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Flexible elements of gas sensors based on conjugated polyaminoarenes

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ABSTRACT

The methods of formation of the free standing flexible gas sensitive films from the composites of conjugated polyaminoarenes (polyaniline, polyorthoanisidine, polyorthotoluidine) with dielectric polymer matrices (polyvinyl alcohol, polyacrylic or polymethacrylic acids) were developed. Synthesis of composites was carried out by “in situ” polymerization of monomers inside the polymer matrix by chemical oxidative polymerization. It has been established that the presence of dielectric matrices in flexible composite films does not alter the nature of optical absorption of polyaminoarenes and provides the possibility of using of the synthesized composites to produce gas sensors. For practical application the optimal are the structures based on the flexible sensor films which change their color under action of gases and may be used as visual indicators of ammonia in the food industry and in environment.

KEYWORDS

Gas sensor;
polyaminoarene; polymer
flexible film; ammonia;
optical absorption

Today many different sensory devices and systems for controlling gas environments have been developed. As sensitive elements in such sensors oxide films, as well as various inorganic and organic semiconductors are used [1–7]. However, despite the successful development and use of intelligent gas-analysis systems of “artificial nose” type and other gas-sensory devices, there is still an acute need in portable low-cost sensors for fast ecological control of the environment “in the field” and monitoring gas environments in the technological processes of the food industry, especially for the control of freshness of food products during their storage (meat, fish, dairy and other products).

In recent years, there is growing interest in the usage of conjugated conducting polymer films in gas sensors, due to their high sensitivity of changes in optical absorption or resistance under the action of gases, as well as the simplicity of synthesis, low cost [8–15]. The electroconductive polymers are particularly important for creating sensory medium for continuous monitoring environment, for the needs of small business and household purposes (refrigerators, warehouses, mini-shops to produce food). It is important that the information signal of such a sensor can be perceived visually, for example, by color change [14]. The performance of such sensors in the form of flexible

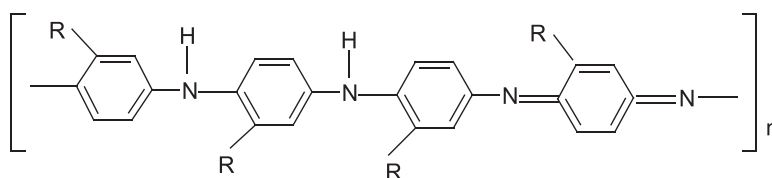


Figure 1. The structure of the repeating unit of polyaminoarenes, where R is functional group: $-H$; $-CH_3$; $-OCH_3$ correspondently for PANi, PoTi, PoA.

films or tapes can significantly expand the scope of their application, for example, as visual indicators of freshness under the packaging of a food product, or in refrigerators, food containers and other devices.

Unfortunately, most electroconductive polyaminoarenes do not themselves form flexible films and are very difficult to process due to low solubility, unsatisfactory mechanical properties. One of the ways to provide a flexibility to conjugated polymers is to deposit them on a flexible or textile substrate [16], using polymer blends in common solvent [17], or creation of composites with high elastic or thermoplastic polymers [15,18], which are mainly dielectrics. In these composites the filler and dielectric matrix have similar values of specific density that provide stability of such systems to stratification.

On the other hand at the loss of the protein foods freshness together with other gases (CO_2 , H_2S , O_2 , H_2 , N_2 , NH_3 , SO_2) the highest amount of ammonia is released [19,20]. The intensity of its releasing and accumulation corresponds to the level of disintegration of proteins, polypeptides and free amino acids, and therefore the information on the concentration primarily of ammonia, will be a reliable criterion of the degree of freshness of protein-containing foods. Thus, there is an urgent need for simple, reliable, cheap and generally accessible ammonia sensors, especially on flexible surfaces, their development is extremely relevant for a variety of control methods, and in the first place, food products.

The purpose of this work was to study the conditions of formation and properties of composite films based on conjugated polyaminoarenes introduced into dielectric polymer matrices, and the creation of flexible sensors on this basis for visual control of ammonia in food industry and environment.

Experimental

Materials

Conductive conjugated polyaminoarenes — polyaniline (PANi) and its derivatives – polyorthoanisidine (PoA) and polyorthotoluidine (PoTi) were used as sensitive components of polymer composites, which can be described by general formula, given in Figure 1.

The monomers – aniline, o-anisidine, o-toluidine were obtained from Sigma-Aldrich Co (USA), before using they were distilled in vacuum.

For the formation of composites as polymer matrices, samples of industrial polymers were used: polyvinyl alcohol (PVA), polyacrylic acid (PAA) and polymethacrylic acid (PMAA). These polymers have a good solubility in water medium and low toxicity.

Obtaining the free flexible films, which would be a composite of conjugated polyaminoarene and a highly elastic polymer matrix, was carried out by oxidative polymerization of 0.01 – 0.025 M solution of aminoarenes at the equimolar content of oxidizer (ammonium persulfate) in an aqueous gel of PVA (PAA or PMAA) with concentration from 0.125 to 5 % (w) during 24 h. The films were formed by the method of pouring of the composition on the surface of Teflon or glass with subsequent monolithization of the film at room temperature over 6-8 h and finally at 331 – 333 K for 1 hour. After separation from the substrate, a homogeneous flexible film was obtained and then used to make the sensor or indicator.

Methods

Optical absorption spectra of polymer films were obtained using the modified Specord M400 dual-beam optical spectrometer with the following measurement parameters: spectral range – 200 ... 1000 nm, slit width – 1 nm, integration time – 1 s, scanning step – 1 nm, recording speed – 10 nm/s. To measure the optical spectra of sensory films in the ammonia atmosphere, a sealed quartz chamber was used of 50 cm² volume, where the required amount of gas (ammonia) was fed. All measurements were carried out at a temperature of 293 ± 1 K. The analysis of the results was carried out using a standard correlation program, in which the relative error did not exceed 1.5 % at the entire range of measurements. Analyzing and processing of experimental data were done using methods described in [21,22].

The surface condition and the morphology of the film samples were studied using a Micromed microscope with a digital camera Nikon-2500. The composite film thickness was measured by micrometer with accuracy ±0.01mm.

Results and Discussion

The most promising method of providing elasticity and thermo-plasticity of polyaminoarenes is the creation of polymer composites in which the mixing of components takes place at the molecular level. This method is used to produce polymer-polymer composites with ordered structure, as well as nanosized composites that cannot be obtained from finished polymers due to the insolubility of one of them. These polymers include conjugated polyaminoarenes, insoluble in water and in most organic solvents.

We used such approaches to obtain the composite of conjugated polyaminoarenes with polymer matrices (PVA, PAA, PMAA), when the polymerization of aminoarenes occurs in a polymer gel whose macromolecules act as “soft” templates [15,23]. It was shown that in such composites the interaction of the functional groups of the polymer matrix with the amino groups of the polymeric filler is possible. The presence of such interaction affects the kinetics of polymerization and all the physical, chemical and mechanical properties of composites [12,15,17,18]. It has been found that the mass fraction of 0,35-1,05 % of the monomer in the initial composition is optimal [23]. Since in the process of oxidative polymerization of aminoarenes within 24 hours at a monomer-oxidizer ratio 1:1, almost complete (95-98%) conversion of the monomer is achieved

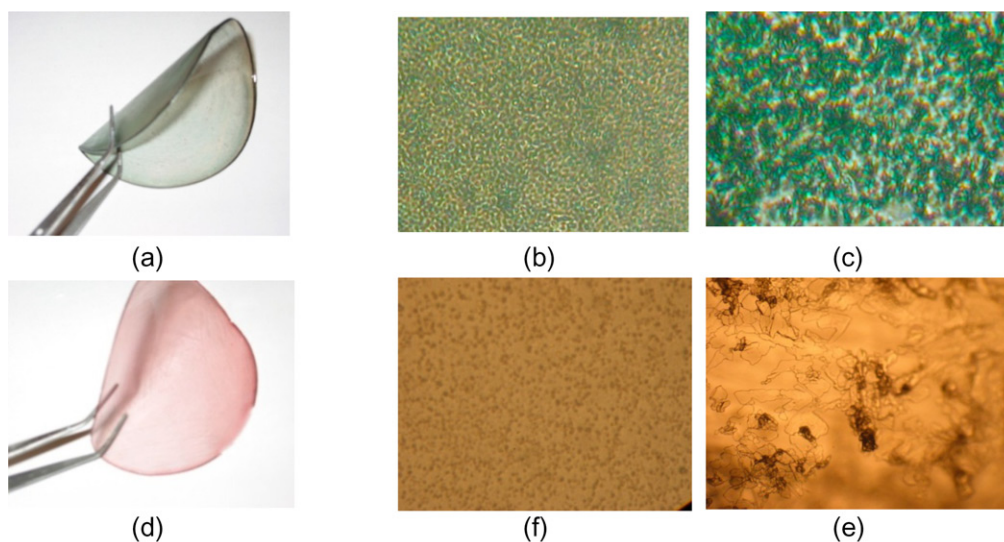


Figure 2. Micro photographs of composite polymer films: PVA-PoTi (a, b); PVA-PANi (c); PMAA-PoA (d, f); PAA – PoTi (e). Zoom 600 (b, c, f, e).

[15] it corresponds to 4.5-15 % mass abundance of the conductive polymer in the final composite.

The obtained polymer-polymer composites form flexible, highly elastic “free” films (Figures 2, a, d), from which it is easy to form indicator tapes. The structure of the film composites based on PVA and polyaminoarenes is sufficiently homogeneous, compact and at the same time its globular nature is preserved (Figures 2, b, c, f). Composites with matrixes based on polymer electrolytes (PAA, PMAA) form not only flexible, but also transparent “glass-like” films (Figure 2, e). The study of the morphology of the resulting film composites confirmed their rather ordered structure.

The appearance of the optical absorption spectra of the resulting composites (Figures 3 and 4) substantially depends on the type of polymer matrix used for the film formation. Indeed, for PoTi-PMAA composites one can observe 2 absorption bands, one – in wavelength range of $\lambda = 400 - 420$ nm ($\pi-\pi^*$ transition in the band gap of polyaminoarene), the other – in the range of $\lambda = 750 - 850$ nm (absorption in the polaron/bipolaron band). For composites PoTi with PAA the second band is observed in the range of $\lambda = 550 - 600$ nm, which is typical for electronic transitions in benzo-quinoid fragments of polyaminoarenes [24].

In the optical spectra of the composites with PVA matrix three absorption bands typical for polyaminoarenes were observed at $\lambda = 375$ nm, 450 nm and at $\lambda > 700$ nm (Fig.4). In the optical spectra of the composites based on PAA, PMAA and PVA matrixes the intensity of absorption increases with the growth of polyaminoarene concentration (Figure 4, a, b).

Film composites of polyaminoarenes in highly elastic polymer matrices under the influence of polar gases (ammonia) exhibit a gas-chromic effect, the general laws of which are like those observed for films of individual polyaminoarenes [14].

Under the action of ammonia, there is a significant change in the optical absorption spectra of composites, first - the general increasing of intensity (Figure 5, a, b), and also

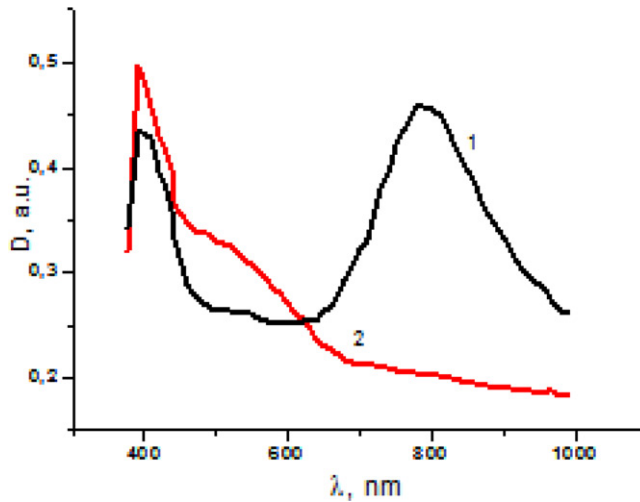


Figure 3. (a) Spectra of optical absorption of film composites PMAA-PoTi (1) and PAA-PoTi (2) at content of conductive polymer 2.5 % (w). Film thickness is 0,12 mm

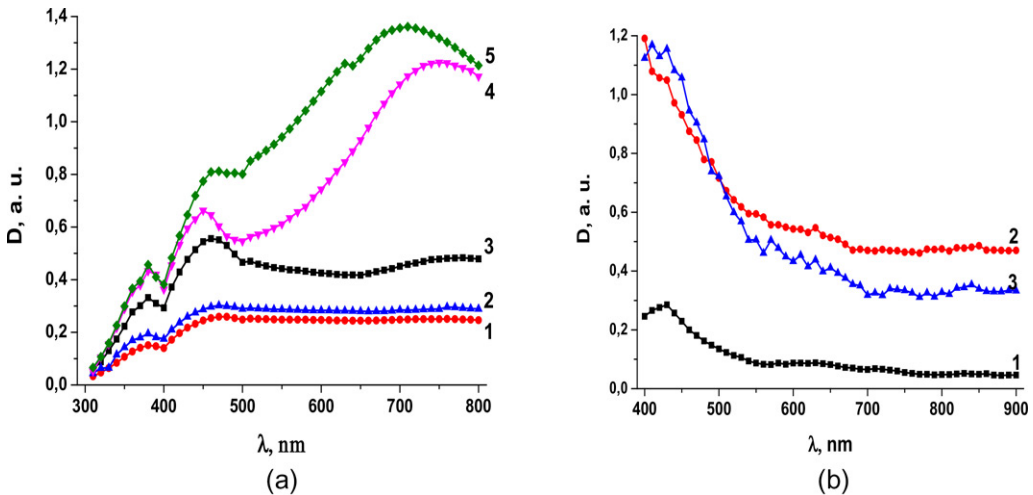


Figure 4. (a) Optical spectra of PVA-PANi films at content of polyaminoarene, %(w): 3.2 (1); 4.3 (2); 7.2 (3); 9.6 (4); 11.2(5); (b) Optical spectra of PVA - PoA films at content of polyaminoarene, %(w): 3.2 (1); 7.0 (2); 9.6 (3)

shifting of the position of the maxima of absorption bands (Figure 5, b). Indeed, in absorption spectra of free standing PVA-PANi films the most significant changes are observed for the band 750 – 830 nm (absorption in the polaron zone). Under the action of ammonia this band is almost completely neglected because of the deprotonation processes with the formation of ammonium cations and the decrease of the carrier's concentration [13,14]. Instead, a band appears in the range of 580 – 620 nm, attributed to the imino-quinone fragments in the structure of polyaminoarenes [24,25].

All this is accompanied by visual changes in the color of the films. At the initial moment, the PVA-PANi film has an intense green color and retains it in the absence of ammonia in the air, or throughout the shelf life, providing the freshness of the food

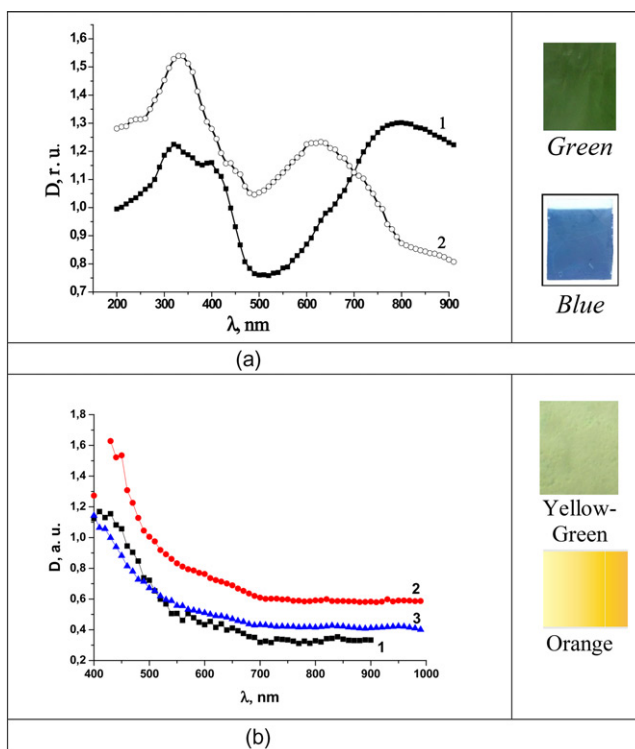


Figure 5. (a) Absorption spectra of free standing composite films PVA– PANi: 1 – on air, 2 – in ammonia environment ($p = 1.4$ kPa). Thickness of the film is 0.15 mm. PANi content in composite is 7.2 %. (b) Spectra of optical absorption of PVA– PoA films: 1 – on air, 2 – in ammonia environment, 3- after resorption in air during 2h. Thickness of film is 0.12 mm. Content of PoA is 8.0 %.

Table 1 Results of the tests of flexible sensors with different indicator substances

Ammonia pressure, kPa	Time of change of color of the sensor (seconds), at different temperatures					
	PANi $t = 18^{\circ}\text{C}$	PVA-PANi $t = 18^{\circ}\text{C}$		PVA-PoTi $t = 1^{\circ}\text{C}$	PoA $t = 25^{\circ}\text{C}$	PVA-PoA $t = 25^{\circ}\text{C}$
1	0.5-1	5	2	12	1	10
0.1	2	15-20	5	60	3	60
0.01	30-40	190	65	360	30-40	420
0.001	60	300	100	450	60	550

product. In the presence of small amounts of ammonia (partial pressure $P = 10 - 30$ Pa) there is visually a change in the color of the indicator from green to blue. The usage of films based on PANi derivatives such as PoTi or PoA allows for a significant increase of the color set. When the freshness of the product is affected, the color of the indicator changes dramatically - from bright green to blue (in the case of PANi and PoTi) or from yellow-green to orange in the case of PoA. If the freshness of the food product deteriorates significantly, the allocation of ammonia is intensified, and the sensory film becomes pale blue (PANi, POT) or burgundy (PoA) color.

The speed of the sensor based on polymer composites depends on the temperature, gas pressure and type of indicator substance embedded in the polymer matrix, but generally ranges from a few seconds to several minutes (Table 1).

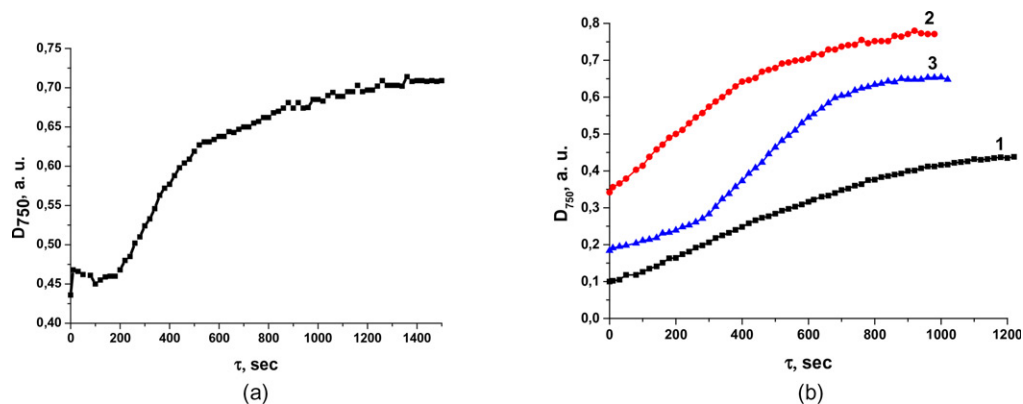


Figure 6. The kinetics of changing optical density of the sensor film PVA-PANi (7.2 %) (a), and sensor film PVA-PoA (b) for different content of PoA, %(w): 3.2 (1); 7.0 (2); 9.6 (3) at ammonia pressure 1.4 kPa

As one can see from Figure 6 and data of the table, the time of reaching the stationary value of the optical density of composite films is higher than polyaminoarene ones. When contact with the ammonia is stopped, reverse processes occur - decay of unstable ammonium cation on the hydrogen ion and ammonia, ammonia desorption and the restoration of the properties of the film. The spectrum of optical absorption retained to its initial shape (Fig.5.b, curve 3). The rate of desorption of ammonia from composite films is rather slow (from 25-30 minutes to 2 hours), and at higher partial pressure of ammonia (more than 10 kPa) the process becomes irreversible.

For practical realization, we offer available flexible indicator films based on the composites of conjugated polyaminoarenes with elastic polymer matrices (PVA, PAA, PMAA), which change their color under the action of gases. The presence of polymer matrices in flexible sensors does not change the nature of their optical absorption, which ensures the use of synthesized composites for the manufacture of gas sensors.

Conclusions

The formation of sensitive flexible films based on polyaminoarenes and polymer matrices significantly improves their functionality and the quality control of food products with their help. The presence of polymer matrices in flexible sensors does not change the semiconductor nature of their optical absorption, which ensures the use of synthesized composites for the manufacture of gas sensors. The structures based on affordable and cheap flexible indicator films that change their color under the action of certain gases, particularly, ammonia, may be used for control of food freshness and gas mediums in the environment.

References

- [1] Harsányi G. (2000). *Sensor Review*, 20, 98.
- [2] Lv. A., Pan Y., Chi L. (2017). *Sensors*, 17, 213.
- [3] Pomogailo D. A., Singh S., Singh M. et al. (2014). *Inorganic Materials*, 50, 296.

- [4] Alizadeha T., Hamedsoltania L. (2014). *J. Envir. Chem. Eng.*, 2, 1514.
- [5] Pavluchenko A.S., Mamykin A.V., Kukla A.L. et al. (2016). *Sensors Actuators B*, 232, 203.
- [6] Kunzo P., Lobotka P., Kovacova E., et al. (2013). *Physica status solidi (a)*, 210, 2341.
- [7] Shukla S. K., Singh N. B., Rastogi R. P. (2013). *Ind. J. Engin. & Mater. Sci.*, 20, 319.
- [8] Bai, H., Shi, G. (2007). *Sensors*, 7, 267.
- [9] Parmar M., Balamurugan C., Lee D.-W. (2013). *Sensors (Basel)*, 13(12), 16611.
- [10] Pandis C., Peoglos V., Kyritsis A., Pissis P. (2011). *Procedia Engineering* 25, 243.
- [11] Kate K.H., Damkale S.R., Khanna P. K., Jain G. H. (2011). *J. Nanosci. Nanotechn.*, 11, 7863.
- [12] Konopelnik O.I., Aksimentyeva O.I., Martynyuk G.V. (2005). *Molec. Cryst. & Liq. Cryst.*, 427, 37.
- [13] Tsizh B. R., Aksimentyeva O. I., Vertsimakha Ya. I., Lutsyk P. M., Chokhan M. I. (2014). *Molec. Cryst. & Liq. Cryst.*, 589, 116.
- [14] Tsizh B. R., Chokhan M. I., Aksimentyeva O. I., Konopelnik O. I., Poliovyi D. O. (2008). *Mol. Cryst. & Liq. Cryst.*, 497, 586.
- [15] Aksimentyeva O. I., Konopelnik O. I., Martyniuk G. V., Yevchuk O. M. Chapter 9. (2017). *Computational and Experimental Analysis of Functional Materials*. (Toronto: Apple Academic Press), 331.
- [16] Tabellout M., Fatyeyeva K., Baillif P.-Y., Pud A. A. (2005). *J. Non-Cryst. Solids*, 351, 2835.
- [17] Aksimentyeva O., Konopelnik O., Opaaynych I., Tzish B., Ukrainets A., Ulansky Y., Martyniuk G. (2010). *Rev. Adv. Mater. Sci.*, 23, 30.
- [18] Aksimentyeva O. I., Konopelnik O. I., Tsizh B. R., Chokhan M. I. (2011). *Sensor Electron. Microsyst. Techn.*, 2(8), 34.
- [19] Vernat-Rossi V., Garcia C., Talon R., Denoyer C., Berdague J. L. (1996). *Sensors and Actuators B*, 37, 43.
- [20] Matindoust S., Baghaei-Nejad M., Abadi M. H. S., Zou Z., Zheng L.-R. (2016). *Sensor Review*, 36(2), 169.
- [21] Angryk R., Czerniak J. (2010). *Internat. J. Approxim. Reason.*, 51, 895.
- [22] Czerniak J. (2009). *Fundam. Informat.*, 92, 43.
- [23] Aksimentyeva O. I., Tsizh B. R., Chokhan' M. I., Yevchuk O.M. (2011). Patent № 65401 (UA). Bul. 23.
- [24] Sverdlova O. V. (1985). *Electron spectra in organic chemistry*. (Leningrad: Khimia).
- [25] Murrell J. N. (1963). *The Theory of the Electronic spectra of Organic Molecules* (L.-N.Y.)