

SORPTION OF NANOPARTICLES AT A LAYER DEPOSITION

The article is dedicated to the study of self-organization processes of conductive layer of polyaniline nanoparticles in heterocoagulation on polyamide fiber. It is shown that the particle size distribution of polyaniline dispersion obtained by the oxidative condensation of aniline is normal with a maximum of 150 nm. It is found out that the resistance of the multilayer fibrous material with a polyaniline coating obtained layer-by-layer depends on the number of layers and the type of the surfactants. The process of heterocoagulation of polyaniline particles on the polyamide fiber is described by the quasi-chemical reaction model. It has been shown that in these conditions, the structures with a limited lifetime and with following self-organization emerge.

Keywords: conductive fiber materials, polyaniline, heterocoagulation, self-organization of nanoparticles.

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. In [5] demonstrated the possibility of obtaining electroconductive fibers by deposition on the surface of the mechanism heterocoagulation (the term is used for the [6; 7]) layer of nanoparticles of polyaniline. The purpose of this work: to characterize the process of self-conductive layer of nanoparticles in the process of heterocoagulation on the example of the system a polyamide fiber – polyaniline nanosize.

Using the deposition of nanoparticles that provide special properties of fibrous material on a substrate is important for many reasons: they provide significantly more surface area than a flat surface that is extremely important for their use; requirements for particles deposited on a surface smaller than conventional coating from solution, and the particles themselves can be used as lining up to follow capsule formation [2]. There are two main approaches for nanoparticles, which in scientific language called as “upward” and “downward”. “Upward” approach covers all methods in which a new phase nanoparticles formed at the interface of homogeneous glut “native” phase.

Saturation can be regulated by changes of physical parameters (pressure, temperature) or changes in the chemical composition. “Downward” approach includes various methods of grinding.

The result of these new synthetic methods is to design and synthesize a much larger range of polymers with the ability to self-organize. This gives an opportunity consider projects complex

building blocks such as functional copolymers that can be connected to large objects, such as block copolymers micelles. If these micelles can organize themselves in a higher level of microscopic structure, the functionality of the original copolymer can be transferred to a higher level of functional unit. This is the essence of the new approach and a key aim nanotechnology – to form highly organized structure [1].

Polymers that are capable of self-organization, on the one hand, can be are ordered to form stable nanostructures on the other – to easily change the form of self even when there is change of external parameters. Usually, the synthesis of nanostructured polymers 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 carried out in the presence of surfactants.

As the sorption of particles of polyaniline the surface polyamide fibrous material is carried out of nanosystems: polyaniline nanoparticle dispersions in a dyeing bath [4] i determined that the main mechanism of formation of polyaniline dyeing during the oxidation of aniline is heterocoagulation polyaniline nanoparticles on the surface of the fibrous material, it is necessary to establish the possibility of achieving self through complex nanostructured surface layer to the application layer (layer by layer), which provides a multistage synthesis of nanoparticles of polyaniline and study of its influence on the properties of colored polyamide fiber material.

The obtaining distribution curve of the particle size of polyaniline dispersion in a numerical proportion of particles depending on their size.

To the nanoparticles attributed on formal grounds a particle size of one of them, less than 100 nm [8].

In fact, the is more faithful approach of S. Lipatov: the particle refers to the colloidal particle (to nanoparticles), if decrease in the size appears of the qualitatively new properties [9].

At the nanosystems is possible wide size distribution: the multiple dispersed or reversible process of aggregation is realized lognormal particle size distribution [10]. In many cases, a set of particles with an average size of between 100 and 1000 nm is also considered as nanoparticles, as part of the particle size is within range of less than 100 nm, and a part of the particles can be dynamic agglomerates consisting of particles smaller than 100 nm. Therefore, the investigated in the work the dispersion of polyaniline are regarded as nanosystems.

The fig. 1 shows the dependence of the optical density of the solutions of polyamide materials, dyeing polyaniline (D), on the concentration of aniline (C) in a presence: 1) preparation OS-20 and 2) alkamon OS-2 is in the coordinates of Langmuir equation [5].

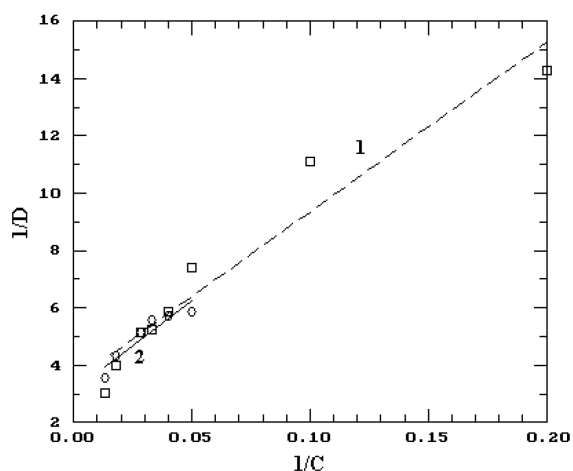
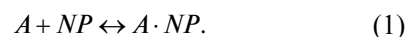


Fig. 1. The dependence of the optical density of the solutions of polyamide materials, dyeing by polyaniline (D), on the concentration of aniline (C) in a presence: 1) preparation OS-20 and 2) alkamon OS-2 is in the coordinates of Langmuir equation

Langmuir equation is derived and is used to describe of the adsorption, for example, the molecules on the surface as a monomolecular layer [11]. It is well known [12; 13] that the deposition of nanoparticles on the surface may be in the form of monolayers by self-organization, in particular, can be synthesized on monolayers polyaniline films [14].

We represent a balance between the process of peptization and heterocoagulation (sorption – desorption) of the colloidal particles on the surface in the form of quasi-chemical reversible reaction (possibly at a sufficiently shallow depth second minimum on the plot of the potential energy of the

interaction of the distance between particles [7; 15]). Using a reversible quasi-chemical reactions generally accepted in the study of molecular adsorption processes [11]. 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 reversible reaction:



If the maximum 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 value $(C_{A,\infty} - C_{A \cdot NP})$. At a concentration of nanoparticles in the dispersion C_{NP} of the equilibrium constant for reaction (1):

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

At the coordinates $1/C_{A \cdot NP} = f(1/C_{NP})$, the equation (2) 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 a monolayer of the particles of the dispersed phase in a reversible process of heterocoagulation sorption isotherm equation similar in form to the Langmuir monomolecular adsorption at the interface. The coincidence of equations for monolayer adsorption [11; 15], to dissolve with the formation of solvates [16], for heterocoagulation of nanoparticles on the surface of the fiber, due to the realization of a situation where a compound is formed with a limited by the lifetime of (reversible process), which creates the conditions for the process of self-organization with the creation of an ordered structure.

The polyamide fiber in acidic media ($\text{pH} < 5$) has a positive surface charge [17], nanoparticles polyaniline synthesized in the presence of anionic surfactant – sulfonol have a negative charge as a result heterocoagulation in this case proceeds according to the classical mechanism [6] as interaction of particles with the opposite charge.

The electrostatic interaction of the particles in this case is sufficiently intense to the irreversibility of the process. As a result, when used as a stabilizer sulfonol dependence of the amount of dye on the fiber concentration of polyaniline in the bath cannot be described by an equation identical in form to the Langmuir equation. The absence of restructuring

possibilities of the deposited layer, apparently, can lead to a layer structure similar fractal structure in the aggregation diffusion limited.

It is known layer deposition (layer-by-layer) polyelectrolytes, proteins, colloidal particles on a substrate [12–14; 18]. Method of layer-by-layer may be applied to increase the electrical conductivity of essentially fiber 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 [12–14; 18]. In the work was carried out multistage synthesis of aniline 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 fiber material.

Fig. 2, *a* shows the change in resistance of the fibrous material from the number of stages at realization the deposition of polyaniline multistage dyeing 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 of nanoparticles.

Thus, during the deposition process was carried out a process of classical heterocoagulation [6; 7], when the process heterocoagulation participate oppositely charged surface (in this case the surface of the particles of polyaniline and the fibrous material) With an increasing number deposited layers significantly changes the resistance of material (two orders). The character of the electrostatic interaction assures regularity decrease in resistance with each subsequent layer (by 3 times). Another character is the dependence of the resistance of the fiber material the number of steps

of deposition of polyaniline in the implementation of the multistage process of dyeing in the synthesis of polyaniline under conditions of use in each step of the same surfactant.

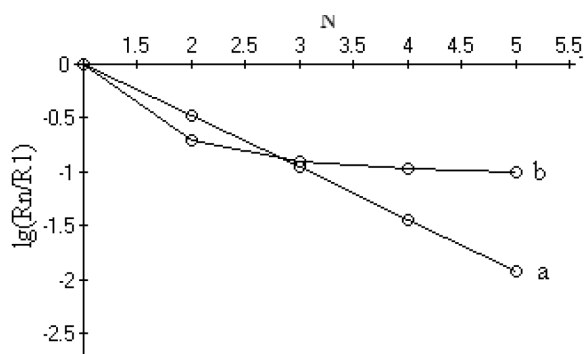


Fig. 2. The resistance change of the fibrous material on the amount of stages of deposition of polyaniline at realization of the multistage process of dyeing in the synthesis of polyaniline. R_n / R_1 – the ratio of the resistance of polyaniline in N layers deposited successively, to the resistance in the same layer

Fig. 2, *b* is characterized by the change in resistance when applied to 5 layers of polyaniline in the presence of anionic surfactant – sulfonol. Constancy charge sign 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 [19] – the interaction energy of the first layer of adsorbed molecules sufficiently greater than the energy of interaction between each successive layer. Thus, the process of a heterocoagulation of polyaniline particles on the polyamide fiber is described by the quasi-chemical reaction model.

References

1. Nanostructured conductive polymers / ed. Ali Eftekhari. – Wiltshire, Great Britain : John Wiley & Sons Ltd, 2010. – 810 p.
2. Nanoparticle assemblies and superstructures / ed. N. A. Kotov. – Boca Raton : Taylor & Francis Group, 2006. – 614 p.
3. Leite E. R. Crystallization and Growth of Colloidal Nanocrystals / E. R. Leite, C. Ribeiro. – NY : Springer, 2012. – 101 p.
4. Born P. G. Crystallization of Nanoscaled Colloids / P. G. Born. – NY : Springer, 2013. – 138 p.
5. Редько Я. В. Отримання електропровідних властивостей текстильних матеріалів в процесі опорядження : дис. ... канд. техн. наук : 05.18.19 / Редько Яна Володимирівна. – К., 2008. – 158 с.
6. Песков Н. П. Физико-химические основы коллоидной науки / Н. П. Песков. – М. : ОНТИ, 1934. – 325 с.
7. Зонтаг Г. Коагуляция и устойчивость дисперсных систем / Г. Зонтаг, К. Штрэнге. – Л. : Химия, 1973. – 152 с.
8. Nanofibers and nanotechnology in textiles / ed. P. J. Brown and K. Stevens. – Cambridge, England : Woodhead Publishing Limited, 2007. – 518 p.
9. Липатов С. М. Физико-химия коллоидов / С. М. Липатов. – М.–Л. : ГНТИ, 1948. – 372 с.
10. Колмогоров А. Н. О логарифмически-нормальном законе распределения частиц при дроблении / А. Н. Колмогоров // Доклады АН СССР. – 1941. – Т. 31, № 2. – С. 99–101.
11. Курс физической химии. Т. 1 / Я. И. Герасимов, В. П. Древинг, Е. Н. Еремин [и др.]. – М. : Химия, 1964. – 624 с.
12. Colloidal Particles at Liquid Interfaces / ed. B. P. Binks, T. S. Horozov. – Cambridge : Cambridge University Press, 2006. – 503 p.
13. Self-Organized Morphology in Nanostructured Materials / ed. K. Al-Shamery, J. Parisi. – Berlin : Springer-Verlag Berlin Heidelberg, 2008. – 175 p.
14. Travas-Sejdic J. Self-assembled polyaniline thin films: Comparison of poly(styrene sulphonate) and oligonucleotide as a polyanion / J. Travas-Sejdic, R. Soman, H. Peng // Thin Solid Films. – 2006. – Vol. 497. – P. 96–102.
15. Фридрихсберг Д. А. Курс коллоидной химии / Д. А. Фридрихсберг. – Л. : Химия, 1984. – 368 с.

16. Романкевич О. В. Изотерма абсорбции при образовании сольватов сорбат – полимер / О. В. Романкевич // Доп. НАН України. – 2006. – № 4. – С. 148–151.
17. Кричевский Г. Е. Химическая технология текстильных материалов / Г. Е. Кричевский, М. В. Корчагин, А. В. Сенахов. – М. : Легпромбытиздат, 1985. – 640 с.
18. Multilayer Thin Films / ed. G. Decher, J. B. Schlenoff. – Weinheim : Wiley-VCH Verlag GmbH & Co. KGaA, 2003. – 524 p.
19. Грег С. Адсорбция, удельная поверхность, пористость / С. Грег, К. Синг. – М. : Мир, 1984. – 306 с.

Романкевич О. В., Редько Я. В.

СОРБЦІЯ НАНОЧАСТИНОК ПРИ ОСАДЖЕННІ ШАРІВ

Статтю присвячено вивченню процесу самоорганізації шару поліанілінових наночастинок при гетерокоагуляції на поліамідних волокнах. Показано, що розподіл за розмірами дисперсії поліаніліну, одержаної окиснювальною конденсацією аніліну, є нормальним з максимумом при 150 нм. Встановлено, що опір багатошарових волоконних матеріалів з поліаніліновим покриттям, одержаним методом layer-by-layer, залежить від кількості шарів і типу ПАР. Процес гетерокоагуляції поліанілінових частинок на поліамідних волокнах описано за допомогою квазіхімічної моделі реакції. Показано, що в цих умовах виникають структури з обмеженою тривалістю існування і з подальшою самоорганізацією.

Ключові слова: волоконні матеріали з провідністю, поліанілін, гетерокоагуляція, самоорганізація наночастинок.

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Халявка Т. О., Камішан С. В.

МЕЗОПОРУВАТІ НАНОКОМПОЗИТИ НА ОСНОВІ ДІОКСИДУ ТИТАНУ ЯК ПЕРСПЕКТИВНІ МАТЕРІАЛИ ДЛЯ ОЧИЩЕННЯ ВОДИ

Отримано мезопоруваті нанорозмірні композитні матеріали на основі оксидів цинку, олова, ванадію та титану за допомогою цитратного методу. За допомогою рентгенофазового аналізу в усіх композитах виявлено фази анатазу та рутилу. Встановлено, що композити складаються з агрегатів округлої форми величиною близько 2 мкм, а розміри їхніх кристалітів у порівнянні з TiO_2 зростають від 9,5 до 21,4 нм. Виявлено, що в спектрах поглинання $\text{V}_2\text{O}_5/\text{TiO}_2$ та $\text{SnO}_2/\text{TiO}_2$ спостерігається батохромний зсув, а у ZnO/TiO_2 – гіпсхромний. Ширина забороненої зони композитів зменшується в порівнянні з чистим діоксидом титану. Наноккомпозитні зразки виявили підвищену фотокаталітичну активність у реакції деструкції органічного барвника сафраніну Т у водних розчинах при УФ-опроміненні в порівнянні з чистими оксидами титану, цинку та ванадію.

Ключові слова: наноккомпозити, оксиди титану, цинку, ванадію, олова, фотокаталіз.

Вступ

При фотокаталітичному способі очищення водних розчинів від токсичних речовин

у більшості випадків використовують діоксид титану, який є дешевим та нетоксичним каталізатором [1, с. 34; 2, с. 1627]. Крім того, після закінчення реакції його можна легко відділити від