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NANOCOMPOSITE POLYMER THIN FILMS FOR SENSORS

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The article is devoted to the study of nanocomposite thin films made from a polyelectrolyte complex of chitosan and chitosan succinamide with single-walled carbon nanotubes as a filler, as well as thin films of polyaniline derivatives. The authors investigate how the morphology of polyaniline derivatives and nanocomposites affects the electrical conductivity, sensitivity to air humidity, and reaction to ammonia vapors in thin-film structures. The surface morphology of the films, which were formed from a solution of the synthesized polymers through centrifugation on sitall and glass substrates, was examined using a scanning electron microscope.

Keywords: *SWCNT, PEC, polyaniline derivatives, morphology, electrical conductivity, sensory sensitivity, substrates, gaps.*

Introduction

New polymer-based materials used in electronic sensor systems have received increased interest due to their cost-effectiveness, ease of production, and the ability to modify their properties through functionalization [1]. Organic polymers, inorganic composites, and ceramics are commonly used in sensor applications for air humidity and various gases [2–4]. Within the field of nanotechnology, polymer nanocomposites have become a prominent area of research and development, encompassing nanoelectronics and polymer biomaterials. These materials exhibit exceptional physico-chemical properties that are not attainable by their individual components alone [5]. Polyaniline (PANI), a widely recognized conductive polymer, has emerged as a promising candidate for a range of electronic devices, thanks to its conductivity, stability, strong resistance to environmental factors, ease of processing, and cost-effectiveness of raw materials and synthesis [6–7]. Polyelectrolyte complexes (PECs) can be used in organic sensors. Polyelectrolyte complexes are polymeric materials that have a high ability for ionic interactions. This makes them useful for creating sensing elements in sensors that can detect various chemicals. Due to their ability to change their structure and properties in response to environmental changes, polyelectrolyte complexes can be used to create effective and highly sensitive organic sensors [8–10]. PECs are compounds consisting of polymers and electrolytes that form stable complexes due to electrostatic interactions between positively and negatively charged parts of the molecules [11]. The polyelectrolyte complex may also include various polymers, kaolin, metal nanoparticles, adhesives, additives for strengthening and modifying material characteristics, as well as other functional additives, for example, to improve adhesion or antiseptic properties [12–13]. Organic humidity sensors play an important role in everyday life, providing humidity control and optimization in a variety of applications [14].

Due to swift growth of industry, the quantity of harmful gases that pose a threat to human health is on the rise, underlining the critical need to identify and quantify the precise levels of toxic pollutants. An example of such a harmful gas is anhydrous NH_3, which can cause irritation to the eyes, skin, and respiratory system [15]. The presence of NH_3, a common pollutant, is widespread across different human activities. Extended exposure to NH_3 levels of 25 ppm or higher can lead to respiratory illnesses and potentially fatal consequences. Studies indicate that NH3 levels in the exhaled breath of healthy individuals typically range from 0.2 to 0.5 m.d. However, patients with kidney disease exhibit significantly higher NH_3 levels, ranging from 0.82 to 14.7 m.d. Thus, elevated NH_3 levels could be an indicator of kidney disease [16]. As a result, there is a pressing necessity to create a gas sensor that can detect NH3 at room temperature.

Currently, there is a high demand for electronic sensors that require high energy efficiency. Existing sensors typically utilize oxide materials and necessitate heating during operation. Moreover, their response and recovery times are often slow. This research aims to explore new composite materials for sensors that offer high performance, low power consumption, minimal hysteresis, and improved efficiency [17–22].

The aim of the study is to investigate how the structure and form of thin films made of polyaniline derivatives and nanocomposites impact their ability to detect changes in air humidity and the presence of ammonia vapors.

Research methods

In the experiments, the power sources used for measurements included MASTESN, DS ROWER SUPPLY HYZ005D-2, and a universal voltmeter V7-21 used as an ammeter. The thickness of thin polymer films was monitored by analyzing SEM images. A sample of the humidity sensor was placed in a hood with a control humidity sensor and a water tank (*Fig.* 1). The input signal values were recorded at specific humidity levels, monitored using a DHT11 sensor.

The humidity values were displayed on a laptop screen using an Arduino UNO and USB connection. The measurements were conducted at a room temperature of 25 °C with a voltage of 30 V applied to the samples. The microstructure of polymers was examined using scanning electron microscopy (SEM) TESCAN MIRA LMS.

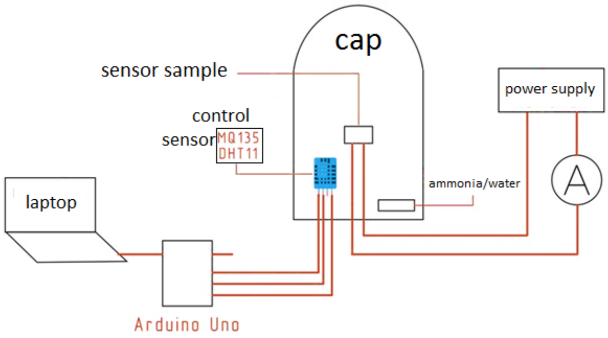


Fig.1. Structure of thin-film resistive sensors.

We created multilayer structures of resistive sensors using thin films of a PANI derivative and PEC with SWCNTs (*Fig.* 1). A sitall (*Fig.* 2a) and a glass (*Fig.* 2b) substrate were used for the resistive sensors. Aluminum electrodes were applied to the substrate using thermal spraying in a vacuum chamber on the UVP-250 installation with a thickness of approximately 400–500 nm, and a gap was created using a shadow mask. A 50-micron PANI film was applied to the gap area between the electrodes for some samples, while others had a polymer PEC with SWCNT. The ohmic nature of the contacts was confirmed by measuring their current-voltage characteristics. SEM studies confirmed the uniformity of the polymer surface in the working area of the resistive sensors. Additionally, the resulting layer underwent thermal annealing at 150 °C for 20–25 min to remove solvent residues.

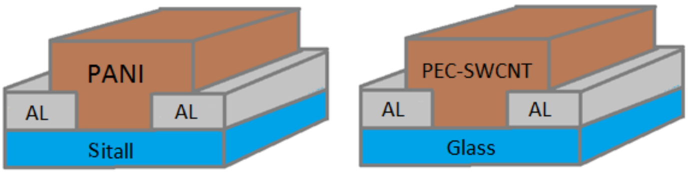
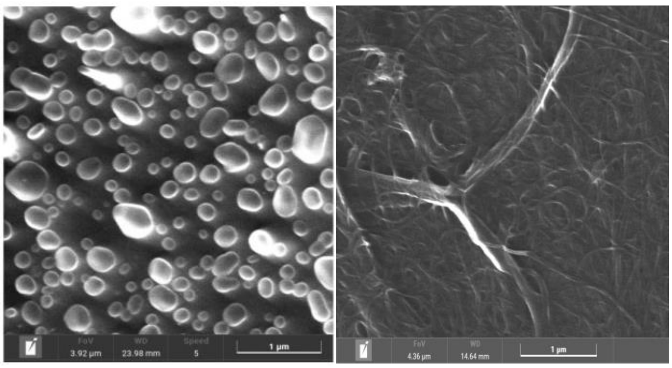


Fig. 2. Structures of thin-film resistive sensors.

Results and discussion

The TESCAN MIRA LMS scanning electron microscope (SEM) and TESCAN Essence software were used to acquire images of the surface of the studied polymers and composites (*Fig.* 3).



a) b)

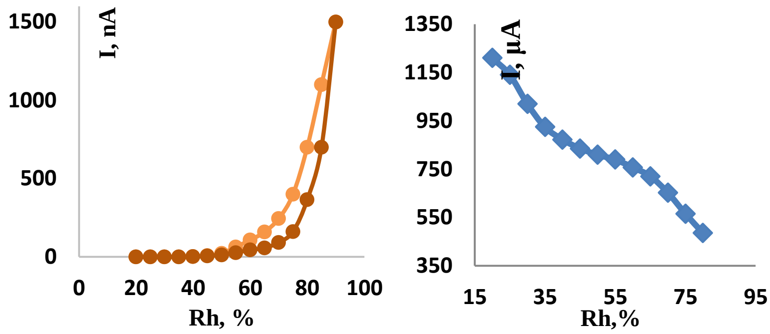
Fig. 3. SEM images of microstructures of film samples:
a) PANI derivative, b) PEC-SWCNT.

In *Fig.* 3a, the surface displays a uniform spherical globular structure that allows for the penetration of numerous gas molecules, while in *Fig.* 3b it appears to be adorned with filament-like formations, possibly indicating the presence of complex structures formed by carbon nanotubes. The roughness measurements were derived using the Gwyddion SEM image processing software, and the RMS roughness values across the Sq area are presented in *Table* 1.

Table 1

The values of the RMS roughness over the Sq area

	Derivative of PANI			PEC-SWCNT		
microns	4	8	100	4	8	100
Root-mean-square roughness in area, microns	229.9	220.8	287.7	0.1	0.1	0.11



a) b)

Fig. 4. Dependence of the current flowing through the films of a) PANI derivative and b) PEC-SWCNT on the relative humidity of the air in the air volume.

The measurement results were used to create graphs showing the relationship between humidity and the current passing through PANI and PEC-SWCNT films (*Fig.* 4). The upper line in *Fig.* 4a represents data collected as humidity increased in the chamber, while the lower line shows data as humidity decreased. The figure demonstrates a clear correlation between substance structure and current values in sensory film samples. It is noteworthy that the current in samples with a PANI derivative only starts to increase at 50% humidity, and this increase is characterized by a sharp rise in current.

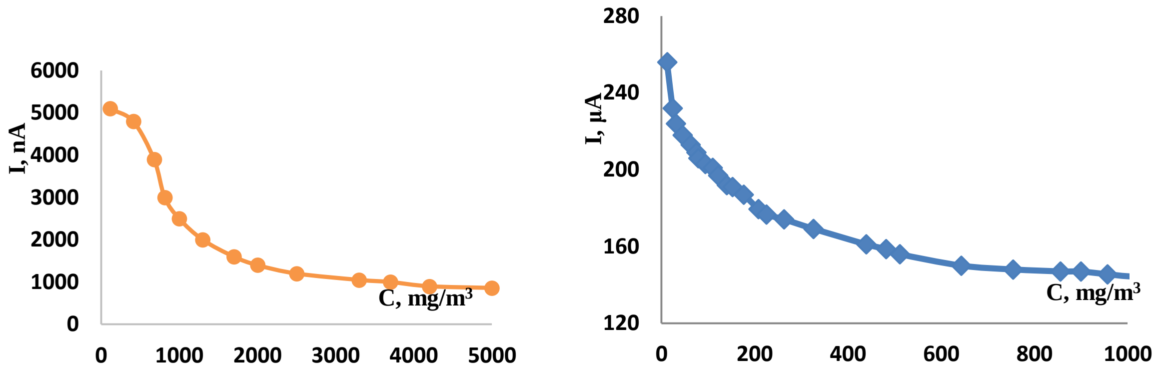
As environmental humidity increases, the electrical conductivity of the polymer film also increases due to the interaction of water with the polymer. During the absorption of moisture, the polymer acquires more ionized groups, which increases electrical conductivity. Due to interaction with moisture, ions can be formed on the surface of the polymer film, which also helps to increase conductivity. This property can be used, for example, in humidity sensors, where the high electrical conductivity of the polymer film in a humid environment can be used to measure the humidity level of the environment.

When the polymer is saturated with moisture, a process called moisture absorption occurs. Water can penetrate into the polymer structure, taking up space between the polymer molecules. This can lead to changes in the physical properties of the polymer, such as an increase in volume, changes in mechanical properties, and a possible decrease in the strength and elasticity of the material. In some cases, interaction with moisture may also cause the polymer to break down or degrade. As a result of the adsorption of moisture on the surface of the polymer, water molecules can be ionized under the influence of an electrostatic field. This means that water can decompose into positively and negatively charged ions – hydrogen ions (H+) and hydroxide ions (OH-), due to the influence of an electrostatic field. As water adsorbs onto the polymer surface and ionizes, it can change the chemical composition and surface properties of the polymer material. The presence of ions on the surface of the polymer can lead to improved adhesion, changes in chemical resistance, and also affect the electrical properties of the polymer.

One of the possibilities for creating an organic humidity sensor is to take advantage of the ability to change the electrical conductivity of polyaniline derivatives under the influence of the environment. It is known that the interaction of individual fragments of a polymer molecule with a hydroxyl group or hydrogen ion can form a charge transfer complex. H+ ions in PANI derivatives lead to protonation of the polymer chain, the formation of emeraldine salt and, as a result, an increase in electrical conductivity. The properties of synthesized polymers can be improved, and the advantages of organic coatings of polymers in the production of electronic materials with unique properties are obvious. These features of PANI polymers allow them to be used as chemical sensors, including humidity sensors.

In the working chamber under the hood, the humidity fluctuated between 20% and 80%, as seen in *Fig*. 4b. *Fig*. 4 displays the current values indicated by the resistive sensor, which range from 450 to 1 250 µA as the humidity levels increase. This relationship is not linear, as the rate of decrease in current value remains relatively consistent across the entire measurement range.

Single-walled carbon nanotubes (SWCNTs) exhibit hole conductivity due to their unique structure and electronic properties. The main mechanism of conductivity in nanotubes is related to their chirality and spin-orbit interaction. Single-walled carbon nanotubes can be classified as p-type semiconductors due to the characteristics of their electronic structure. As a result of the electric field, electrons can move freely along the nanotube to form a current, but there are free electron holes in the material that can also participate in conduction. This leads to hole conduction and classification of nanotubes as p-type semiconductors. Such properties make single-walled carbon nanotubes potentially useful for a variety of electronic and optical applications, including semiconductor devices, sensors, and photonic devices.



a) b)

Fig. 5. Dependences of the flowing current through the films of the a) derivative of PANI and b) PEC-SWCNT at 25 °C.

Polyaniline derivative films exhibit a decrease in electrical current when exposed to ammonia vapor in the environment (*Fig.* 5a). This response is attributed to the protonation/deprotonation of the polymer chain. As the concentration of ammonia in the environment increases, the degree of doping in the polymer decreases. It is hypothesized that the interaction between the polymer and NH3 results in the absorption of protons from PANI by ammonia molecules, leading to the formation of energetically favorable ammonium (NH4+). As a result, PANI undergoes deprotonation, leading to a decrease in conductivity.

The PEC-SWCNT derivative films shown in *Fig.* 5b exhibit a decrease in electrical current in response to the presence of ammonia vapors in the surrounding environment. The current decreases from 260 µA to nearly 140 µA as the concentration of ammonia vapor changes from 0 to 1 000 mg/m^3. The maximum allowable concentration of ammonia is 20 mg/m^3. The response is non-linear: the current decreases rapidly up to a concentration of 200 mg/m^3, after which the rate of decrease slows significantly.

Conclusion

The study findings indicate that the sensitivity of the films' surface morphology and total area has a greater impact than the RMS roughness on the results. Interestingly, the sensitivity of polyaniline derivative samples does not show much difference when taking error into account.

The use of new PANI derivatives as sensor elements allows for the creation of thin films with a well-developed and analyte-permeable surface. The resistive sensors studied exhibit low inertia and rapid response times. The PANI derivative samples displayed high sensitivity, quick response times, and efficient recovery, making them highly practical for air humidity sensors and detecting ammonia vapors in the air.

Research on the surface morphology of PEC-SWCNT nanocomposite found that it is coated with filamentous carbon nanotube formations, as observed using SEM. Additionally, the resistive thin-film nanocomposite structures were found to be sensitive to changes in air humidity and ammonia vapors, with current flow through the structures showing dependence on relative air humidity and ammonia vapor concentration.

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REFERENCES

1. Vychuzhanin V. Measurement of air humidity by Honeywell sensors // Modern electronics. 2008. Vol. 5. P. 8–10.
2. Mustafin A. G., Latypova L. R., Andriianova A. N. et al. Polymerization of new aniline derivatives: synthesis, characterization and application as sensors // RSC advances. 2021. Vol. 11(34). P. 21006–21016.
3. Tuktarov A. R., Salikhov R. B., Khuzin A. A. et al. Photocontrolled organic field effect transistors based on the fullerene C60 and spiropyran hybrid molecule // RSC advances. 2019. Vol. 9(13). P. 7505–7508.
4. Markov V. F., Vinogradova T. V., Zarubin I. V., Maskayeva L. N. Thin-film chemical sensors based on $Ag_xPb_{1-x}s$ for determination of No_2, No and Co content in the air environment // Analytics and control. 2012. Vol. 4. P. 410–414.
5. Bazunova M. V., Mustakimov R. A., Salikhov R. B., Mullagaliev I. N. Film Materials Based on Polymer Blends of N-Succinyl Chitosan Sodium Salt with Poly-N-vinylpyrrolidone // Russian Journal of Applied Chemistry. 2022. Vol. 95(6). P. 828–835.
6. Salikhov R. B., Zilberg R. A., Mullagaliev I. N. et al. Nanocomposite thin film structures based on polyarylenephthalide with YHT and graphene oxide fillers // Mendeleev Communications. 2022. Vol. 32(4). P. 520–522.
7. Latypova L. R., Andriianova A. N., Usmanova G. S. et al. Influence of copolymer composition on the properties of soluble poly(aniline-co-2-[2-chloro-1-methylbut-2-en-1-yl] aniline)s // Polymer International. 2023. Vol. 72(4). P. 440–450.

8. Yi Y., Yu C., Zhai H. et al. A free-standing humidity sensor with high sensing reliability for environmental and wearable detection // Nano Energy. 2022. Vol. 103. P. 107780.
9. Xuan W., He X., Chen J. et al. High sensitivity flexible Lamb-wave humidity sensors with a graphene oxide sensing layer // Nanoscale. 2015. Vol. 7(16). P. 7430–7436.
10. Zhang X., Wang A., Chen Y. et al. Intestinal barrier dysfunction induced by ammonia exposure in pigs in vivo and in vitro: The protective role of L-selenomethionine // Ecotoxicology and Environmental Safety. 2022. Vol. 248. P. 114325.
11. Zhang D., Wu J., Cao Y. Ultrasensitive H_2S gas detection at room temperature based on copper oxide/molybdenum disulfide nanocomposite with synergistic effect // Sensors and Actuators B: Chemical. 2019. Vol. 287. P. 346–355.
12. Manivannan S., Saranya A. M., Renganathan B. et al. Single-walled carbon nanotubes wrapped poly-methyl methacrylate fiber optic sensor for ammonia, ethanol and methanol vapors at room temperature // Sensors and Actuators B: Chemical. 2012. Vol. 171. P. 634–638.
13. Bardócz S. Polyamines in food and their consequences for food quality and human health // Trends in Food Science & Technology. 1995. Vol. 6(10). P. 341–346.
14. Timmer B., Olthuis W., Van Den Berg A. Ammonia sensors and their applications – a review // Sensors and Actuators B: Chemical. 2005. Vol. 107(2). P. 666–677.
15. Li H. Y., Lee C. S., Kim D. H., Lee J. H. Flexible room-temperature NH3 sensor for ultrasensitive, selective, and humidity-independent gas detection // ACS applied materials & interfaces. 2018. Vol. 10(33). P. 27858–27867.
16. Ivanov A. N., Kuzin Y. I., Evtugyn G. A. SPR sensor based on polyelectrolyte complexes with DNA inclusion // Sensors and Actuators B: chemical. 2019. Vol. 281. P. 574–581.
17. Andriianova A. N., Salikhov R. B., Latypova L. R et al. The structural factors affecting the sensory properties of polyaniline derivatives // Sustainable Energy & Fuels. 2022. Vol. 6(14). P. 3435–3445.
18. Mustafin A. G., Latypova L. R., Andriianova A. N. et al. Synthesis and Physicochemical Properties of Poly (2-ethyl-3-methylindole) // Macromolecules. 2020. Vol. 53(18). P. 8050–8059.
19. Salikhov R. B., Mullagaliev I. N., Badretdinov B. R. et al. Effect of the morphology of films of polyaniline derivatives poly-2-[(2E)-1-methyl-2-butene-1-yl] aniline and poly-2-(cyclohex-2-en-1-yl) aniline on sensory sensitivity to humidity and ammonia vapors // Letters on materials. 2022. Vol. 12(4). P. 309–315.
20. Khuzin A. A., Tuktarov A. R., Venidiktova O. V. et al. Hybrid molecules based on fullerene C60 and dithienylethenes. Synthesis and photochromic properties. Optically controlled organic field-effect transistors // Photochemistry and Photobiology. 2022. Vol. 98(4). P. 815–822.
21. Salikhov R. B., Safargalin I. N., Badretdinov B. R. et al. Nanocomposite-based thin film carbon monoxide sensors // Petroleum Engineering. 2023. Vol. 21. No. 4. P. 154–165.
22. Yumalin T. T., Salikhov R. B., Abdrakhmanov V. Kh. et al. Wireless environmental quality monitoring system // Petroleum Engineering. 2023. Vol. 21. No. 3. P. 232–242.

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