

SURFACE MODIFICATION OF POLYMERS TO IMPART ANTISTATIC PROPERTIES

Alexandra ISAKOVA¹, Vladimir TVERSKOY², Andrey INDENBOM^{1,3}, Victor IVANOV¹,
Oxana GRIBKOVA¹, Aleksandr NEKRASOV¹

¹*Russian Academy of Sciences A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS,
Moscow, Russian Federation,*

Isakova_Aleks@list.ru, oxgribkova@gmail.com

²*Moscow Technological University, Institute of Fine Chemical Technologies of M. V. Lomonosov,
Moscow, Russian Federation*

³ *Moscow Institute of Physics and Technology (State University), Dolgoprudny,
Moscow Region, Russian Federation*

Abstract

Static electricity on the surface of dielectric polymers can be dangerous in various areas of human life. Antistatic agents reduce or eliminate accumulation of static electricity by creation a conductive layer on the polymer surface. The most known antistatic agents are surfactants. They increase surface conductivity by absorbing moisture from the air. But this effect is short-lived and depends on the temperature and air humidity. Modification of a thin surface layer of polymers by conductive polymer, e.g., polyaniline (PANI), is a promising method. In this work fragments of polyacrylic and polystyrenesulfonic acids were grafted onto the surface of polyethylene films before the synthesis of PANi. This technique allows to create long lasting antistatic effect. Synthesis of PANi on the modified polyethylene films was studied by optical spectroscopy. The autocatalytic character of this process was proved. Optimal synthesis conditions for obtaining homogeneous films were defined. The electrical characteristics of the obtained materials were measured. Thus, the possibility of synthesizing PANi on polyethylene films with incorporated fragments of sulfonated polystyrene or with its mixture with acrylic acid was demonstrated. The minimum sheet resistance of the modified PE film was achieved with the maximum content of styrene sulfonic acid. It was shown that the proposed technique is promising for the creation of antistatic coatings of polymers. The proposed method is also suitable for application of antistatic coatings on the inner surface of polymer containers of complex shape.

Keywords: Polyaniline, polyethylene, antistatic properties, conductive polymers

1. INTRODUCTION

The occurrence of static electricity on the surface of dielectric polymers can be dangerous in various areas of human life. The resulting electrical discharge can cause combustion or explosion of flammable substances, lead to breakdown of various electronic devices, etc. Static charge on polymer surface can be significantly reduced. Depending on the conditions and the environment of use, two methods to reduce or eliminate accumulation of static electricity can be distinguished. The first method is to create a surface hydrophilic layer that promotes the emergence of a thin film of water under natural moisture conditions and temperatures above 0°C. Various kinds of surfactants are commonly used as such substances, including nitrogen-containing compounds (long-chain amines, amides or quaternary ammonium salts), sulfonic acids, polyols and their derivatives, etc. The second method consists in introducing into the surface layer various electroconductive additives (nanoparticles, carbon materials, etc.) that provide the electrical conductivity of the surface layer irrespective of atmospheric humidity and temperature. Despite the wide choice of antistatic additives, their introduction can lead to a deterioration in the physico-mechanical properties of the polymers being modified. Many additives can not be used to modify industrially important polyolefins (thermoplastics - polyethylene, polypropylene, polybutylene), and the antistatic effect persists for a short time. In addition, some antistatic agents are difficult to use at low temperature and low relative humidity (for example, in the conditions of the

Far North and the Arctic). In our opinion, the most promising method of imparting antistatic properties to polymers is their modification with special additives that, after chemical interaction with the base polymer, create a thin layer of new electrically conductive polymeric material. In this case, the electrostatic properties not only do not depend on the environmental conditions, but are also most resistant to various external influences.

A promising polymer for use as an antistatic agent is polyaniline (PANI). It is easily synthesized, resistant to oxidation in air, and has sufficient electrical conductivity. A method for synthesizing PANi in hydrochloric acid in a matrix of porous polyethylene was described [1]. The authors showed that this method leads to the production of conductive composites. The disadvantage of this synthesis is the influence of the polyethylene film relief on the uniformity of the PANi distribution. We have previously shown that the use of polysulfonic acids together with polyaniline allows to obtain coatings with improved properties [2,3]. Complexes of PANi with polysulfonic acids contain hydrophilic fragments, which gives the modified material additional electrostatic properties. However, such complexes are soluble in water and form easily removable films on the surface of polymers (for example, polyethylene). More stable coatings of this type could be obtained by synthesizing PANi on polyethylene with grafted fragments of polysulfonic acids.

2. MATERIALS AND METHODS

We used polyethylene (PE) films with grafted polystyrene sulfonic acid fragments (PE-PSSA) and PE films with grafted fragments of copolymer of acrylic and styrene sulfonic acids (PE-ASA). The main characteristics of the films are shown in **Table 1**.

Table 1 Physico-chemical properties of PE films

Film thickness, μm	Fraction of grafting, $\Delta p(\%)$	
	[St]	[acrylic acid]
50	93	-
50	39	-
50	28	-
22	17.8	58.7
16	13.6	57.0
14	16.8	56.9

Ammonium persulfate (reagent grade) employed as an oxidizer was used as received. Aniline (reagent grade) was distilled in vacuum in nitrogen atmosphere, and a fraction with a boiling temperature of 82-84°C (20 mmHg) was collected. Polymerization experiments were performed with the as-distilled product ($n_d^{20} = 1.583$)

Polymerization of aniline on PE-PSSA and PE-ASA films was carried out at a temperature of 25 ° C. Few days before the synthesis, the PE-ASA was transferred from Na⁺ to the H⁺-form by placing in a 1M HCl solution, and then washed with water and dried in air.

For PANi synthesis, PE-PSSA and PE-ASA films were left for a few days in 0.1 M aniline solution, washed with water and air-dried. Thus, the aniline-treated film was transferred to a PSA solution for the aniline polymerization. After polymerization, the films were washed with water and dried.

For comparison, the oxidative polymerization of aniline in an aqueous solution of polystyrene sulfonic acid (PSSA, Aldrich Mw ~ 7 × 10⁴) was carried out. The molar ratio of aniline to oxidizer was 1:1 mol/mol, the ratio of aniline to a sulfonic group of PSSA was 1:2 mol/g-eq. sulfonic groups. Aniline concentration was equal to 0.003 M. [3].

Spectral measurements in the visible region of the spectrum during the matrix synthesis were carried out using a high-speed scanning single-beam spectrophotometer Avantes 2048, equipped with flexible light guides. Instrument control, data acquisition and processing were done by a computer equipped with the appropriate software. The spectral range of was 300 to 900 nm, the recording time was 100-150 ms, which made it possible to neglect the change in the shape of the spectrum during its recording. The spectra of the modified films in the 250-3200 nm region were recorded using a two-beam spectrophotometer "Shimadzu UV-3101PC".

The sheet resistance was measured using digital ohmmeter by applying two narrow contacts made of silver conductive paste onto 2 opposite edges of a rectangular sample (1 cm X 1 cm) of the modified films.

3. RESULTS AND DISCUSSION

3.1. Synthesis of polyaniline in polyethylene films with grafted polystyrene sulfonic acid

The changes in the optical absorption spectra during the synthesis of PANi on the films of PE-PSSA (a) and in the solution of polystyrene sulfonic acid-PSSA (b) are shown in **Figure 1**. Synthesis of PANi on PE-PSSA reveals some similarity to the synthesis of PANi in the PSSA solution. Thus, during the synthesis of PANi on PE-PSSA, as well as in the case of PANi synthesis in the PSSA solution, the growth of absorption bands attributed to cation-radical (430 nm) and quinoneimine (600 nm) forms is observed. In the future, a shift of the absorption maximum to the long-wavelength region around 750 nm, which is caused by the formation of localized polarons is observed. Changes in the absorption spectra during the synthesis on PE-PSSA films are less pronounced, in comparison with the PANi synthesis in the PSSA solution. This may be due to several factors, including the spatial distribution of aniline and its orientation over the surface/inside the film, the presence of a crystalline phase of polyethylene, the formation of a surface layer of PANi contributing to delocalization of oxidized fragments, and others.

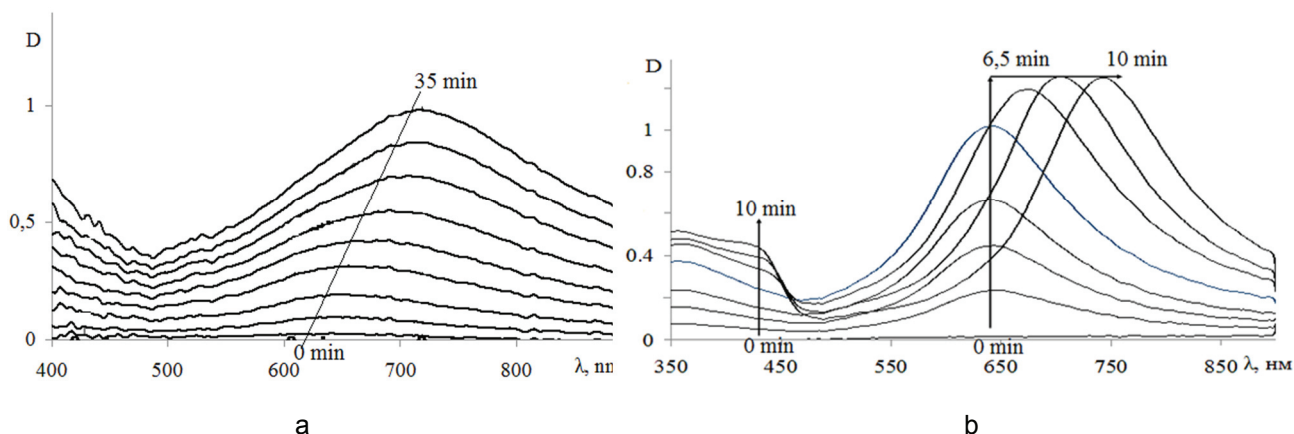


Figure 1 Spectrum changes during PANi synthesis on PE-PSSA films (a) and in the presence of PSSA (b). The proportion of grafted PS in case (a) is 39 %. The reagent ratio for (a): nAn: n PSSA = 1: 2, nAn: nOx = 1: 1; for (b): nAn: nOx = 1: 1

The polymerization of PANi on PE-PSSA has an autocatalytic character, as evidenced by the S-shaped kinetic curves (**Figure 2**). It should be noted that the rate of synthesis is influenced by the ratio of reagents. Thus, rapid oxidation of aniline (the case with an excess of oxidizer, nAn / nOx = 1/2) leads to the acceleration of polymerization process by approximately a factor of 2.

Figure 3 shows the PANi polaron absorbance changes depending on the proportion of grafted polystyrene. It can be seen that the growth rate (slope of the linear part of the curve) reaches maximum in the interval 28-39 % and then does not change up to 93 %. The induction period of polymerization is hard to be determined at the polystyrene concentration of $\Delta p = 28$ %. With a further increase in the proportion of grafted polystyrene

from 39 to 93 % (i.e. 2.38 times), the induction period increases from about 20 to 47 min (2.35 times), i.e. approximately proportionally to the increase of fraction of grafted polystyrene.

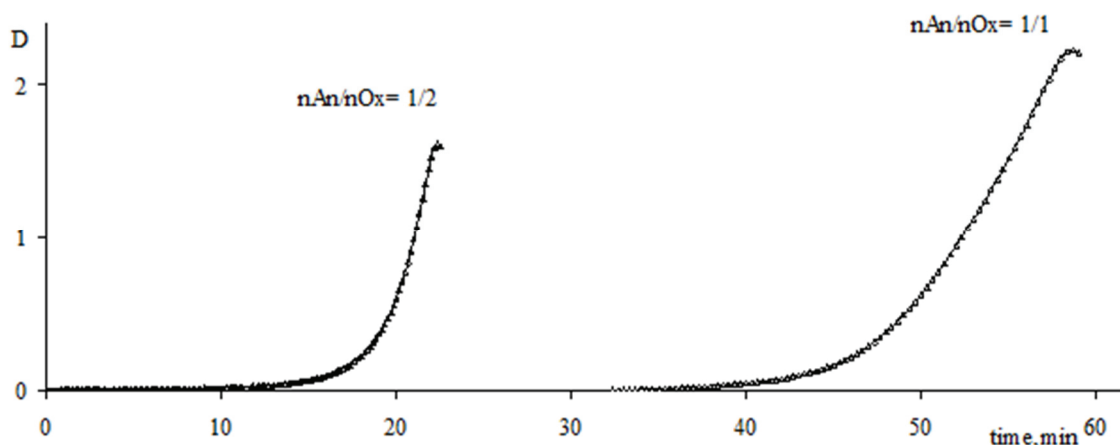


Figure 2 Absorbance changes at 750 nm (polaron absorption) during PANi synthesis on PE-PSSA ($\Delta p=39\%$), depending on the ratio of reagents

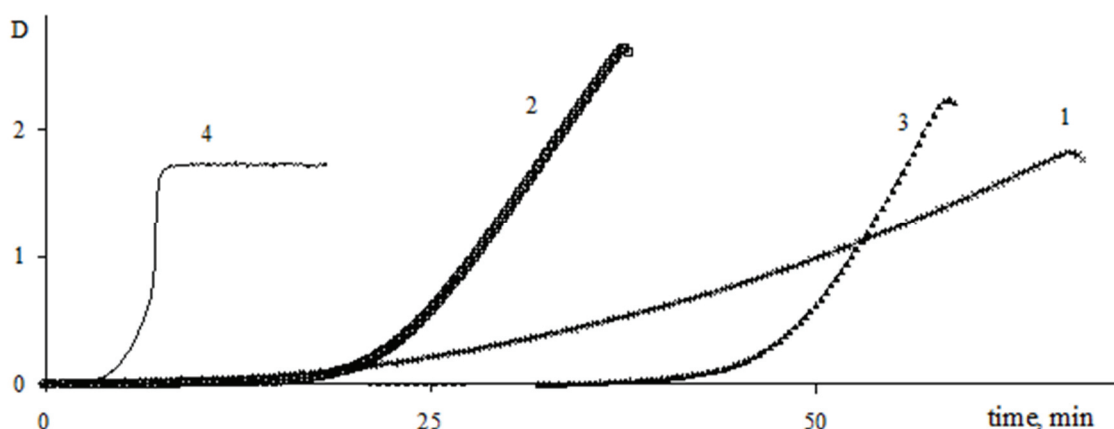


Figure 3 Change in the absorption at 750 nm (polaron form of PANi) during synthesis in PE-PSSA films depending on the proportion of grafted polystyrene. Curve 1 - PANi-PE-PSSA ($\Delta p=28\%$); 2- PANi-PE-PSSA ($\Delta p=39\%$), 3- PANi - PE- PSSA ($\Delta p=93\%$), 4- PANi-PSSA (synthesis of PANi in the solution of PSSA for comparison).

For PE films with grafted fragments of the copolymer of acrylic (AA) and styrene sulfonic (SSA) acids the effect was studied of total proportion of grafted acids and the ratio of the AA and SSA on the shape of final electronic absorption spectra of the films at a given PSA concentration.

The change in the composition of the film with a partial replacement of SSA by AA groups led to a significant slowdown in the synthesis of PANi (the synthesis occurred for a day or more). Analysis of the spectra of optical absorption of grafted copolymers (**Figure 4**) shows the presence of characteristic absorption bands of PANI.

The position of the maximum in the region of localized polarons (750 nm) shows that the optimum is PE-ASA with a grafting degree of 70.6 %, including 57.0 % AA and 13.6 % SSA. Differences in the characteristic absorption spectra for PE-ASA films with $\Delta p = 70.6$ and $\Delta p = 76.5$ (58.7 % AA+ 17.8 % SSA) indicate that it is necessary to select a specific concentration of PSA for each film to avoid the formation of short oligomers, as in the case of a film with $\Delta p = 73.7\%$ (56.9 % AA+ 16.8 % SSA)

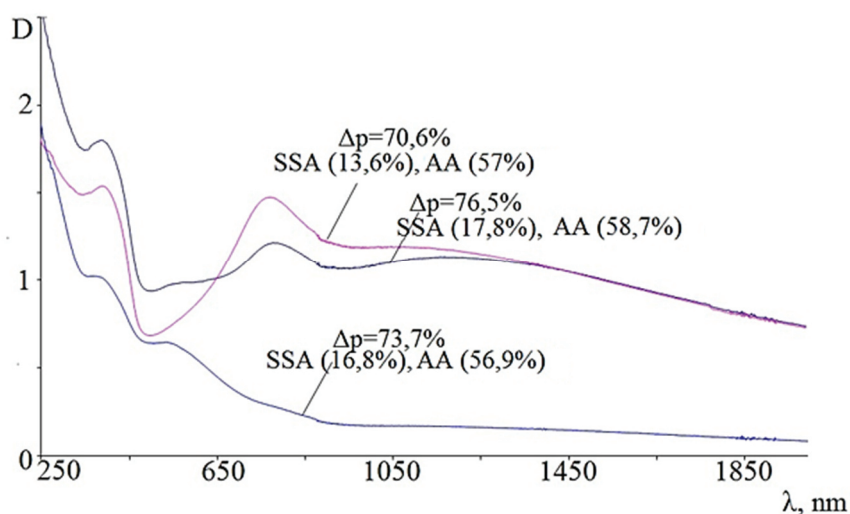


Figure 4 Electronic absorption spectra of modified PE-ASA films with different ratios of AA and SSA groups in the graft copolymer at a total PSA concentration of 5.7 mM.

The sheet resistance of polyaniline-modified PE-PSSA films was measured. The results, presented in **Table 2**, indicate successful modification of these films by PANi. It can be seen that the film with the maximum degree of polystyrene grafting has the lowest sheet resistance. Unfortunately, the sheet resistance of PANi-PE-ASA films could not be measured despite the electronic absorption spectrum proper to PANi. Apparently, this is due to irregular distribution of the conductive areas of PANi phase in the polyethylene film. In particular, the frequency and regularity of the arrangement of the sulfonic groups, the distribution of the crystalline and amorphous phase in polyethylene can affect the uniformity of the distribution.

Table 2 Surface resistance of modified PE-PSSA*

Films	Sheet resistance, MOM/□
PANi-PE-PSSA 93 %	0.08
PANi-PE-PSSA 39 %	3.6
PANi-PE-PSSA 28 %	5

*The measurement temperature is 22 °C, relative air humidity is 45 %.

Thus, the possibility of synthesizing PANi on polyethylene films with incorporated fragments of sulfonated polystyrene or with its mixture with polyacrylic acid was demonstrated. The minimum sheet resistance of the modified PE film was achieved with the maximum content of styrene sulfonic acid. It was shown that the proposed technique is promising for the creation of antistatic coatings of polymers.

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