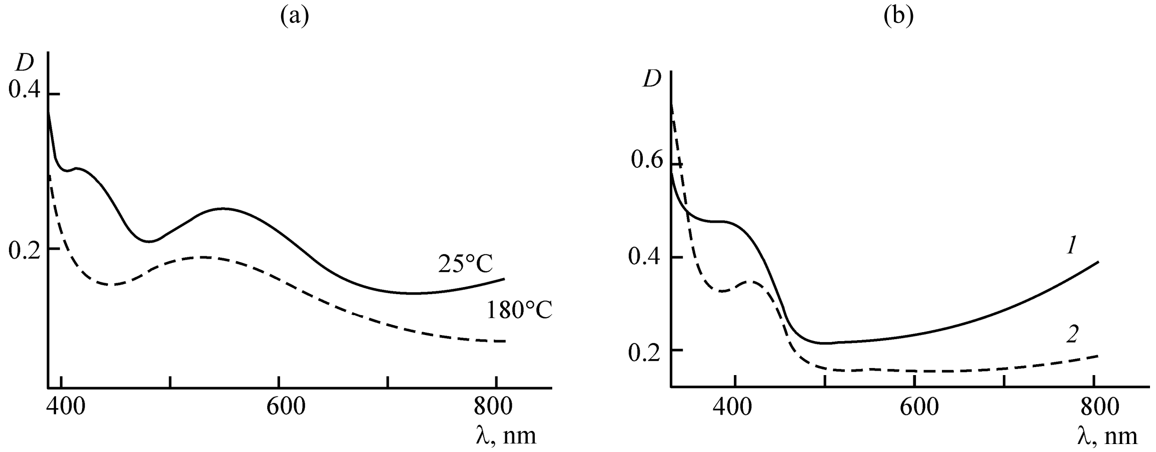

Fig. 2. Electronic absorption spectra of coatings. (*D*) Optical density and (λ) wavelength; the same for Figs. 3 and 4. (a) PANI coating + PTFE sublayer; (b) (*1*) PANI–sulfamic acid (1 : 1) and (*2*) PANI–aluminum chloride (1 : 3).

as a result of surface charging and appearance of braking electric field. The same features are characteristic of the process of PTFE dispersion [11].

The absorption spectra of coatings formed by electron-beam dispersion of PANI contain in the visible range a broad band with a maximum at about 420 nm, which is assigned to the absorption of radical cations [12, 13]. Absorption bands characteristic of quinone imines (600–650 nm) and localized polarons (750–800 nm) are lacking.

The IR spectra of PANI coating contain all the absorption bands characteristic of the starting powder. However, the optical density of the bands in the range 1200–1100 cm^{-1} considerably decreases.

For comparison, Fig. 2 shows the electronic spectra of coatings formed by electron-beam dispersion of mechanical mixtures of PANI powders with sulfamic acid and aluminum chloride. These coatings are dark green, in contrast to dark blue PANI coatings.

In the electronic spectra of coatings, there are bands in the region of absorption of radical cations and localized polarons. In the IR spectra, there is strong absorption in the range 1200–1100 cm^{-1}, attributable to the effect of acids on formation of –NH$^+$– groups [7, 8].

Conductivity of coatings

Coating	*s*, μS cm^{-1}
PANI	0.51
PANI–sulfamic acid	100
PANI–aluminum chloride	70

Data on the conductivity of the coatings formed are given in the table.

It is known that, to increase the conductivity of PANI layer, it is treated in some cases with strong acids [14]. Similar reactions, apparently, occur in the course of electron-beam deposition, both directly in the crucible (in the polymer melt) and on the support, between the products of electron-beam dispersion of PANI and acid. Sulfamic acid, in contrast to aluminum chloride, readily melts under the action of an electron beam, passes into the gas phase, and is deposited on the support. Protonation of PANI with sulfamic acid can occur both in the crucible and on the support. Aluminum chloride, apparently, can intensely interact with PANI only directly in the crucible. These facts account for the higher conductivity of the PANI–sulfamic acid coating, compared to that of the PANI–aluminum chloride coating.

The results of spectroscopic studies and conductivity measurements confirm the possibility of chemical reactions of electron-beam dispersion products in the course of deposition of PANI-based coatings.

We examined the effect exerted by activation treatment of the quartz support with Ar$^+$ ions on the structure of PANI-based composite layers. We found that the optical density of the absorption band of radical cations in deposition of PANI coatings onto the support treated with argon ions was considerably higher (by a factor of more than 4) than that of the similar band in deposition onto the untreated support.

In deposition of PANI coating, a PTFE sublayer strongly affects the electronic spectrum (Fig. 2). In the spectrum, along with absorption in the range of radical cations, absorption appears in the range 480–700 nm, assignable to quinone imine fragments arising in the coating. Weak absorption also appears in the range corresponding to localized polarons. Deposition of PANI coating onto a support with a PTFE sublayer, heated to 180°C, is accompanied by disappearance of the absorption in the range of radical cations and localized polarons. At the same time, a broad band in the range 440–760 nm is observed. An increase in the mobility of fragments forming the PANI coating initiates the reaction of radical cations with each other, with the formation of imine units, in agreement with Ivanov's data [6].

In deposition of coatings onto quartz supports treated with Ar^+ ions and untreated, we found no significant differences in the electronic absorption spectra of composite PANI–PTFE coatings with component weight ratios of 2 : 1 and 1 : 1. Change in the weight ratio of PU and PANI from 1 : 1 to 1 : 2 led to appearance of absorption in the region of 700 nm. Absorption bands at ~700 nm were recorded only in the case of deposition of PANI–PU (2 : 1) coating onto the support that had not been treated with Ar^+ ions. The absence of the absorption maximum at 700 nm in the electronic spectra of composite PANI–PTFE coatings is attributable to low segmental mobility of fragments of PTFE molecules, preventing the reaction of PANI fragments with each other.

The molecular structure of composite coatings based on PU and PANI is determined by the ratio of the components forming the composite layer and by the surface energy of the support (Fig. 3). The relative content of the polyurethane component in the coating also, apparently, affects the adsorption mobility of dispersion products, in particular, PANI.

Whereas the electronic absorption spectra of PANI–PU (1 : 1) are characterized by a weak absorption in the region corresponding to radical cations (450 nm), a decrease in the PU fraction in the coating leads to appearance of absorption in the region of localized polarons (750 nm).

It should be noted that thermal vacuum sputtering of PANI resulted in formation of a block structure including amine (absorption at ~320 nm) and quinone imine (absorption at ~650 nm) blocks, and localized polarons formed in the course of subsequent chemical

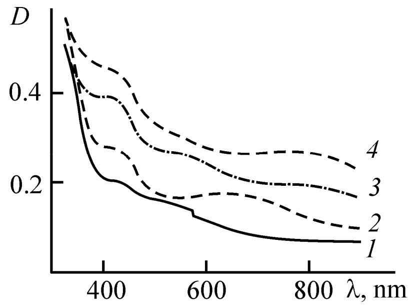

Fig. 3. Electronic absorption spectra of composite PANI–PU coatings: (*1*) PANI–PU (2 : 1), (*2*) PANI–PU (2 : 1) + PTFE sublayer, (*3*) PANI–PU (3 : 1), and (*4*) PANI–PU (3 : 1) + PTFE sublayer.

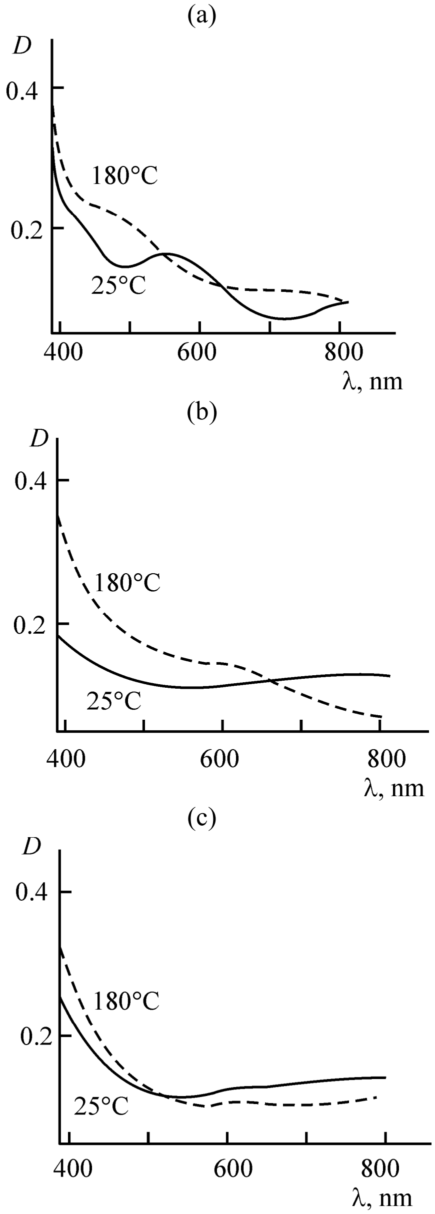

Fig. 4. Electronic absorption spectra of PANI–PU coatings formed on PTFE sublayer. PANI : PU: (a) 3 : 1, (b) 2 : 1, and (c) 1 : 1.

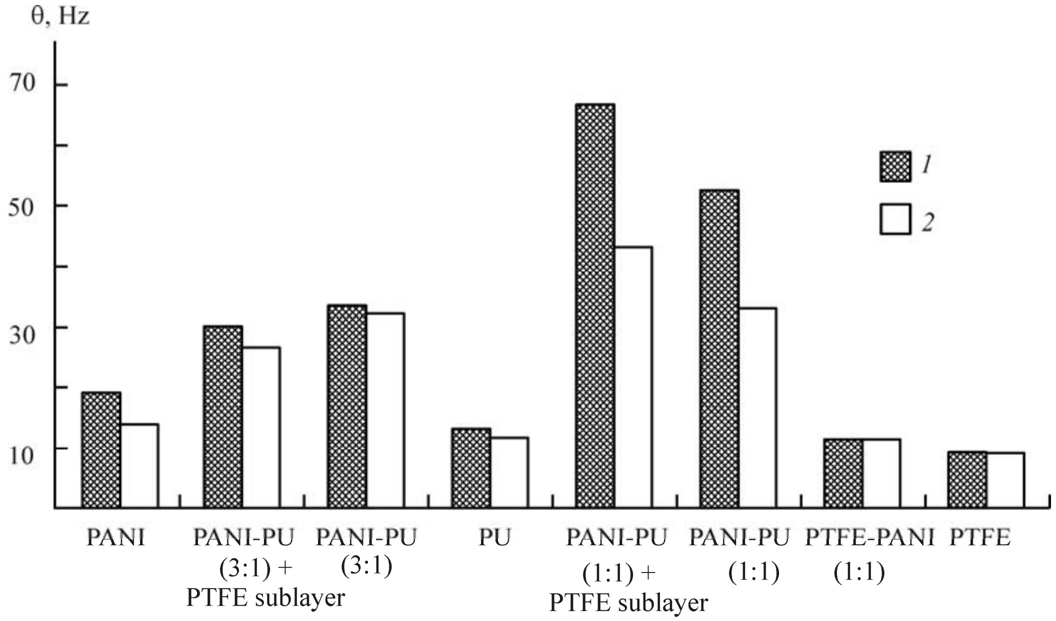

Fig. 5. Sensitivity of sensor elements θ with deposited coatings to ammonia. Response: (*1*) maximal and (*2*) steady-state.

or electrochemical oxidation of the coatings [6]. Application of a PTFE sublayer prior to deposition of PANI–PU composite coatings leads to significant changes in the structure of the layers. In the electronic spectrum of PANI–PU (2 : 1) coatings, intense absorption appears in the range corresponding to radical cations, and also in the range 500–800 nm, suggesting formation of quinone imine fragments and localized polarons. For the PANI–PU (3 : 1) coating, the presence of a PTFE sublayer leads to an increase in the absorption intensity in the region corresponding to localized polarons.

The electronic spectra of composite coatings formed in different process cycles can differ from each other in the shape, which may be due to nonstationary mode of dispersion of PANI and PU powders (Fig. 4).

Enhancement of the segmental mobility of the dispersion products forming the polymer layer, provided by heating the support with the PTFE sublayer, significantly affects the electronic spectrum of the coating (Fig. 4). Pronounced absorption bands appear in the spectra of PANI–PU coatings at weight ratios of 2 : 1 and 1 : 1, which suggests the occurrence of intermolecular interaction of PU and PANI dispersion products, decreasing the adsorption mobility of PANI fragments.

We assessed the efficiency of using the composite coatings prepared as active elements of adsorption-type sensors. As a gas being analyzed we chose ammonia. The results of evaluating the adsorption activity of coatings are shown in Fig. 5.

For PANI coatings formed from the active gas phase, a correlation is observed between the conductivity and adsorption activity toward ammonia. PANI coatings formed by electron-beam dispersion of PANI with sulfamic acid and aluminum chloride show the highest adsorption activity toward ammonia. However, in the course of operation of sensor elements with such coatings, in some cases the adsorption activity of the deposited layer can drastically decrease or increase.

Sensor elements with the deposited composite layers show high stability in operation. The sensor sensitivity does not change noticeably in operation with different concentrations of ammonia in the gas mixture. The lack of clear correlation between the adsorption activity of the composite layer and its electronic absorption spectrum, in particular, for PANI–PU coatings, may be due to active participation of oxidized areas in cross-linking of the composite layer.

CONCLUSIONS

(1) Specific features of deposition of composite polymeric coatings based on polyaniline and thermoplastic polymers by electron-beam dispersion were determined. In dispersion of a mixture of these products, the target surface temperature in the area

exposed to electron beam is appreciably lower than in dispersion of straight PANI.

(2) The structure of the forming coatings is determined by the support parameters (surface energy, temperature).

(3) Sulfamic acid and aluminum chloride efficiently promote oxidation of polyaniline coatings deposited from the active gas phase both in the step of gas phase generation and in the course of formation of the coating on the support.

(4) The polyaniline–polyurethane coating deposited onto a polytetrafluoroethylene sublayer shows the highest adsorption activity toward ammonia molecules.

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