INFLUENCE OF SUPERFICIAL MODIFICATION ON ELECTRICAL CONDUCTIVITY OF POLYACRYLONITRIL FIBER

Olga Garanina, Igor Panasyuk, Ievgeniia Romaniuk and Yana Red'ko

Kyiv National University of Technologies and Design, Nemirovich-Danchenko Street 2, Kyiv, Ukraine
helgaranina@gmail.com, evromanuk@gmail.com

Abstract: *Purpose - to determine the influence of surface functionalization on the electrical conductivity of fibrous material on the basis of polyacrylonitrile (PAN). Fibrous based materials possess a number of PAN properties, in particular, "wooly". However, the products based on copolymers of acrylonitrile have unpleasant disadvantages, among which should be a significant accumulation of electrical charge.* Radzyshevsky *reaction is effective in holding surface functionalization of PAN-based material. It decreases the electrical conductivity of fibers. Thus, during exploitation of the finished product a more intense and rapid process of draining the formed electrical charges will occur, which, in turn, minimizes the number of accumulated charges.*

Keywords: *superficial modification, electrical conductivity, polyacrylonitrile fiber.*

1 INTRODUCTION

Today, the use of synthetic fibers as a raw material predominates [1]. PAN textile materials have valuable properties, but they also have disadvantages, such as the ability to accumulate electrical charge during using. Accumulation of static charge of the fibers it hampered their processing and deteriorates hygienic properties of the products [2, 3]. The grade of the accumulation of static charge is depends on the humidity of the environment or fiber, and on the composition of the surface layers of the fiber. The value of the static charge is determined by the: presence of moisture, surface contamination, the presence of antistatic agents and the nature of the contact. Each type of fiber has a certain maximum charge, however, the rate of increase (accumulation) of the charge for different fibers varies, with other things being equal [5]. Moreover, the electrical charges can occur not only in friction, but also in tension and compression [8]. One way to reduce or remove of static charge is to treat products from synthetic fibers with antistatic agents. Antistatic agents absorb moisture or interact with it. They form a layer on the surface of the material which dissipates the charges and reduces the material's static charge [7-10]. The determining effect on the electrical properties of fibrous materials is exerted by their surface [11]. The state of the surface is associated with the maintenance of functional groups on it. Their composition is changed by adjusting their hydrophilic properties and value of the electrical conductivity of the textile material.

The aim of this work is to study the effect of the functionalization of the surface of PAN fibers using the Radzyshevsky reaction on electrical conductivity [4].

PAN-based fibrous materials have a range of valuable properties, in particular “wool-like”. However, products based on acrylonitrile copolymers are characterized by rather unpleasant disadvantages, among which a pronounced ability to accumulate an electrical charge during operation is highlighted. When electrostatic charge accumulation of the fibers, their processing is difficult and the hygienic properties of the products are deteriorating. When using such materials for the manufacture of clothing, their high static charge can influence blood pressure, increase fatigue, irritability, etc. [11]. The degree of static charge accumulation largely depends on the humidity of the environment or fiber, on the composition of the surface layers of the fiber. Polyacrylonitrile fibers absorb a small amount of moisture, so reducing the static charge of the filament is a complex and important problem to solve. In this research the Radzyshevsky reaction was used of the way to reduce of static charge of fibrous materials, on the basis of copolymers of acrylonitrile in the conditions of treatment. The effect is achieved by replacing a part of the nitrile groups on the surface of the fiber on the amide groups. Amides are obtained by partial hydrolysis of nitriles. The reaction mechanism of Radzyshevsky provides for a nucleophilic attack of the nitrile group by a hydroperoxide anion. The result is an unstable intermediate that is an oxidizing agent. Subsequently, the hydride transfer from the second water molecule to the intermediate formation of the hydroperoxide carboximide follows (Figure 1).

In an alkaline solution, hydrogen peroxide restores the intermediate to the amide with the release of oxygen.

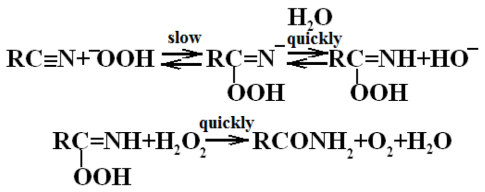

Figure 1 The hydride transfer from the second water molecule to the intermediate formation of the hydro-peroxide carboximide

In research [13] the mechanism of action of hydrogen peroxide as a nitrile activator in the medium of methyl alcohol in the presence of alkali is considered.

An interest is the analysis of the action of hydrogen peroxide in the preparation of the product with the content of amide groups. The concentration of hydrogen peroxide in the reaction of hydration depends on the structure of the output nitriles. Usually 3% of hydrogen peroxide is used. For heavy hydrating nitriles use more concentrated peroxide hydrogen (up to 30%). The concentration of sodium hydroxide varies from lowest to 50%. The reaction is conducting out when heated in an aqueous solution of ethanol or methanol.

A variation of the Radzyshevsky reaction is hydration of the nitrile group, which proceeds with the synchronous oxidation of other functional groups. In this case, the reactive groups may belong to either one or a different compound. As reagents can be used unsaturated nitriles, mixtures of nitriles with olefins and other compounds. Generally, the reaction is carried out in aqueous ethanol or methanol. Reaction temperatures are 40-70°C. As a result aromatic amides is 80-90%, aliphatic 40-60%.

However, as mentioned earlier, it was necessary to obtain an experimental confirmation of the possibility of conducting a Radzyshevsky reaction in an aqueous medium with the participation of nitrile groups of copolymer of acrylonitrile.

2 MATERIALS AND METHODS

The samples for functionalization were made on a flat knitting machine of 10th class. The yarn for samples is nitron D (factory Polimir, Republic of Belarus), with a direct linear density of 15 tex. The composition of the copolymer: acrylonitrile 91%, methyl acrylate 8%, AMPS (2-acrylamide-2 methyl-propanesulfonic acid) 1%. For processing fiber material based on PAN fibers was used a different amount of 35% hydrogen peroxide solution in the presence of ammonia (pH 10.5) and tetraborate (pH 8.0) buffer systems. To study the electrical conductivity, samples of PAN knitted fabrics were used. The studies were performed according to the standard.

Functionalization of the textile material was performed by the Radzyszewski reaction, varying the amount of hydrogen peroxide at pH 8 and pH 10.5. Functionalization of the samples was performed at a temperature of 80°C, bath modules 1:20, the amount of hydrogen peroxide (35%) varied from 50 to 100 g/l. The duration of processing was 60 minutes After functionalization, washing with water was performed until neutral.

Traditional methods of textile materials research, classical methods of textile materials technology, physical and colloid chemistry, standardized methods of textile materials science were used for the research. All methods used are defined by current international or State standards of Ukraine for the relevant textile products.

It is known that for the oxidation reaction of nitriles to amides, Radzyshevsky treated nitrides by 3% solution of H_2O_2 in KOH at pH=8.0, temperature of the process 40°C for 90 minutes.

However, the processing by 3-5% solution of hydrogen peroxide at temperatures below 80°C does not increase the ability to dye by active dyes. The reason is to get the low number of amide groups.

In addition to the main tasks (increasing hydrophilicity and reducing electrical conductivity) peroxide hydrogen is able to participate in the bleaching of PAN fibers. The bleaching is carried out at a temperature of 70°C for 90 minutes in a solution, containing 10 g/L hydrogen peroxide at pH 6.5. However, in [14] it was noted that when bleaching cotton, the active action of H_2O_2 is manifested at pH 10.5-11.0 and at temperature increase to 85-90°C.

Thus, the reactionary modification was carried out in the conditions of finishing production (the Radzyshevsky reaction in aqueous environment) using buffer solutions with pH 8.0 and pH 10.5 at temperature of 95-98°C.

3 RESULTS AND DISCUSSION

The magnitude of the emerging static charge on the surface of the fibrous material is determined by many factors: the presence of moisture, contamination of surfaces, the presence of specially applied anti-static substances, the presence of inevitable external fields, the nature of the contact and the characteristics of the measurement method [15].

A number of researches [4, 16] indicate the property of a unified theory of electrical action. It proposes to reduce the study of the mechanisms of generation and dispersion of static charge to the resistivity of textile materials. The author of the scientific paper [16] determined that for each type of fiber there is a certain maximum charge, however, the rate of growth (accumulation) of charge under other equal conditions for different fibers is different.

This is the reason for determining the ability of static charge accumulation of the fiber by its maximum charge. At the same time, other methods of measuring of static charge of the fibers and fibrous materials on their basis [16] are also available, but the results of these studies often contradict each other. Thus, the resistivity of textile fibers varies within the range of 10^6-10^{13} Ω.cm.

In our research we assume that the determining influence on the electrical properties of fibrous materials is given by their surface. In turn, the state of the surface is closely related to the content of functional groups on it. Directed change in their content can serve as an effective way of regulating, for example, hydrophilic properties, and, as a consequence, the electrical conductivity of a textile material [16-18].

The electrical conductivity is determined by the following indicators: strength of the electrical field, unit of electrical charge, surface density, electrical polarity, specific volumetric electrical resistance and specific surface resistance. In turn, if the electrical conductivity is characterized by the appearance of electrical charges on their surface when friction fibers of the finished product, then the electrical conductivity can be considered the emergence of electrical current. As electrical conductivity is the process of charge transfer, as the main conditions are: the presence in this environment of charged particles (charge carriers), a certain mobility of these carriers, which ensures their movement under the influence of electrical field forces. To evaluate the electrical conductivity of functionalized PAN-fibrous materials, we used the characteristic of the surface electrical resistivity in Ω.m^2.

Important factors affecting the electrical conductivity of the material are relative humidity and the speed of motion of the contacting surfaces. If a relative humidity of 85% or more the static charge accumulation of the material process is practically not manifested, as the electrical resistance of the moistened fabric decreases. At low humidity, the electrical resistance of the fabric is high and flow of electrical charge from a static charge accumulation of clothing occurs by means of a spark discharge between fabric and metal, dielectrical parts of the equipment or the ground. Electrical spark energy may be sufficient to ignite a flammable or an explosive mixture.

In [17-19] the effect of surface modification of fibers on the capillary properties of synthetic textile materials was investigated. It is stated that the increase of hydrophilicity decreases the static charge accumulation of textile materials.

The influence of PAN functionalization on its hydrophilic properties is investigated. With increasing concentration of hydrogen peroxide, the capillarity of textile material increases.

Graphical dependences, obtained as a result of our research, (Figure 2) confirm that as a result of surface functionalization, the conductivity of the fibrous material decreases by 5 orders of magnitude (at pH 8.0) and 7 orders of magnitude (at pH 10.5).

The Radzyshevsky reaction is effective in the functionalization of the surface of the PAN and leads to a decrease of the electrical conductivity index. Thus, during the operation of the finished product will be more intensive and faster process of draining of the formed charges. This minimizes the amount of charge accumulated.

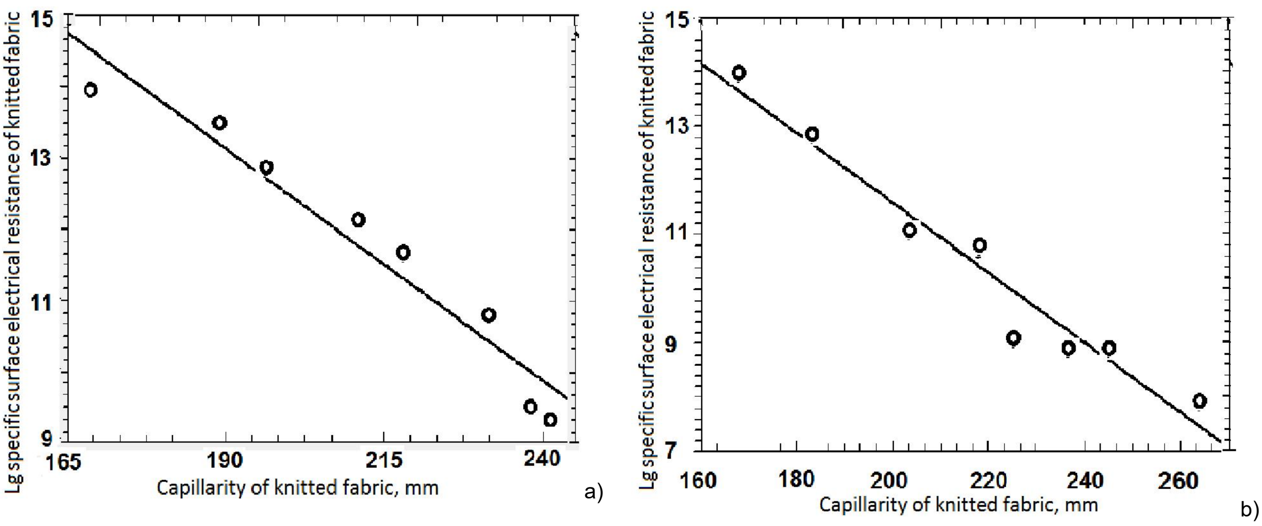

Figure 2 The dependence lg specifics surface electrical resistance on the capillarity of knitted PAN-fibrous material at: a) pH 8.0; b) pH 10.5

The presence of a clear correlation between the specific conductivity and the capillarity of the fibrous materials indicates the Radzyshevsky reaction on the fiber surface and the improvement of the hygienic properties of PAN.

Accept that the sample PAN before functionalization PAN-0, after functionalization with a concentration of hydrogen peroxide:
50 g/l at pH 8.0 - PAN-50(8),
100 g/l at pH 8.0 - PAN-100(8),
120 g/l at pH 8.0 - PAN-120(8),
140 g/l at pH 8.0 - PAN-140(8),
180 g/l at pH 8.0 - PAN-180(8),
100 g/l at pH 10.5 - PAN-100(10.5).

Figure 3 presents typical micrographs of SEM samples before functionalization PAN-0 and after functionalization with different conditions PAN-100(8) and PAN-100(10.5). It is established that as a result of functionalization changes of the surface of PAN occur (Figures 3b and 3c). It is worthy of note that after functionalization at pH 8.0 (Figure 3b) there are changes in the morphology of the fiber with the formation of longitudinal "furrows" on the surface. After functionalization at pH 10.5 (Figure 3c) the surface of fibrous materials in addition to the longitudinal has transverse "furrows", which indicates deeper transformations at pH 10.5.

The nature and size of the formed "grooves" (depressions) are shown in Figure 4. The surface of the sample PAN-0 (Figure 4a) has a relatively uniform, smooth, without visible heterogeneity microrelief. After functionalization on the surface of the samples PAN-50(8), PAN-100(8), PAN-120(8), PAN-140(8), PAN-180(8) (Figures 4b-f) the following morphological changes are observed: nanosized "caverns" and "furrows" appear.

The calculations showed that as the concentration of H_2O_2 changes, the shapes and sizes of the "caverns" very clearly change: the average numerical value of the size of the "caverns" varied from 30 to 150 nm. The formation of a similar size and shape of "caverns" in the studied samples, of course, is associated with carrying out functionalization, which changes the surface microrelief in the structure of the sample.

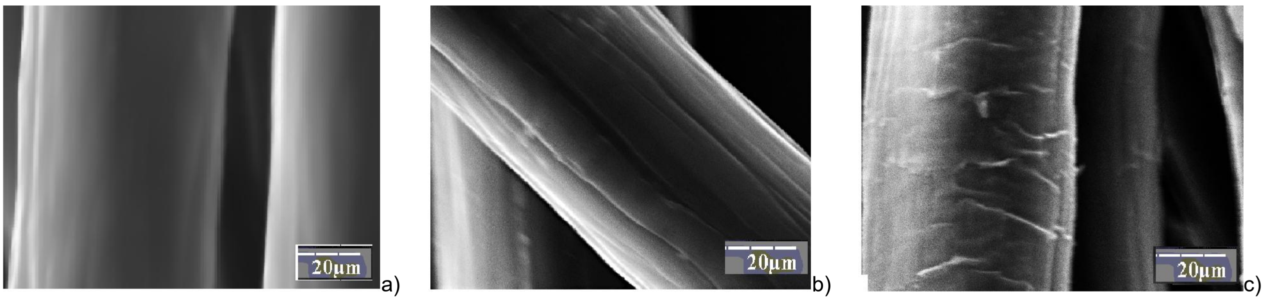

Figure 3 SEM micrographs of samples of PAN-fibrous materials: a) original sample PAN-0; b) PAN-100(8); c) PAN-100(10.5)

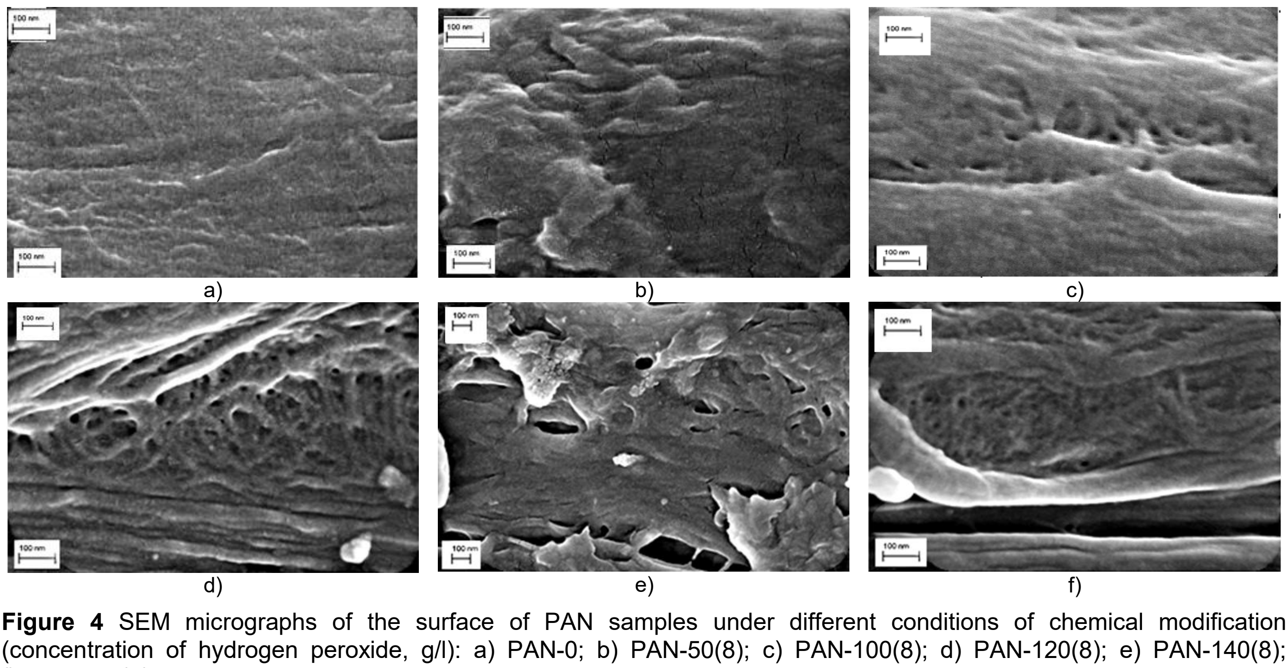

Figure 4 SEM micrographs of the surface of PAN samples under different conditions of chemical modification (concentration of hydrogen peroxide, g/l): a) PAN-0; b) PAN-50(8); c) PAN-100(8); d) PAN-120(8); e) PAN-140(8); f) PAN-180(8)

4 CONCLUSION

The Radzyshevsky reaction is effective in the functionalization of the surface of the PAN material: it leads to a decrease in the electrical conductivity of the textile material. When operating the finished product, a more intensive and faster process of draining the formed charges will occur, this, in turn, minimizes the number of accumulated charges.

The presence of a clear correlation between the specific electrical conductivity and the capillarity of fibrous materials, on the one hand, indicates the progress of the Radzyshevsky reaction on the surface of the fiber, and on the other – the improvement of the hygienic properties of fibrous materials based on PAN fibers.

5 REFERENCES

1. Heller B.E.: Status and prospects of development of production of polyacrylonitrile fibers, Chemical Fibers №3., 2002, pp. 3-10
2. Pakshver E.A.: Carbochain fibers, Chemistry, Moscow, 1973, pp.7-163
3. Morton W.E., Hearle J.W.S.: Physical Properties of Textile Fibres, Woodhead Publishing 2008, 796 p., ISBN: 978-1-84569-220-9
4. Levy J.B., Wakelin J.H., Kauzmann W.J., Dillon J.H.: Relation of charge to frictional work in the static electrification of filaments, Textile Research Journal 28(11), 1958, pp. 897-911, https://doi.org/10.1177/004051755802801101
5. Yuan X.Y., Sheng J., Shen N.X.: Surface modification of acrylonitrile copolymer membranes by grafting acrylamide III. Kinetics and reaction mechanism initiating by Fe^{2+}/H_2O_2, Journal of Applied Polymer Science 69(10), 1998, pp. 1917–1921, https://doi.org/10.1002/(sici)1097-4628(19980906)69:10<1917::aid-app4>3.0.co;2-h
6. Kurhanskyi A., Bereznenko S., Novak D., Kurganska M. Sakovets V, Bereznenko N, Haranina O.: Effects of multilayer clothing system on temperature and relative humidity of inter-layer air gap conditions in sentry cold weather clothing ensemble, Vlakna a Textil (Fibres and Textiles) 25(3), 2018, pp.43-50
7. Red'ko Y., Suprun N.: XRD and SEM analysis of iron oxide nanoparticles formation in polyamide textile material, Vlakna a Textil (Fibres and Textiles) 25(3), 2018, pp. 63-67
8. Pan W., Yang S.L., Li G., Jiang J.M.: Electrical and structural analysis of conductive polyaniline/polyacrylonitrile composites, European Polymer Journal. 41(9), 2005, pp. 2127–2133, https://doi.org/10.1016/j.eurpolymj.2005.04.003
9. Matveitsova D, Paraska O, Karvan S.: Developing compositions based on nanoparticles for final treatment of textile materials, Eastern-European Journal of Enterprise Technologies 5(10), 2016, pp. 19-25, http://dx.doi.org/10.15587/1729-4061.2016.79809
10. Van Krevelen DW, Te Nijenhuis K.: Chapter 11 - Electrical Properties, Properties of Polymers, Elsevier, Amsterdam, 2009, pp. 319-354, ISBN: 978-0-08-054819-7
11. Kukin G.N., Soloviev A.N., Koblyakov A.I.: Textile Materials Science [in Russian], 2nd ed., Vol. 2, Legprombytizdat, Moscow, 1989, pp 352
12. Romankevich O.V., Garanina O.A., Bardash N.A.: Affinity of Cationic Dyes for Polyacrylonitrile Fiber, Fibre Chemistry 46(3), 2014, pp. 161-164, http://dx.doi.org/10.1007/s10692-014-9581-x
13. von Holleben M.L.A, Livotto P.R., Schuch C.M.: Experimental and theoretical study on the reactivity of the $R\text{-}CN/H_2O_2$ system in the epoxidation of unfunctionalized olefins, Journal of the Brazilian Chemical Society12(1), 2001, pp.42-46, http://dx.doi.org/10.1590/s0103-50532001000100005
14. Rustamov M.K., Karimov M.M., Mukhamediev M.G. and etc.: Synthesis of fibrous ion-exchange materials based on polyacrylonitrile and their physicochemical properties, Mountain Spring of Uzbekistan 4(43), 2010, pp.93-96
15. Polonik P.A.: The fight against static electricity in the textile and light industries [in Russian], Light Industry, Moscow 1966, pp. 186
16. Alekseeva L.V.: Theoretical aspects of predicting the electrostatic properties of textile materials, Fibre Chemistry 39, 2007, 225–226, https://doi.org/10.1007/s10692-007-0047-2
17. Prorokova N.P.: Dissertation abstract, Directional change in the surface properties of fibrous materials in the processes of chemical-textile production, Ivanovo, 2006, pp. 34
18. Prorokova N.P., Vavilova S.U., Buznik V.M., Zavadsky A.E.: Modification of polypropylene fibrous materials with ultradispersed polytetrafluoroethylene. High molecular weight compounds [in Russian], Akademizdatcenter Nauka, 55(11), 2013, pp. 1333-1342, http://dx.doi.org/10.7868/s0507547513110044
19. Etzler F.M.: Characterization of surface free energies and surface chemistry of solids, Contact Angle, Wettability and Adhesion 3, Utrecht, The Netherlands, 2003, pp. 219-26