

# MULTILAYER TEXTILE MATERIAL COATED WITH NANOPARTICLES OF ELECTROCONDUCTIVE POLYANILINE

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**Abstract:** *The article is devoted to the study of self-organization processes of conductive layers of polyaniline nanoparticles in heterocoagulation on polyamide textile material. It is shown that the particle size distribution of the polyaniline dispersion has a normal distribution with a maximum of 150 nm. It is found that the electrical resistance of the multilayer textile material with a polyaniline coating obtained by method of the layer-by-layer depends on the number of layers and the type of the surfactants. The process of a heterocoagulation of polyaniline particles on the polyamide textile material is described by the quasi-chemical reaction model.*

**Keywords:** multilayer textile materials, polyaniline, heterocoagulation, self-organization, nanoparticles.

## 1 INTRODUCTION

Electroconductive nanostructured materials not containing metals are of interest in several areas of their use [1]. This is possible due to the self-organization of nanoparticles formation of different structures. The character of formed structures, the ability to control their formation is of interest as from the scientific [2-4], and from a practical point of view because of the influence on the properties of nanosystems. The possibility of obtaining electroconductive fibers by deposition of nanoparticle layers of polyaniline on the surface of nonconductive fabric by heterocoagulation mechanism (the term firstly was used in [5]) is demonstrated in [56].

The use of deposition of nanoparticles that provide special properties of textile material as a substrate is important for many reasons. Textile material provides a much larger surface area than a smooth surface, which is extremely important for their use. The particle size applied to the surface of the textile material should be smaller than for particles forming a conventional coating of the solution. The nanoparticles deposited on the textile material can be used as a substrate for the subsequent formation of the next layer of nanoparticles by the layer-by-layer method.

The saturation of nanoparticles of a particular substrate can be regulated by changes in physical parameters (pressure, temperature) or changes in chemical composition [2]. The result of these new synthetic methods is the development and synthesis of a much larger range of polymers with the possibility of self-organization. This is the essence of the new approach and the key aim

of nanotechnology is to form a highly organized structure [1].

The purpose of this work is: 1) to characterize the process of self-organization of the electrically conductive layer of nanoparticles in the process of heterocoagulation on the example of polyamide textile material – nanosize polyaniline; 2) to obtain multilayer textile materials with electroconductive properties.

## 2 EXPERIMENTAL

Polyamide (PA) yarn with a linear density of 15.6 tex was used for the study. Knitted PA fabric obtained from this polyamide yarns was used as a textile substrate for the experiments.

Conductive textile material was prepared as follows. Aniline is subjected to oxidation in a processing solution at a certain bath module in the presence of surfactant (SAS) and textile material.

Non-ionic OS-20 (NSAS), cationic alkamon OS-2 (CSAS) and anionic sulfonol (ASAS) were used as surfactants. Ammonium peroxydisulphate was used as an oxidizer. Equivalent oxidizer/aniline ratio was 1:1.3. The treatment process lasted for 15-30 min at the temperature of 18-22°C. Thus, nanodispersed aniline was formed on the polyamide textile by heterocoagulation mechanism [5, 6]. Next, the conductive textile material was washed with distilled water and dried. The specific electrical resistance of the processed textile material was determined by a two-zone compensating method which allows determining both bulk and surface resistance ( $R$ ) using ohmmeter.

The particle size distribution was determined using Mastersizer 2000 (Malvern, UK) with appropriate software which includes the Mie theory. Using the device allows to obtain the size distribution curves as a function of the numerical fraction of particles according to their size.

The surface morphology of the treated polyamide materials was characterized by scanning electron microscopy (SEM) MIRA 3 LMU, Tescan with a resolution of  $\pm 1$  nm and energy-dispersive spectroscopy (EDX) with chemical analysis Oxford X – MAX 80 mm<sup>2</sup> with appliance uncertainty  $\pm 1\%$ .

The amount of polyaniline on the textile substrate was determined by photocolometry. The concentration of polyaniline in the bath is assumed to be proportional to the concentration of aniline before synthesis (characterized by optical density  $D$ ).

### 3 RESULTS AND DISCUSSION

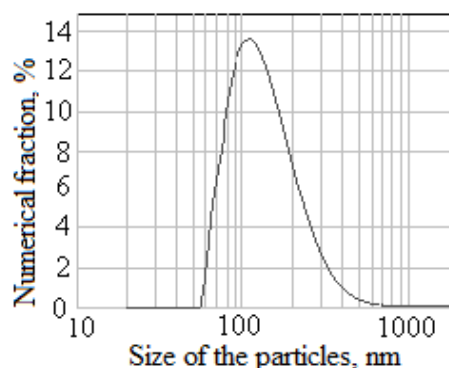
#### 3.1 The self-organization of the conductive nanoparticles on the textile material

Polymers capable of self-organization, on the one hand, can form stable nanostructures, on the other – easily change the form of self-organization, even under the influence of external factors [7, 8]. Usually, the synthesis of nanostructured polymers is carried out in the presence of hard or soft (micelles, surfactant solutions, polymer gels, emulsions) template. In our case, the controlled synthesis of nanostructured polyaniline is carried out in the presence of surfactants.

It was established that the deposition of polyaniline particles on polyamide textile material is carried out from the nanosystem: dispersion of polyaniline nanoparticles in the treatment bath. Figure 1 shows the distribution curve of the particle size of polyaniline dispersion in a numerical proportion of particles depending on their size.

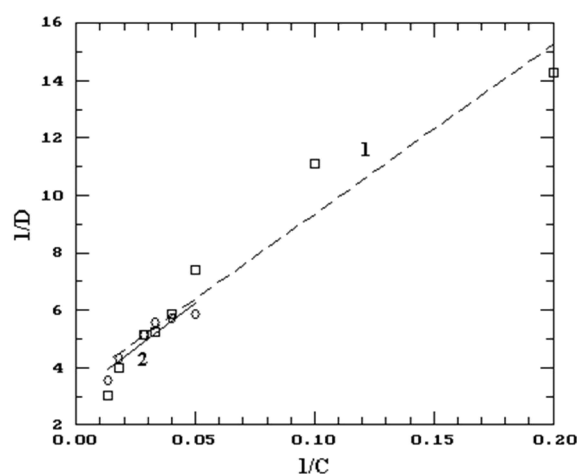
According to the formal features, the nanoparticles are particles which particle size is less than 100 nm. In fact, there is a more correct approach: a particle belongs to a colloidal particle (nanoparticles), if the reduction of size affects the achievement of new properties.

Nanosystems usually have wide size distribution of particles: the multiple dispersed or reversible process of aggregation is realized by a lognormal particle size distribution. In many cases, a set of particles with an average size between 100 and 1000 nm is also considered as nanoparticles, because part of the particle size is within the range less than 100 nm and a part of the particles can be as dynamic agglomerates consisting from particles smaller than 100 nm. Therefore, the investigated dispersion studied in this work was found as nanosystem.



**Figure 1** Differential curve of polyaniline particles sizes distribution

Figure 2 shows the dependence of the optical density  $D$  of the solutions of polyamide materials on the concentration of aniline  $C$  in a presence of OS-20 preparation (1) and alkamon OS-2 (2), in the coordinates of Langmuir equation [5]. Langmuir equation is derived and is used to describe of the adsorption, for example, the molecules on the surface as a monomolecular layer [9]. It is well known [7, 8] that the deposition of nanoparticles on the surface can be in the form of monolayers by self-organization and multilayer coatings [10].



**Figure 2** The dependence of the optical density  $D$  of the solutions of treated polyamide materials on the concentration of aniline  $C$  in presence of OS-20 (1) and alkamon OS-2 (2), in the coordinates of Langmuir equation

The balance between the process of peptization and heterocoagulation (sorption - desorption) of colloidal particles on the surface, in the form of a quasi-chemical reversible reaction (possibly at a relatively small depth of the second minimum in the area of potential energy of interaction between particles), is presented. The using of reversible quasi-chemical reactions is generally accepted in the study of molecular adsorption processes [9].

The equilibrium between the surface "active" centers  $A$ , the nanoparticles of dispersion  $NP$  and temporarily settled on the surface of the nanoparticles  $A \cdot NP$  is determined by quasi-chemical equation of reversible reaction:



If the maximum of concentration  $A$  (the active sites of surface), with the potential to form compounds with the nanoparticles in the 1: 1 ratio, is  $C_{A,\infty}$ , the concentration of active centers remaining free is determined as value  $(C_{A,\infty} - C_{A \cdot NP})$ . The equilibrium constant for reaction (1) at a concentration of nanoparticles in the dispersion  $C_{NP}$  is:

$$K = \frac{C_{A \cdot NP}}{C_{NP}(C_{A,\infty} - C_{A \cdot NP})} \quad (2)$$

The equation (2) at the coordinates  $1/C_{A \cdot NP} = f(1/C_{NP})$  is converted into a linear equation:

$$\frac{1}{C_{A \cdot NP}} = \frac{1}{C_{A,\infty}} + \frac{1}{KC_{A,\infty}} \cdot \frac{1}{C_{NP}} \quad (3)$$

Analysis of the equations (2) and (3) shows that the formation of particles' monolayer of the dispersed phase in the reverse process of heterocoagulation of the isotherm sorption equation has similar shape as the Langmuir monomolecular adsorption equation on the interface. This equation is characteristic for monolayer adsorption [9]. In the process of heterocoagulation of nanoparticles on the surface of textile material, a compound with a limited lifetime is formed (reverse process). This creates the conditions for the process of self-organization with the emergence of an orderly structure.

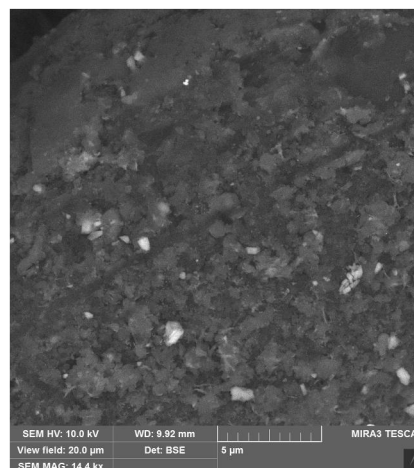
The polyamide textile material (TM) in acidic media ( $\text{pH} < 5$ ) has a positive surface charge, polyaniline nanoparticles synthesized in the presence of anionic surfactant – sulfonol have a negative charge as a result of heterocoagulation and in this case, interactions between particles with opposite charges occur according to the classical mechanism [5].

The electrostatic interaction of the particles in this case is sufficiently intense to the irreversibility of the process. As a result of the use of sulfonol stabilizer, the dependence of the amount of polyaniline on the fabrics and the concentration of polyaniline in the bath cannot be described by an equation identical to the Langmuir equation. The absence of restructuring possibilities of the deposited layer can apparently lead to a layered structure similar to fractal structure in the limited aggregation diffusion.

It is determined that the main mechanism of formation of polyaniline coating in the process of aniline oxidation in the presence of surfactants is heterocoagulation of polyaniline nanoparticles on the surface of textile material. In this regard, it is necessary to establish the possibility of achieving self-organization of nanoparticles

by the layer-by-layer method [11–13] to obtain multilayer textile materials with electrically conductive properties. The formation of nanostructured surface layers provides multi-stage synthesis of polyaniline nanoparticles with a change in the surfactant type and, as a consequence, with a change in the surface charge of the polyaniline nanoparticles. It is interesting to study the effect of the process of multistage heterocoagulation of polyaniline nanoparticles on the conductive properties of polyamide textile material.

The results of morphological studies indicate the uniform deposition of polyaniline particles on the surface of textile materials (Figure 3). Perhaps, this is due to the increased affinity of the organic substrate and the organic disperse phase. The proposed method for polyaniline synthesis ensures the formation of polyaniline particles with bimodal size distribution, namely, isomorphic particles of polyaniline of small size ( $87 \pm 15$  nm) and anisomorphic particles in the form of plates with an average linear size of 496 nm – 180 nm and a thickness of about 90 nm.



**Figure 3** The SEM images of the treated polyamide materials with polyaniline nanoparticles

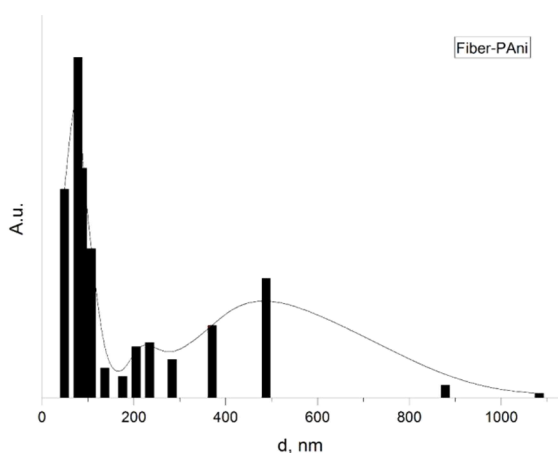
The relatively high content of nitrogen in the surface layer of the composite (experimentally 6.8%, theoretically 15.3%), obtained from the results of elemental analysis by the method of energy-dispersion spectroscopy, confirms the high degree of coating the surface of the textile material with particles of polyaniline.

Small-size particles also practically do not form aggregates, as evidenced by their distribution on the histogram and low polydispersity (Figure 4).

When the ratio between the aggregation and sorption stability of micelles with solubilized polyaniline changes, the particles, which are stabilized by adsorption of ASAS, cause the transition to the heterocoagulation mechanism

of treatment with nanostructured polyaniline instead of possible absorption (dissolution) of polyamide. Management of sorption stability is also required for other processing processes that occur in different ways of nanoscale processing in order to obtain special properties of textile materials.

Thus, the distribution of the polyaniline particles (conjugated organic polymer), synthesized in the presence of ASAS according to its sizes in the initial dispersion (Figure 1), shows the synthesis of nanoparticles in the treatment bath and the distribution of polyaniline particles on the polyamide textile material (Figures 3 and 4). It also shows the detection of sorption affinity of the particles of the dispersed phase to the surface of the polyamide textile material.



**Figure 4** The histogram of distribution of the polyaniline particles in sizes on the textile material

However, high frictional properties are evident from the deposited polyaniline nanoparticles on the surface of PA textile material by the heterocoagulation mechanism.

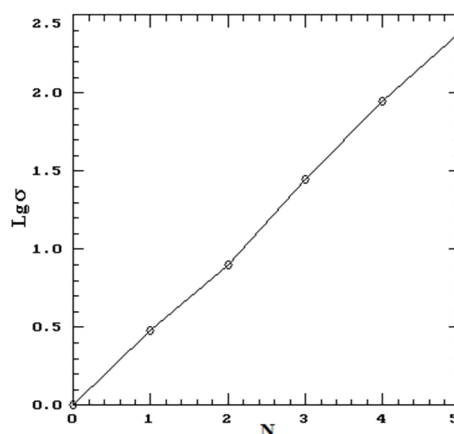
It should be noted that the surface layer of polyaniline forms the plates of polyaniline. The formation of aggregates of polyaniline particles, which is associated with the conditions of their synthesis when using surfactants, is uncharacteristic. As a result, a layer of polyaniline on the surface of a textile material consists of a monolayer of planar particles of polyaniline, whose thickness is about 90 nm.

Layer deposition (layer-by-layer) of polyelectrolytes, proteins, colloidal particles, films on a substrate is well known [7, 8, 10-13]. Method of layer-by-layer may be applied to increase the electrical conductivity of essentially textile composite material – electrically conductive polymer layer on the surface. In the method of layer-by-layer of like or different charges and the surface of the deposited particles of different nature plays an important role [10–13].

### 3.2 The obtaining of the multilayer textile materials with electroconductive properties

In this work, the multistage synthesis of polyaniline conductive layer using at each stage of the dispersions stabilized by surfactants, form micelles with a charge opposite to the charge of the surface of the textile (Figure 5) was carried out.

A multilayer coating on the surface of the textile material was obtained using the layer-by-layer method under the condition of changing the surfactant type. This contributes to the increase of the specific electrical conductivity of TM by an order of magnitude from  $1 \times 10^2$  S/m to  $1 \times 10^3$  S/m (Figure 5). The linear dependence of the electrical conductivity of the treated TM on the number of stages of polyaniline deposition in the presence of different types of surfactants was obtained. This indicates that differently charged polyaniline nanoparticles, stabilized alternately ASAS and CSAS, form electrically conductive layers. This is done due to the implementation of the mechanism of self-organization of polyaniline nanoparticles by forming a multilayer coating on the surface of polyamide TM with a stable ordered nanostructure.

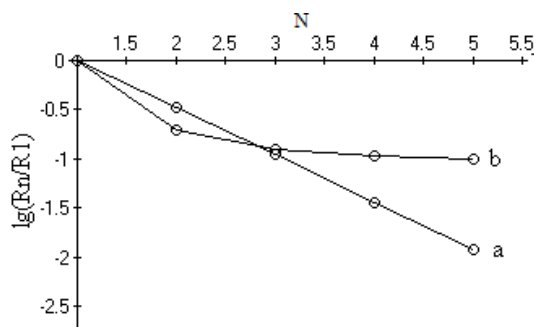


**Figure 5** Dependence of the specific electrical conductivity of TM ( $\sigma$ ) on the number of stages of deposition of nanoparticles (N) with a change in the type of surfactant (SAS)

Figure 6a shows the change of electrical resistance of the textile material depending on number of stages during realization of deposition of polyaniline multistage treatment process in the synthesis of polyaniline. Each subsequent stage of the deposition was carried out with the change of the type of surfactant, and as a consequence, the change of the charge of polyaniline nanoparticles.

A process of classical heterocoagulation [5, 6] was carried out during the deposition process when the process of heterocoagulation participate oppositely charged surface (in this case the surface

of the particles of polyaniline and the textile material). With increasing number of deposited layers, the electrical resistance is decreasing significantly (two orders). The character of the electrostatic interaction assures the regular decrease of electrical resistance with each subsequent layer (by 3 times).



**Figure 6** The resistance change of the textile material  $R$  on the amount of stages of deposition of polyaniline  $N$ : a) with the change of the SAS type; b) in the presence of ASAS;  $R_n / R_1$  is the ratio of the polyaniline resistance in  $N$  layers deposited ( $R_n$ ) successively to the resistance in the same layer ( $R_1$ )

The dependence of the electric resistance on the number of deposition steps of polyaniline nanoparticles, in the implementation of the multistage process of treatment in the synthesis of polyaniline under conditions of use in each step of the same SAS, is another character.

Figure 6b is characterized by the change in resistance when applied to 5 layers of polyaniline in the presence of anionic surfactant – sulfonol. Constancy charge polyaniline particles leads to an efficient adsorption of the first layer, followed by deceleration resistance decrease with increasing number of layers (and, presumably, with progressive decrease in the quantity of sorbed polyaniline). This situation is similar to the adsorption BET [9] – the interaction energy of the first layer of adsorbed molecules sufficiently greater than the energy of interaction between each successive layer.

#### 4 CONCLUSION

Thus, the example system of polyamide textile material – polyaniline shows that the change in the balance of forces of interaction with the surface of the nanoparticles by changing conditions of heterocoagulation (deposition) may be used for the various structures in the process of self-organization of nanoparticles and, consequently, nanosystems with different properties. The resulting conductive textile material is proposed to be used as a textile neutralizer. A modern highly efficient way of removing static charges of electricity in the finishing industry has been developed. Textile neutralizer is environmentally friendly, inexpensive

and easy to use. It is recommended to use electrically conductive textile materials as technical special purpose textiles in the production of clothing for protection against the influence of powerful electromagnetic fields, clothing with antistatic properties, heating of clothing, antistatic and reinforcing additives to fabrics and polymers.

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