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Plasma-treating of polymeric membranes for separation of water-oil emulsions

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Abstract. The effect of high-frequency capacitive low-temperature plasma of reduced pressure of glow in different gas atmospheres on polymeric membranes has been investigated. Increased roughness of plasma-treated PES membranes and smoothing of PAN and PSA filters is shown. For all membranes, oxidative processes are observed as a result of plasma exposure, which is confirmed by the increased C-O content of the IR-spectroscopy group. The growth in wetting capacity of membranes treated with plasma of gas atmospheres is also demonstrated. They contain nitrogen and air and an increase of hydrophobicity in the case of propane and butane gas atmosphere. The increasing in hydrophilicity has been determined experimentally, thus raise of efficiency of water-oil emulsion separation.

Plasma is a tool, and for membrane filters it is a tool for modifying their properties to provide the mass-exchange required characteristics. The traditional method is to synthesize a polymer and produce membranes based on it with the required performance properties. An alternative direction is the modification of available filters, the advantage of which is that no additional polymer production is necessary. The modification can be carried out by chemical reagents or by electromagnetic radiation using heat, radiation, laser or plasma as the processing agent. Each of these methods is an effective solution with due care. The advantage of plasma technology is the ability to vary the parameters of modification over a wide range when choosing the type of discharge, the gas medium, the power and the processing time, which makes it more likely that positive results will be obtained.

The polymer membrane is a complex structure consisting of successively arranged surface, porous and supporting layers, the combination of them determines the performance and selectivity characteristics [1, 2]. When charged particles of non-polymeric plasma interact with the membrane, the following processes occur: ablation and etching, resulting in increased pore size and the formation of new ones that it leads to increase of surface roughness; chemical modification of the surface layer, which contributes to the breaking and stitching of polymer chains, which can change the morphology of the surface by reducing roughness; precipitation of polymer fragments or volatile products formed from the etched surface helps to narrow the pores and smooth the surface. At the same time, the indicated phenomena are carried out both sequentially and in parallel depending on the plasma modes, which together lead to a complex change of the properties of the membrane filter. Therefore, determining the
relationship between the variation of membrane characteristics from different polymers depending on plasma processing parameters is one of the main objectives of this research [3-8].

Based on the above methods of atomic force microscopy (AFM), infrared (IR) spectroscopy of impaired full internal reflection (IFPI) and sitting drop (SD), X-ray phase analysis of polyestersulfon (PES), polyacrylonitrile (PAN) and polysulfonamide (PSA) Membranes treated with high-frequency capacitive (HFC) low-temperature (LT) plasma of reduced pressure of glow in the different gas atmospheres and modes are presented in Table 1.

**Table 1. Membrane plasma-treating parameters.**

| Membrane polymer | Pore size, kDa | Gas atmosphere of plasma | Anode voltage, kV | Plasma-treated time, min |
|------------------|---------------|-------------------------|------------------|------------------------|
| PES              | 30            | Argon and nitrogen (70:30) | 3.5              | 4                      |
|                  |               | Argon and air (70:30)     |                  |                        |
|                  |               | Propane-butane           |                  |                        |
| PAN              | 25            | Argon and nitrogen (70:30) | 5.5              | 4                      |
|                  |               | Argon and air (70:30)     |                  |                        |
|                  |               | Argon and propane butane (70:30) |          |                        |
| PSA              | 20            | Argon and nitrogen (70:30) | 1.5              | 1.5                    |
|                  |               | Argon and air (70:30)     |                  |                        |
|                  |               | Air                      | 7.5              | 4                      |

The total result of all plasma running processes on the surface of a polymer film is a change in its topography, the qualitative confirmation of which is embodied in the form of microimages and quantitative corresponding protrusion histograms, obtained by the AFM method with the aid of a probe microscope of the brand «MultiMode V» and membranes are presented for the PES in figures 1 and 2.

**Figure 1. Images of the PES membrane surface: a) initial; plasma-treated; b) in argon and nitrogen medium; c) in argon and air medium; d) propane and butane medium.**
Analyzing of the images presented in Figure 1 shows surface deformations of modified PES filter elements (figure 1b-d) compared to the original sample (figure 1a), clearly with the membrane plasma treated in propane and butane (figure 1d) has a different structure. Similar phenomena have been identified for PAN membranes. In the case of PSA filter elements, the gas atmosphere of argon and propane butane is replaced by air as a more economical carrying agent. Thus, the visual changing of the PSA membrane surface, plasma-treated in the air is similar to the deformations of the PSA membrane plasma-treated in argon and nitrogen, argon and air.

As a result of the PES modification of the membranes in the samples under investigation, in all cases the increase in the roughness of the elevation of the protrusions is observed, as shown in figure 2, due to the predominance of the etching process in plasma-treating. In the case of the PAN and PSA filter elements, a decrease in roughness and, accordingly, smoothing of the surface due to the greater influence of the processes of chemical deformation and deposition of gaseous destruction products have been identified.

One of the processes at the action of plasma is the oxidation of the polymer surface, and therefore with the analysis of the method IFPI of IR-spectrography with the use of the IR-spectrometer «Avatar-360» investigations of plasma-treated membranes have been studied.

As a result of IR-analysis of the initial PAN of membrane absorption bands specific for polyacrylnitrile structural fragments were marked. Stretch vibration of bond C-H of group CH2 2850 and 2919 cm⁻¹, nitrile group C≡N at 2242 cm⁻¹, stretch vibration at 923 cm⁻¹, as well as pendular oscillations CH₂ at 722 cm are referred to the latter.

The greatest difference of absorption bands of the considered spectra between the initial and plasma-treated PAN membrane in hydrophilic medium of argon and nitrogen, argon and air is observed in the area of stretch vibration C=O which also advance to increase the amount of absorbed water recorded in the area of 3300 cm⁻¹ wide band. For PAN membrane processed in hydrophobic medium of argon and propane-butane changes in the absorption bands mentioned above is less significant. Besides, deformation vibrations of aliphatic CH₂, CH₃ for all plasma-treated filter-elements are recorded in the area of 1452 cm⁻¹.
Likewise an increase in the spectral bands of plasma-treated PES and PSA membranes is observed in hydrophilic media of argon and nitrogen, argon and air, and air in the region of the C-O group formed as a result of oxygen cleavage of the C=O and C=C bonds on the polymer surface.

The end result of plasma modification of polymer membranes is a change in their contact properties, in particular, wettability, which is especially important when separating liquid media. In this regard, the wetting angle was measured by the SD method using the Kruss DSA 20E apparatus, the results of which for PSA membranes are shown in figure 3.

![Figure 3. Wetting angle wetted with distilled water drop of PSA membrane surface: a) initial, plasma-treated: b) in argon and nitrogen medium, c) in argon and air medium, d) in air medium.](image)

As shown by the data presented in figure 3, as a result of plasma treatment of the initial PSA membrane, which wetted by the water drop angle value was $\alpha = 59.6^\circ$ (figure 3a) in argon and nitrogen medium the considered parameter is decreased up to $\alpha = 47.9^\circ$ (figure 3b), in argon and air medium up to $\alpha = 43.5^\circ$ (figure 3c), in air medium up to $\alpha = 19.5^\circ$ (figure 3d), thus the surface becomes more hydrophilic. Also, an increase in wettability occurs as a result of plasma treatment of PES and PAN filters in argon and nitrogen, argon and air media, and when exposed to argon and propane-butane plasma, the parameter under consideration increased from $\alpha = 75.3^\circ$ to $\alpha = 97.9^\circ$ and from $\alpha = 34.3^\circ$ to $\alpha = 74.5^\circ$, respectively, which causes an increase in the hydrophobicity of these membranes.

The increase in hydrophilicity determines the purposefulness of the plasma modification of membranes under the parameters mentioned above in order to intensify the separation of the hydrophilic phase from hydrophobic components in liquid mixtures. Such systems correspond to oil-water emulsions (OWE), which are formed in industry in the form of lubricants, washing solutions, refinery drains, etc. In this regard, the testing of studied plasma-modified membranes in the process of separation of OWE was conducted.

Table 2 shows the results of separation of 3% OWE PSA by membranes with a mass of cut-off particles of 20 kDa, processed by plasma in air at a voltage of $U = 1.5-7.5$ kV and an exposure time $\tau = 1.5-7$ minutes. The chemical oxygen demand (COD) was selected as the component to be determined as a complex indicator of the total content of organic components of OWE before and after membrane separation. OWE is prepared by mixing 3% I-20A oil, 0.3% Kosintol-242 surfactant and 96.7% distilled water, respectively. The membrane is a flat round filter element with a surface area of 0.0017 m$^2$. The experiment was carried out in a laboratory ultrafiltration separation unit under the pressure of 0.2 MPa in the “cross-flow” mode with a volume of the separated mixture of 50 cm$^3$. 

Table 2
Table 2. COD of the emulsion in the process of PSA separation by membranes.

| U, kV | COD, mg O/dm³ | τ, min |
|-------|---------------|--------|
|       | 1.5 | 4 | 7 |
| 1.5   | 1617 | 1590 | 334 |
| 3.5   | 1858 | 1281 | 474 |
| 5.5   | 882  | 807  | 454 |
| 7.5   | 831  | 98   | 474 |
| Initial membrane | 2311 | |
| Emulsion | 22750 | |

According to the data from table 2, in all cases the content of organic matters after separation of OWE by plasma-treated membranes is less compared to the initial filter, which indicates their greater efficiency. The least value COD = 98 mg O/dm³ was revealed when using a PSA membrane treated with air plasma at U = 7.5 kV and τ = 4 min. Thus, the efficiency was more than 99%. Note, that the obtained result is the best among all gaseous media, and also the best among all tested membranes. Hydrophobic PES and PAN filters processed by the gaseous medium plasma contained propane-butane mixture did not separate the emulsion, as expected.

Generally, when testing hydrophilic PES membranes, in 87 results of 96 obtained results (90.6 %) enhancement of efficiency after plasma treatment (43 in argon medium, 44 in argon and air medium) was registered, and productivity increases in all cases. For PAN filter elements, 48 results are presented, 32 of which (66.7%) show an increase in efficiency as a result of plasma exposure (19 in argon and nitrogen medium, 13 in argon and air medium) and in all cases there is also an increase in productivity. 23 results of 36 results of plasma-treated PSA membranes (63.9%) showed an increase in efficiency (2 in argon and nitrogen medium, 9 in argon and air medium, 12 in air medium), productivity in most cases increases.

Thus, HFC LT plasma impact on polymeric membranes contributing to an increase in their hydrophilicity contributes to an increase in the performance of polymer membranes in the process of separation of a water-oil emulsion.

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