

Infrared Spectroscopic Studies of the PTFE and Nylon Membranes Modified Polyaniline

Dinar Dilshatovich Fazullin¹, Gennady Vitalevich Mavrin¹, Michael Pavlovich Sokolov¹ & Ildar Gilmanovich Shaikhiev²

¹ Kazan Federal University, Naberezhnye Chelny, Prospect Mira, Russia

² Kazan National Research Technological University, Kazan, Russia

Correspondence: Dinar Dilshatovich Fazullin, Kazan Federal University, Naberezhnye Chelny, Prospect Mira, 68/19, Russia.

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Abstract

Ion-selective membranes have a high degree of separation of the solutions, both with low and high concentrations of dissolved salts. Besides solutions using ion selective membrane occurs in the low operating pressures of 0.1-2 bar, depending on the substrate to which the working layer is applied. Lately, in the production of conductive polymers are used, such as polyaniline (PANI), for example for the manufacture of solar cells, sensor devices, for making protection from electrostatic charges and corrosion, as well as ion-exchange membranes. Use in the preparation of PANI, or modification has the advantages of ion exchange membranes in the communication and availability of raw materials and ease of manufacture and also because of such quality as high selective permeability. Modification of membranes to form on the surface and in the pores of the PANI layer, which is a cationic, allows to obtain ion-exchange membranes are not inferior in selectivity by reverse osmosis on a number of cations. The aim is to establish the chemical nature of using FTIR spectroscopy layer surface modification of PTFE and nylon membranes by polymerization of aniline and the study of possible changes in the properties of membranes such as exchange capacity and moisture content. In this operation the composite membranes prepared from cation-modified surface layer on the substrate a polyaniline and nylon of PTFE. The results of the study by infrared spectroscopy of the molecular structure of polyaniline and a number of materials on its basis.

Keywords: IR spectroscopy, membrane Polyaniline, Nylon, PTFE, moisture

1. Introduction

In recent time, various studies have been conducted to prove the high electrical conductivity of the organic polymer polyaniline (Bredas et al., 1991, Paoli et al., 1985, Niwa et al., 1987, Zinger & Kijel, 1991, Wang et al., 1990, Dogan et al., 1992, Selampinar et al., 1994). Many researchers have reported polyaniline composite supported by various insulating matrices, such as polyvinyl chloride (Srivastava et al., 2006), nylon-6 (Byun & Im, 1998) and nylon-66 (Khalid & Mohammad, 2009).

Since past few decades there has been much emphasis on polymer modification. Quite a few methods adopted by the researchers are grafting, curing, blending etc. Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain. The various techniques include chemical, radiation, photochemical, electrochemical and enzymatic grafting. Conducting polymers are being extensively used because of their potentiality in different applications such as electrochromic displays, optoelectronic devices, batteries and sensors etc. In the past different studies have been carried out to prove the high electrical conductivity in organic polymers. But these polymers suffer from certain drawbacks. It has been reported that the composite system by blending PANI with a useful polymer improves its mechanical properties. Li et al also prepared different PANI grafted co-polymers. In order to overcome the limitations such as poor mechanical properties and problems in processing as well as instability under the relevant ambient conditions; it was decided to graft polyaniline-emeraldine salt onto nylon 6. Now the reason for choosing this insulating polymer (nylon 6) is its good mechanical properties. Grafting provides a potential technique to overcome these limitations on both of these polymers to improve the process ability of conducting polymers (Jadhav & Kelkar, 2012).

In this work (Fazullin et al., 2014), we obtained ion-selective membranes with polyaniline (PANI) as a working layer. Studies were performed on a laboratory membrane separation installation. PTFE and nylon membranes with pore size 0.45 μm . were used as the matrix for polymerization of aniline. Modification of membranes with forming PANI layer on the surface and in the pores, which is a cation-active, makes it possible to obtain ion-exchange membranes that are not inferior to the reverse osmotic ones in selectivity by the number of cations. Membranes with PANI surface distribution were synthesized by polymerization of aniline directly in the matrix of the membranes. In the former case, the membrane had been pre-treated for 5 hours in a solution of ammonium persulfate (method 1), in the latter, it had been kept in the solution of aniline hydrochloride for 5 hours (method 2). After that, the membrane was placed in a solution of the second reagent. PANI particles formed directly in the matrix of the membrane, which fact was evidenced by changing the polymer color to dark green. Duration of membrane processing with each reagent was 5 minutes with constant stirring with a laboratory shaker. Concentration of the solutions was 1 mol/l each. In order to study membranes swelling, samples with diameter 45 mm were placed in distilled water and membrane weight was measured using analytical weigher with accuracy 0.0001 grams before and after the experiment. Exchange capacity was determined under dynamic conditions by passing certain amounts of model solutions with known concentrations of cations through the membrane. Using the AAS method, concentration of cations in the filtrate was determined, and weight of cations absorbed by the membrane was calculated. Filtering was continued till selectivity decreased to 10%. Exchange capacity was calculated per 1 gram of the membrane. After each experiment, the membrane was regenerated by placing it in 3% solution of hydrochloric acid followed by rinsing it in deionized water. Cation-exchange membranes have been obtained by polymerizing aniline in the structure of nylon and PTFE membranes. Physicochemical properties of the membranes have been determined. Membranes selectivity has been proven for cation ions in test solutions of metal salts. However, in case of high concentrations of metal ions, in dynamic conditions, selectivity drops abruptly. Ion-exchange capacity of the obtained nylon-PANI membrane is not inferior to some commercially available cation-exchange membranes.

A simplified method to prepare polysulfone (PSf)/polyaniline (PANI) nanocomposite membrane was proposed. With this method, aniline was polymerized using ammonium peroxydisulfate as oxidant and N-methyl-2-pyrrolidone (NMP) as solvent, which was also the solvent of PSf. The mixture after aniline polymerization containing PANI nanospheres, PANI oligomers, NMP and inorganic ions, named PANI/NMP, was added directly into the solution consisting of PSf and NMP without any post-processing to form membrane casting solution. Then, PSf/PANI nanocomposite membranes were prepared via immersion phase inversion process using the casting solution. This method is called in situ blending method. PANI oligomers were soluble in both water and organic solvent while PANI nanospheres were dispersed in both water and organic solvent. The behaviors of PANI oligomers and PANI nanospheres during membrane formation were investigated and analyzed. A large portion of PANI oligomers and a small portion of PANI nanospheres would be leached out of the casting film during the phase separation and act as pore formers, inducing the enhancement of membrane porosity and surface pore size. A large portion of PANI nanospheres and a small portion of PANI oligomers residing in the prepared membranes favored the enhancement of membrane hydrophilicity, breaking strength and thermal stability. Compared with PSf membrane, PSf/PANI nanocomposite membranes obtained with this method had more hydrophilic surface, higher porosity, larger surface pore size, less acicular pores, thicker skinlayer, wider pores beneath the skinlayer, better vertically interconnected finger-like pores and less macrovoids. Pure water fluxes of PSf/PANI nanocomposite membranes were 1.7–4.1 times that of PSf membrane and BSA rejections of the membranes were all above 96%. During BSA ultrafiltration, PSf/PANI nanocomposite membranes showed slower flux decline rate and higher flux recovery ratio values after simple water flushing than PSf membrane (Song Zhaoa et al., 2011).

The grafting of polyamide nylon 6 (N6) with polyaniline-emeraldine salt (PANI-ES) was accomplished by in situ polymerization of the monomer on the nylon 6 film using chemical method of polymerization. The primary goal of the work is to graft a conducting polymer onto a non-conducting one and likewise study the structural changes. The grafting of PANI-ES onto nylon 6 film was verified by X-ray diffraction (XRD) analysis. The graft parameters such as % grafting, % efficiency and total conversion were also calculated. The results thus obtained show that grafting has altered the crystallinity of the host polymer. From the analytical study and its discussions it can be concluded that polyaniline-emeraldine salt grafted nylon 6 films show an overall structural modification, asserting formation of a different crystal structure irrespective of the parent polymers (Jadhav & Kelkar, 2012).

Polymer chain conductive polyaniline (PANI) consists of regularly alternating benzene rings and nitrogen-containing groups. This structure provides polyconjugation chain (regular alternation of single and double bonds). The polymer chain forming the zigzag lying in one plane, wherein the π -electron clouds above

and below the overlap plane of the chain. The charge carriers are formed in such a polymer is its oxidation. PANI oxidation centers are nitrogen atoms having not involved in the chemical valence bonds pair of electrons. Upon oxidation, i.e. withdrawal of one of the electrons in the polymer chain there is a positive charge (Compan et al., 2012).

According to the literature it is known that the products of polymerization of aniline are oligoaniline containing protonated and quinonediimine fenoldiaminnye fragments (Laska & Widlarz, 2005, Winokur & Mattes, 1998).

Some of the cation exchange material with a surface layer are characterized by high selectivity PANI transfer (Ivanov et al., 2004). For conducting PANI its forms doped with various acids. Interestingly the use of polymer membranes as a matrix for the polymerization of aniline (Stenina et al., 2008).

The purpose of the study of the chemical nature of composite communication systems nylon and PTFE modified polyaniline, by IR spectroscopy.

In this paper, according to IR-spectroscopic analysis of the chemical nature of the produced composite systems based on nylon and PTFE, and a conductive polymer -polyaniline (PANI).

IR spectrum of polytetrafluoroethylene (PTFE) is relatively simple (Figure 1), which is explained by a simple chemical structure of the polymer macromolecules $(-CF_2-)_n$. The most intense bands are stretching vibrations of CF_2 (1211 and 1154 cm^{-1}) and vibration ν (CC), which manifests itself in the form of inflection at $\sim 1233\text{ cm}^{-1}$. In the region below 650 cm^{-1} are located outside the planar deformation and vibrations of CF_2 : rolling vibrations γ_w (CF_2) appear at 639 cm^{-1} , strips 555 and 516 cm^{-1} is characterized by oscillations of the pendulum and the deformation CF_2 -groups, respectively (Ignatief & Bouznik, 2008).

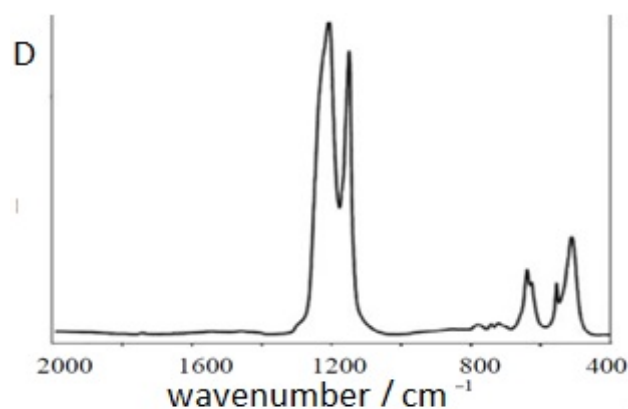


Figure 1. IR absorption spectrum polytetrafluoroethylene F-4

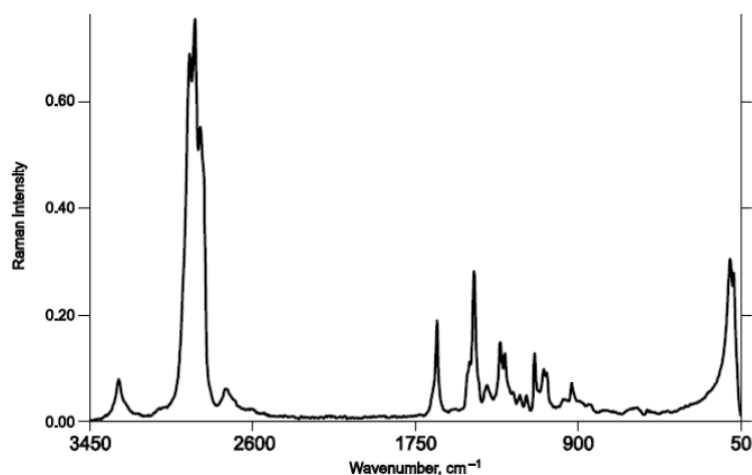


Figure 2. IR absorption spectrum of the standard sample of nylon (Krylov et al., 2005)

For polyaniline characterized by a number of absorption bands: 3450 and 3370 cm^{-1} (stretching vibrations of

N-H); 3010 cm^{-1} (stretching vibrations of C-H in benzene ring); 1590 cm^{-1} and 1500 cm^{-1} correspond to bending vibrations of quinoid and benzenoid rings; 1307 cm^{-1} - corresponds to vibration of the C-N of an aromatic secondary amine; 1167 cm^{-1} - corresponding planar deformation oscillations CH groups (Laska & Widlarz, 2005).

2. Methods

Since past few decades there has been much emphasis on polymer modification. Quite a few methods adopted by the researchers are grafting, curing, blending etc. Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain. The various techniques include chemical, radiation, photochemical, electrochemical and enzymatic grafting. Conducting polymers are being extensively used because of their potentiality in different applications such as electro chromic displays, opto electronic devices, batteries and sensors etc. (Song Zhaoa et al., 2011).

In this work, we obtained ion-selective membranes with polyaniline (PANI) as a working layer. PTFE and nylon membranes with pore size $0.45\text{ }\mu\text{m}$. were used as the matrix for polymerization of aniline. Modification of membranes with forming PANI layer on the surface and in the pores, which is a cation-active, makes it possible to obtain ion-exchange membranes that are not inferior to the reverse osmotic ones in selectivity by the number of cations.

The template for the polymerization of aniline was used PTFE membranes brand Phenex AF0-0514 and nylon brand Phenex AF0-0504 with a pore size of 0.45 microns. Synthesis of membranes with surface distribution of PANI polymerization of aniline was carried out directly in the matrix membranes. The membrane was pre-incubated for 5 h in a solution of 1 mol of aniline hydrochloride. The membrane was placed in a 1 mol solution of ammonium persulfate. Polymerization was carried out for 10 minutes at 25°C . After the reaction, the membrane was washed with distilled water.

Potentiometric pH value changes were made with a pH meter "Ionomer-I 160" standard pH selective electrode with a digital output to a personal computer.

To prove modified polyaniline membranes were measured infrared spectra of the raw PTFE and nylon membranes and the membranes modified nylon and nylon-PANI PTFE. If the spectrum of the analyzed sample contains all the absorption bands of the reference material, it can be assumed that the material is really contained in the sample. The study of the IR spectra of samples was performed on spectrometer Bruker Vector 22 in the Chemical Institute A.M. Butlerova KFU.

To study the membrane wetness samples of 45 mm diameter were wetted with distilled water, and the moisture content was determined using a moisture analyzer A&D MX-50. In principle implemented moisture analyzer thermogravimetric analysis in which the drying specimen using a halogen lamp and the determination of the moisture content, as well as other values that are calculated based on the difference between the wet and dry weight.

3. Results

Figure 3. Shows the IR absorption spectra of the PTFE samples before and after modification of PANI. The figures show that the IR spectra of the original and modified membranes are different.

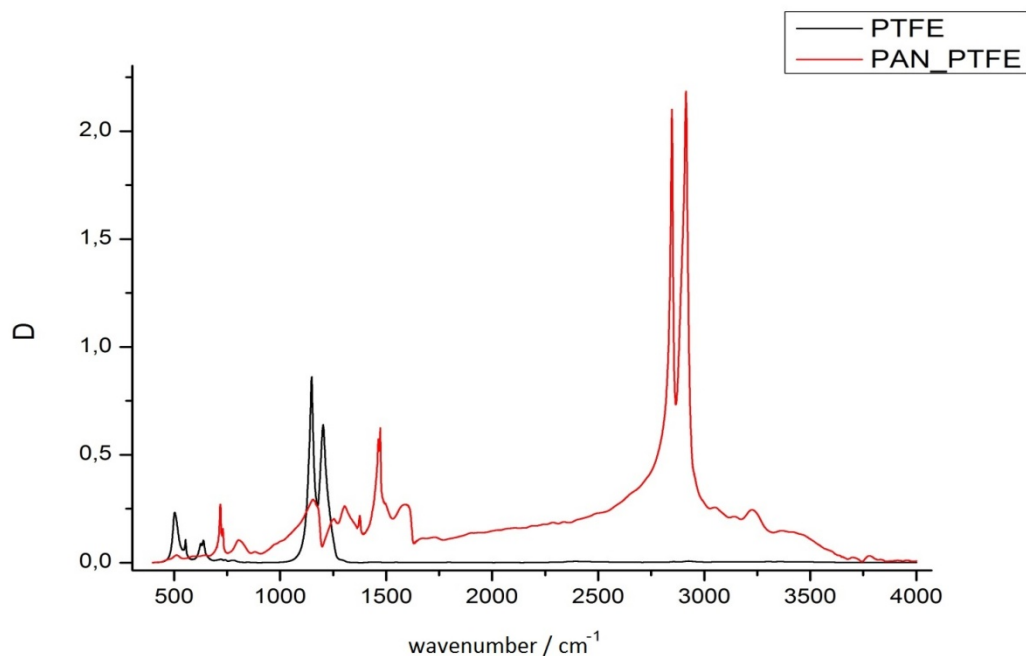


Figure 3. IR absorption spectra of PTFE: lower - PTFE, PTFE top-system-PANI

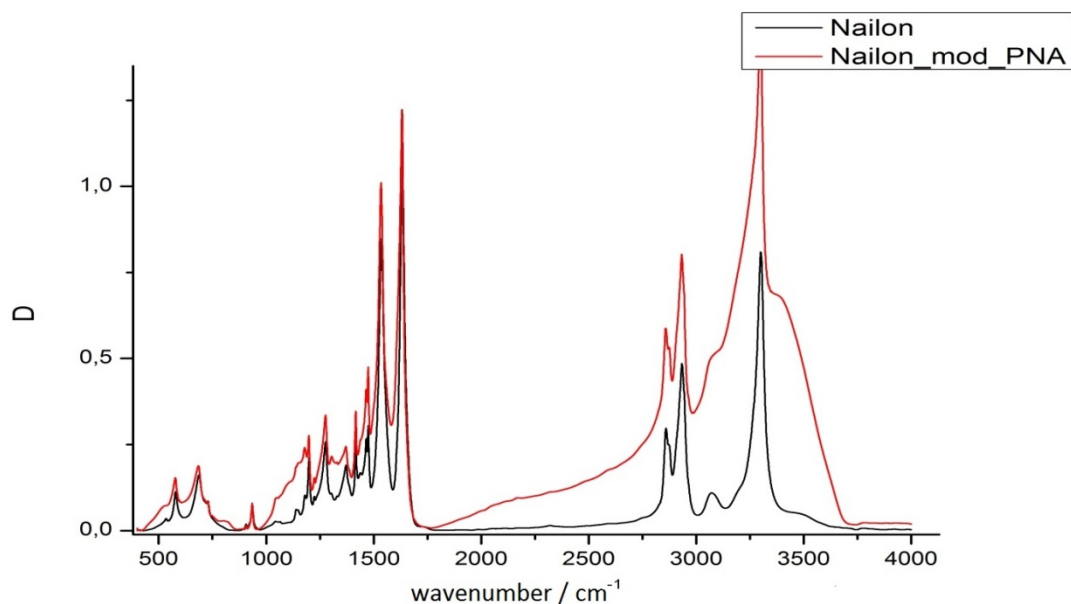


Figure 4. The IR absorption spectra of nylon: lower – nylon, upper - Nylon-PANI system

Water absorption capacity membranes are essential characteristics of ion-exchange membranes, which determine the availability of ion-exchange groups and the speed with which the ion-exchange equilibrium (Table). As a result of the modification of nylon membrane moisture content increased by 4% PTFE membrane became hydrophilic after inoculation. Increase dehumidifying ability membranes due to the presence of polyaniline in the membrane structure.

The table shows that the polyaniline modified membranes appears exchange capacity.

Table 1. Physico-chemical properties of membranes

Membranes	Exchange capacity mmol / g	Moisture content,%
Nylon-PANI	0,59	71,7
PTFE-PANI	0,17	3,6
Initial membrane Nylon Phenex AF0-0504	0	67,4
Initial membrane PTFE Phenex AF0-0514	0	<0,1

4. Discussion

The FTIR spectra of polyaniline: nylon-6,6 composites are presented in work (Khalid et al., 2011). The band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene rings appears at 824 cm^{-1} . The bands corresponding to stretching vibration of N-B-N and N=Q=N structures appear at 1497 cm^{-1} and 1587 cm^{-1} respectively where -B- and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C-N bond appear at 1143 cm^{-1} and 1302 cm^{-1} respectively. The band close to 1130 cm^{-1} is described as being characteristic of the conducting polymer due to the delocalization of electrical charges caused by deprotonation. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline. The characteristic bands at around 688, 1642, 3303 cm^{-1} attributed to nylon-6,6 are present in all the composites. As-prepared polyaniline: nylon-6,6 composite shows a strong band around 1650 cm^{-1} corresponding to carbonyl group of nylon-6,6. For polyaniline, the band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene ring appears around 824 cm^{-1} . The bands corresponding to stretching vibration of N-B-N and N=Q=N structure appear around 1377 cm^{-1} and 1500 cm^{-1} respectively (where -B- and =Q= stand for benzenoid and quinoid moieties in the polymer). The band corresponding to stretching mode of C-N bond appears at 1504 cm^{-1} . The band corresponding to hydrogen bonding between $>\text{C}=\text{O}$ of nylon-6,6 and $>\text{N}-\text{H}$ of polyaniline appears at 3650 cm^{-1} . The gradual increase in the intensities of the bands corresponding to polyaniline and decrease in the intensities of bands corresponding to nylon-6,6 support the gradual change in the composition of the composite samples.

When comparing the IR spectra of PTFE and PTFE-PANI reveals several differences. They consist in the appearance in the spectra of PTFE-PANI additional bands with frequencies 720, 790, 1313, 1490, 2823, 2900 cm^{-1} and changes in the shape and intensity ratio of the majority of the bands (Figure 3).

One of the reasons for the observed changes in the spectrum can be the appearance in the field of new bands associated with the emergence of new groups. So absorption bands at 720, 790 and 1154 cm^{-1} correspond to the deformation and vneplskostnym vibrations of CF_2 , at 1233 cm^{-1} - vibration (SS), which manifests itself in the form of inflection, band at 1313 cm^{-1} can be attributed to the stretching and deformation vibrations of the symmetric CN aromatic amines, but at 1490 cm^{-1} correspond to planar stretching vibrations of the C = C and C-quinonediimine C phenyldiamine PANI fragments.

Background The strong absorption at wave number higher than 2000 cm^{-1} is characteristic of electro conductive PANI form - emeraldina salt which is a polycation radical.

Study the resulting membranes presented in Figure 4, by FT-IR spectroscopy showed that the spectrum of the composite present absorption band at 1260 cm^{-1} , characteristic of the cation radical and in the fields 1581-1600 and $1494-1500\text{ cm}^{-1}$ corresponding quinonediimine phenyldiamine fragments and (Laska & Widlarz, 2005). Background The strong absorption at wave number higher than 2000 cm^{-1} is characteristic of electro conductive PANI form - salt of emeraldin which is a polycation radical.

Modification of nylon polyaniline leads to the appearance in the IR spectra of samples of well-resolved absorption bands characteristic for polyaniline ($1589, 1506, 1313, 1164$ and 833 cm^{-1}), so for neylon ($1635, 1539\text{ cm}^{-1}$). This comparison of the IR spectra of these membranes with an IR spectrum of the original nylon, reveals their qualitative matches. In both spectra contain intense absorption bands in the regions 1580-1590 and $1490-1510\text{ cm}^{-1}$, corresponding to planar stretching vibrations of the C = C bonds in quinonediimine and C-C fragments phenyldiamine PANI, the intensity ratio of which to assess the degree of oxidation of the polymer. Intense bands at 1164 and 1313 cm^{-1} can be attributed to the stretching and symmetric deformation vibrations of aromatic amines in the CN. Absorption band at 833 cm^{-1} in the IR spectra corresponds to bending vibrations of CH groups in 1,4-substituted benzene ring.

The IR spectrum of the composite material has been a shift of the absorption bands 1584, 1496, 1295 and 1141 cm^{-1} , characteristic of PANI, in the long wavelength region and bands 1643 and 1544 cm^{-1} , bands 1643 and 1544 cm^{-1} , which is characteristic of nylon - in the short wavelength region. These spectral changes indicate the formation of hydrogen bonds between PANI and nylon.

Thus, the data of IR-spectroscopy showed that the composite material is formed in the form of PANI salts emeraldina comprising phenylamino quinonediimine and fragments.

5. Conclusions

Analysis of the IR absorption spectra of the initial and modified membranes show the presence of polyaniline in the matrix membranes. In the modified PTFE membrane, the background absorption at wave numbers above 2000 cm^{-1} is characteristic of an electrically conductive form of PANI - salt of emeraldine. Spectral changes in the original nylon membrane indicate the formation of hydrogen bonds between PANI and nylon PANI formed in the form of a salt emeraldina containing phenyl amine and quinonediimine fragments. After modifying polyaniline an increase dehumidifying ability of membranes. Consequently, on the surface and within the pores of the starting nylon and PTFE membrane after modifying them aniline layer formed of polyaniline. Wherein the polyaniline is in the membrane in the form of a salt emeraldina which the membrane comes to the ion exchange capacity. The greater the amount of polyaniline in the membranes, the higher sorption capacity and the moisture capacity of the membrane. The obtained membrane can be used for purifying wastewater, process water from metal ions, also be used for concentration of solutions of the components with a low content of the solution.

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