

SURFACE POLYMERIZATION OF MONOMERS ON THE POLYETHYLENE TEREPHTHALATE MEMBRANE IN LOW TEMPERATURE PLASMA FOR WATER TREATMENT

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The plasma-chemical method of track-etched polyethylene terephthalate membranes' surface modification by monomers with different chemical structure was developed. Physicochemical properties of modified membranes were investigated. The authors showed the possibility of obtaining membranes with the required properties.

Keywords: polyethylene terephthalate membranes, plasma-chemical modification, functional monomers, surface properties.

Introduction

Membrane filtration is one of the most prospective technological processes of complex mixtures separation. Track membranes take an important place among the materials used in this process (TM) [1, 2]. Due to a number of properties, especially low thickness and high homogeneity of pores, TM have insignificant resistance to the flow through the filtering medium, high selectivity of separation, low adsorption of solutes and ease regeneration. All this favorably distinguishes TM from other filtering materials and makes them widely used in medicine and biotechnology.

A new trend has been developed in technology of track membranes in recent years – membranes' surface modification, which refers to a deliberate change in the structure of membranes' surface layer, which leads to obtaining of required properties. There are a lot of physical and chemical methods of modifying the surface properties of polymeric materials.

The plasma-chemical method has the greatest advantage over the others [3 – 6]. Specific effect of low temperature plasma on different materials defined its widespread use in solving various technological problems in scientific research practice. This specificity is the combination of high chemical activity with low gas temperature, which makes plasma an effective tool in polymer modification. An additional advantage of plasma action is that it only impacts small depths, not exceeding a few micrometers, keeping the bulk properties of a material unchanged. Thus, plasma treatment actually converts the polymer into a new composite material.

The main advantage of the plasma-chemical method is the possibility to use it for modification of a wide range of chemical compounds (both organic and inorganic). Chemical reactions that take place in plasma discharge and determine the polymers' surface modification are mainly defined by the composition of the plasma gas. When monomers of organic compounds are injected into plasma, the following processes are observed: monomer polymerization and deposition of polymer film onto the polymers' surface. New surface properties largely depend on the type of chemical compound used as the plasma gas. The process of applying a thin polymer layer on the membrane's surface in plasma is particularly interesting, as it allows obtaining a membrane with predetermined functional characteristics.

It can thus be concluded that polymerization initiated by plasma is a highly effective method of polymers' and polymer membranes' surface modification. This method allows for very precise and purposeful modification by plasma processing of polymers or plasma-initiated polymerization. It is worth noting, that this method is applicable for almost any polymeric material.

The purpose of our study was:

- to study track membranes' surface modification in low-temperature plasma;
- to develop a way of modifying PET membranes by plasma with monomers of different chemical nature to obtain membranes with predetermined functional characteristics.

Experimental part

2.1 Materials

Track-etched polyethylene terephthalate (PET) membranes with pore diameter of 0.05 mm and thickness of 10 microns (production of JINR Dubna, Russia) were used in this work.

Functional monomers for modification are methacrylic acid (MAC), vinylpyrrolidone (VP), tetrafluoroethane (TFE).

2.2 Methods

Grafting of monomers to the polyethylene terephthalate (PET) membrane's surface was conducted in the developed plasma-chemical installation using high-frequency (HF) discharge of 13.56 MHz. The conditions of membranes' surface plasma-chemical modification were experimentally chosen: pressure 13.32 Pa., temperature 40-50 °C, monomer flow rate 8 – 10 cm³/min, power 25 – 30 W (Fig. 1)

The efficiency of plasma-chemical modification was estimated by measuring: membrane surface contact angle, grafting degree of functional monomers, and volumetric water flow through the membrane by the standard methods [7].

Results and their discussion

Physicochemical modification of hydrophobic membrane allows:

- to make the surface hydrophilic (including the surface of pores), which reduces their susceptibility to contamination (such as proteins, humic substances, etc.),
- to provide specific separation characteristics of membranes due to the formation of certain functional groups on membranes' surface. Plasma-induced graft polymerization is one of the most effective and easy methods membranes surface hydrophilisation among many others.

The following chemical reactions occur in oxygen plasma during membrane's modification: the C–O bond is broken, radicals are formed and then oxidized, and, as a result, a carboxyl group and a double bond are formed (Fig. 1).

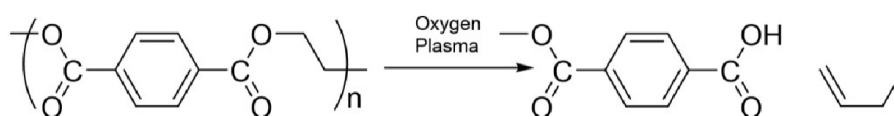


Fig. 1. Chemical transformations in oxygen plasma.

During the plasma-chemical modification of membrane with methacrylic acid, radicals of acrylic acid and radicals on the membrane's surface are formed, Carbon chain is grafted and growing, and polymethylmethacrylate is formed (Fig. 2).

During the membrane surface modification with vinylpyrrolidone (Fig. 3) and tetrafluoroethane (Fig. 4) similar chemical reactions occur, by radical addition and formation of respective polymer on membrane's surface.

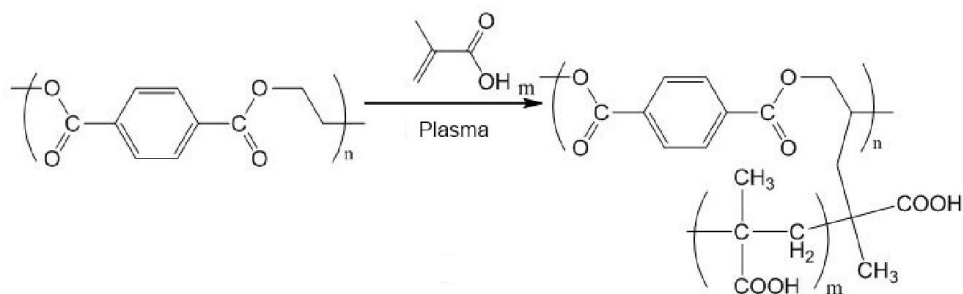


Fig. 2. Chemical changes in methacrylic acid plasma.

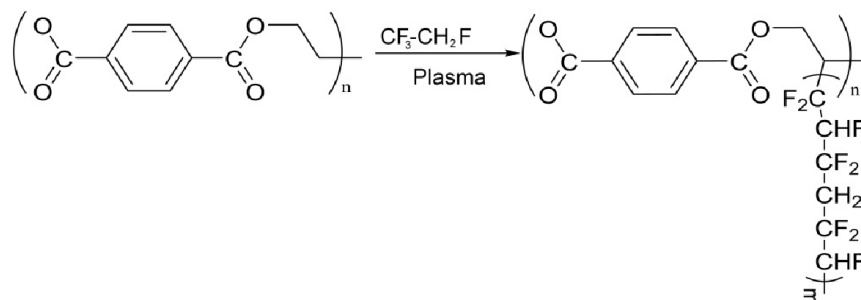


Fig. 3. Chemical changes in vinylpyrrolidone plasma.

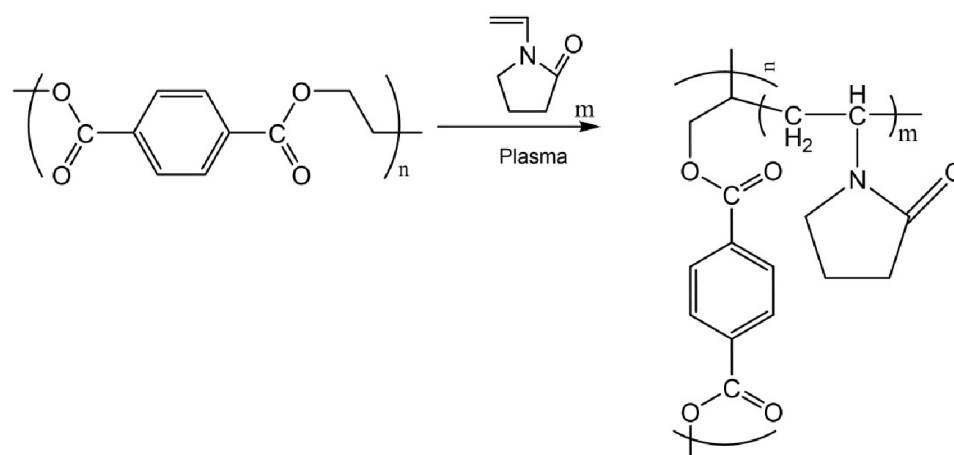


Fig. 4. Chemical changes in tetrafluoroethane plasma.

The structural changes of membrane surface were studied by IR-spectroscopy. Spectrum of the membrane, modified in oxygen plasma, shows an increase of a peak at 1708.33 cm^{-1} , which confirms that during modification the bonds are broken and carboxyl groups are formed.

Analysis of the IR-spectrum of the membrane surface, modified with polymethacrylic acid, indicates the intensity of stretching vibrations of the C=O carboxyl group (1706.42 cm^{-1}) compared to unmodified membrane. New absorption band also appears at 3423.10 cm^{-1} , which corresponds to the stretching vibrations of O-H bond; at 2964.17 cm^{-1} , which corresponds to the asymmetric stretching vibrations of polymethacrylic acid's CH₃-group; and at 1178.44 cm^{-1} , which corresponds to the stretching vibrations of C-O bond.

Grafting of polymethacrylic acid is additionally confirmed by the increasing intensity of O-H deformation vibration in carboxyl group at frequency of 1408.41 cm^{-1} . Analysis of the IR-spectrum of membrane surface modified with vinylpyrrolidone revealed the appearance of a new absorption peak with a wavelength of 1655 cm^{-1} , which corresponds to fluctuations of amide-carbonyl group in the N-vinyl-2-pyrrolidone ring. Furthermore, when increasing the degree of PVP grafting, the intensity of these peaks increased as well. Absorption at 1713 cm^{-1} is typical

for aromatic compounds with C–H and C=O bonds. Also, there is an increase of peak intensity at 3394 cm^{-1} in the IR-spectrum. It also indicates that grafting is actually happening.

Research of the tetrafluoroethane-modified membrane surface structure by IR spectroscopy, shows the presence of several bands that are characteristic for polytetrafluoroethylene. These are bands with wavelengths of 1160 and 1220 cm^{-1} , which correspond to symmetric and asymmetric $-\text{CF}_2-$ stretching vibrations of polytetrafluoroethylene; absorption bands at 513 and 555 cm^{-1} are associated with $-\text{CF}_2-$ circular and polygonal deformation vibrations; absorption bands in the $1400\text{--}1450\text{ cm}^{-1}$ region correspond to C–C stretching vibrations in main polymer chain and band with wavelength of 990 cm^{-1} corresponds to $-\text{CF}_3$ symmetric stretching vibrations. IR spectroscopy data confirm the fact that polymer, which was synthesized by plasma discharge of 1,1,1,2-tetrafluoroethane, consists of $-\text{CF}_2-$ groups.

While studying modification of track-etched membranes with monomers, it was found out that increase of processing time leads to sample mass growth due to the grafting of monomers to the membrane's surface (Fig. 5). The opposite effect is observed while using oxygen as the aerogenous gas – the sample weight decreases due to the destruction and etching of the track-etched membrane's surface.

The surface properties of PET membranes modified with oxygen, methacrylic acid and vinylpyrrolidone using the plasma-chemical method were studied by water contact angle measuring. The results are shown in Table 1.

Table 1. The membranes' surface contact angles

Plasma gas	Duration(sec)			
	30 sec	120 sec	210 sec	300 sec
Oxygen	28	23	23	23
Methacrylic acid	57	49	45	45
Polyvinylpyrrolidone	47	39	34	34

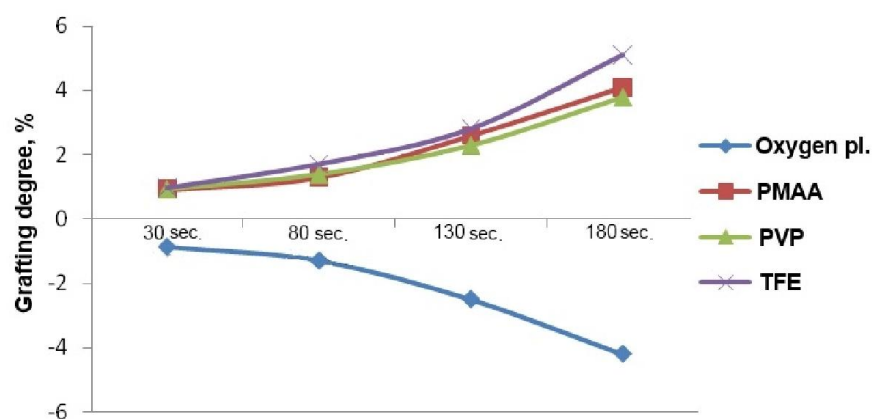


Fig. 5. Dependence between the grafting degree and the time.

The extrapolation of data was shown using the graphs, which represented the dependence between the membrane surface contact angle and plasma processing time. Summary of membrane hydrophilicity is also given (Fig. 6 – 7).

The investigation of the process of track-etched membrane modifications has shown that the hydrophilicity of all membranes, except when using TFE (Fig. 7), increases. This graph also represents that the optimal time for sample modification is 80 sec, because all significant changes in the values of contact angles occur up to 80 sec and then almost no change take place.

Protein adsorption on plasma-modified membrane surface was also studied in a variety of conditions.

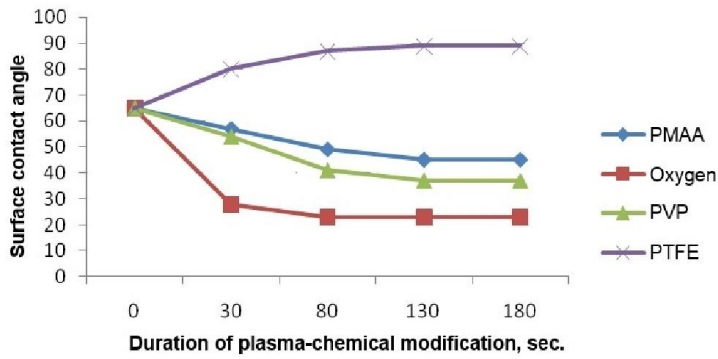


Fig. 6. Dependence between the surface contact angle and plasma processing time of the track-etched membranes.

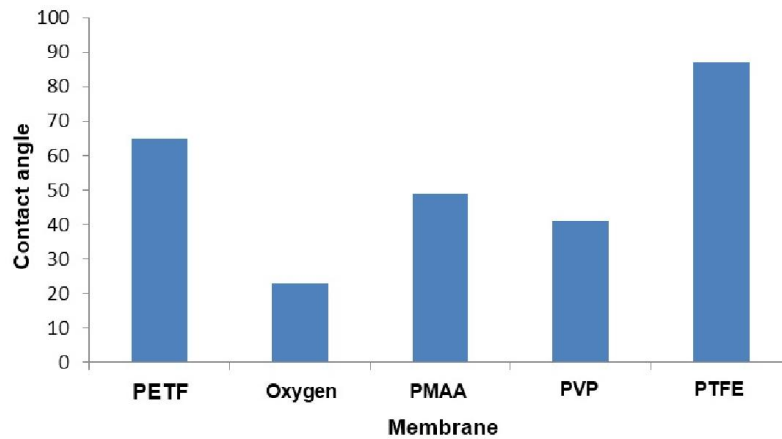


Fig. 7. The contact angles obtained at the optimal time of modification by low-temperature plasma.

Plasma graft polymerization leads to the decrease in the effective radius of membrane pores, which causes transmembrane volumetric water flow value to drop. Thus, the degree of grafting can be characterized by the change of volumetric water flow through the membrane before and after modification.

As shown in Fig. 8, there was a strong decrease of the volumetric water flow through the membranes, which were plasma-treated for 30 and 120 sec, which can be explained by monomer grafting to the surface. In case of longer modification time the gradual decrease of the volumetric water flow occurs. After 120 sec of treatment, the decrease becomes less visible, which can be explained by surface saturation with monomers. Considering the results above, the optimal duration of modification is 120 sec.

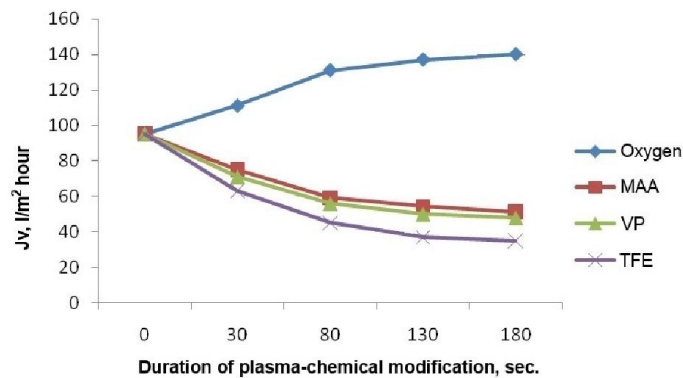


Fig. 8. Dependence between the volumetric water flow through the membrane and the duration of plasma-chemical modification.

Conclusions

In this study, the plasma-chemical methods of the PET track-etched membrane surface modification were developed with the purpose of changing their hydrophilic/hydrophobic characteristics. Optimal modification parameters to obtain the membranes with predetermined functional properties of their surface (pressure 10 – 20 Pa, frequency 13.56 MHz, temperature 40-60 °C, power 25 – 30 W, gas flow rate 8.10 sm³/hv) were experimentally obtained. The presence of characteristic absorption bands for modifiers was proven by infrared spectroscopy (C=O 1706.42 cm⁻¹; –CF₂– 1160 cm⁻¹ and 1220 cm⁻¹). The authors showed the possibility of plasma-chemical surface modification of PET track-etched membranes with the purpose to obtain the required properties.

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ПОВЕРХНОСТНАЯ ПОЛИМЕРИЗАЦИЯ МОНОМЕРОВ НА ПОЛИЭТИЛЕНТЕРЕФТАЛАТНОЙ МЕМБРАНЕ ПРИ ВОЗДЕЙСТВИИ НИЗКОТЕМПЕРАТУРНОЙ ПЛАЗМЫ ДЛЯ ОБРАБОТКИ ВОДЫ

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Разработана плазмохимическая методика модификации поверхности полиэтилен-терефталатной мембраны мономерами различной химической структуры. Исследованы физико-химические свойства модифицированных мембран. Авторы продемонстрировали возможность получения мембран с требуемыми свойствами.

ПОВЕРХНЕВА ПОЛІМЕРІЗАЦІЯ МОНОМЕРІВ НА ПОЛІЕТИЛЕНТЕРЕФТАЛАТНЬОЇ МЕМБРАНИ ПРИ ДІЇ НИЗЬКОТЕМПЕРАТУРНОЇ ПЛАЗМИ ДЛЯ ОБРОБКИ ВОДИ

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Розроблена плазмохімічна методика модифікації поверхні поліетилен-терфталатної мембрани мономерами різної хімічної структури. Вивчено фізико-хімічні властивості модифікованих мембран. Автори продемонстрували можливість отримання мембран з потрібними властивостями.