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ОСАЖДЕНИЕ ПОКРЫТИЙ НА ПОЛИУРЕТАН В ДИЭЛЕКТРИЧЕСКОМ БАРЬЕРНОМ РАЗРЯДЕ АТМОСФЕРНОГО ДАВЛЕНИЯ В ПАРАХ C_2H_4-He

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В работе показана возможность использования диэлектрического барьерного разряда для осаждения полимерных пленок на поверхность полиуретановых подложек. Планарный барьерный разряд атмосферного давления возбуждался в проточной камере в атмосфере этилена при фиксированном расходе газа. В качестве газа-носителя выступал гелий. Расходы газа-носителя и рабочего газа были фиксированными и составляли 10 мл/с. Частота диэлектрического барьерного разряда составляла 50 Гц, средний ток разряда был 2 мА при полной мощности, вкладываемой в разряд 16 ВА. Время осаждения варьировалось в диапазоне от 30 до 1200 с. Показано, что в исследованных условиях разряд имеет диффузную форму. Исследование морфологии поверхности и элементного состава осажденной пленки выполняли методом сканирующей электронной микроскопии и методом энергодисперсионной спектроскопии, а также с использованием атомно-силовой микроскопии. Смачиваемость поверхности определяли методом краевых углов смачивания методом фотофиксации капель. Метод краевых углов смачивания по полярным (дистиллированная вода) и неполярным (дийодометан, глицерин, минеральное масло) жидкостям показал, что смачиваемость осажденных покрытий выше, чем у исходной подложки. Рост полимерной пленки в низкотемпературной плазме состоит из трех этапов – образование равномерной пленки, повторяющей рельеф поверхности, рост макромолекулярных конусов на поверхности уже образовавшегося покрытия и деструкция и травление пленки. Показано, что в нашем случае осажденная пленка имеет островковый характер, «островки» равномерно распределены по поверхности, расположены близко друг к другу и имеют практически одинаковый размер.

Ключевые слова: газоразрядная плазма, барьерный разряд, осаждение, этилен

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FILMS DEPOSITION ON POLYURETHANE USING ATMOSPHERIC PRESSURE DIELECTRIC BARRIER DISCHARGE IN C_2H_4-He

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The paper demonstrates the possibility of using a dielectric barrier discharge for the deposition of polymer films on the surface of polyurethane substrates. A planar barrier discharge of atmospheric pressure was excited in a flow reactor in an atmosphere of ethylene at a fixed flow rate. Helium as the carrier gas was used. The carrier gas and working gas flow rates were fixed at 10 ml/s. The frequency of the dielectric barrier discharge was 50 Hz, the average discharge current was 2 mA at a total power put into the discharge of 16 VA. The deposition time varied in the range of 30–1200 s. It was shown that under the conditions studied, the discharge has a diffuse form. The study of the surface morphology and elemental composition of the deposited film was carried out using scanning electron microscopy and energy-dispersive spectroscopy, and atomic force microscopy. Surface wettability was determined by the contact angle method and the method of photofixation of drops. The contact angle method for polar (distilled water) and non-polar (diiodomethane, glycerol, mineral oil) liquids showed that the wettability of the deposited coatings is higher than that of the original substrate.

Keywords: gas discharge plasma, barrier discharge, deposition, ethylene

INTRODUCTION

Current environmental issues include the increasing amount of industrial oil-containing wastewater, such as from oil refineries. In addition, frequent leaks of organic solvents are observed during various industrial processes [1, 2]. In recent decades, selective removal of oils and non-polar organic solvents from water resources has been considered as an effective strategy for cleaning/restoring water resources [3]. An example is the approach that involves the use of functional materials with simultaneous superhydrophobic and superoleophilic properties (having a water contact angle of more than 150° and an oil contact angle of less than 10°), that is, materials with sharply opposite wettability in relation to water and oils, as well as to non-polar organic solvents [4-6].

Highly porous three-dimensional (3D) structures with high absorption capacities are used as sorbents [7-9]. However, to impart selectivity to such materials with respect to liquids of different chemical nature, as a rule, it is necessary to change the chemical composition of its surface and its morphology. Various methods, mainly of a purely chemical nature, are used to functionalize the surface.

Today, low-temperature gas discharge plasma has become widely used as a tool for processing and modifying the surface of various materials [10-12]. Some studies have shown the significant potential of atmospheric pressure plasma for effective modification of the surface of three-dimensional porous materials [13-21]. This paper proposes a method for depositing coatings on the surface of glass substrates in an atmospheric pressure dielectric barrier discharge in an atmosphere of ethylene vapor and helium carrier gas.

EXPERIMENTAL SETUP AND EXPERIMENTAL PROCEDURE

A plane-parallel dielectric barrier discharge (DBD) system consisting of two parallel electrodes separated by a dielectric glass barrier was used in the work (Fig. 1). A high-voltage alternating voltage with a frequency of 50 Hz was applied to the upper and lower electrodes (electrode size 25 × 25 mm), due to which a dielectric barrier discharge was excited in the dielectric gap (d = 2 mm). Alkaline-aluminosilicate glass with a thickness of 0.97 mm was used as a dielectric barrier. The geometric dimensions of the glass were selected in order to prevent discharge leaks bypassing the dielectric barrier.

Glass cover glasses were used as a substrate and were placed on the lower electrode of the DBD cell. A mixture of helium (grade B, Khimreaktiv, Russia) and ethylene (C_2H_4, high purity (99.99%), Khimreaktiv, Russia) was used as a plasma-forming gas. The helium and ethylene flows were 10 ml/s. Before the deposition process, the sealed chamber was purged with pure helium for 2 min at a flow rate of ~45 ml/s. Two minutes after the start of the purging and the establishment of the working gas flows, the discharge was excited. The deposition time varied in the range from 30 to 1200 s.

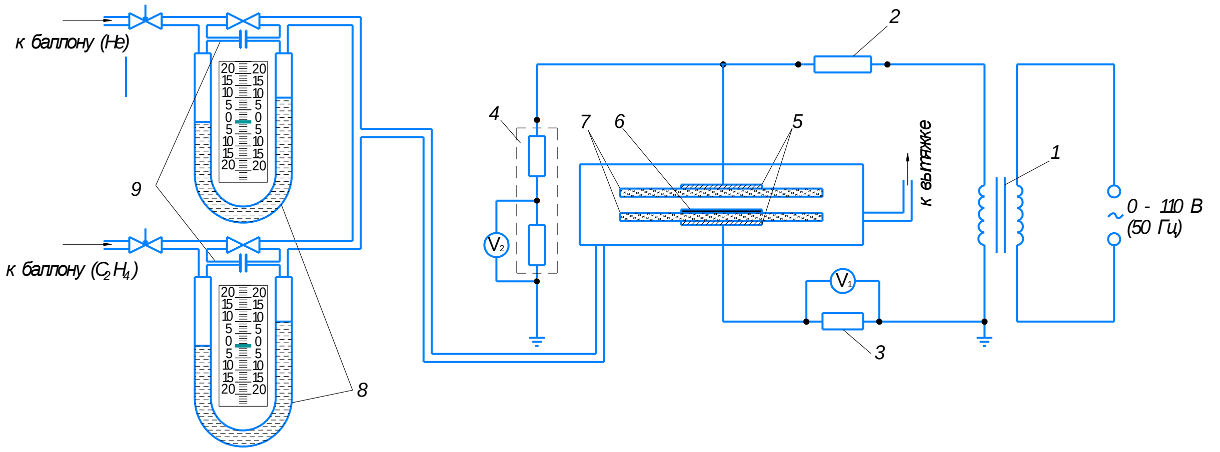
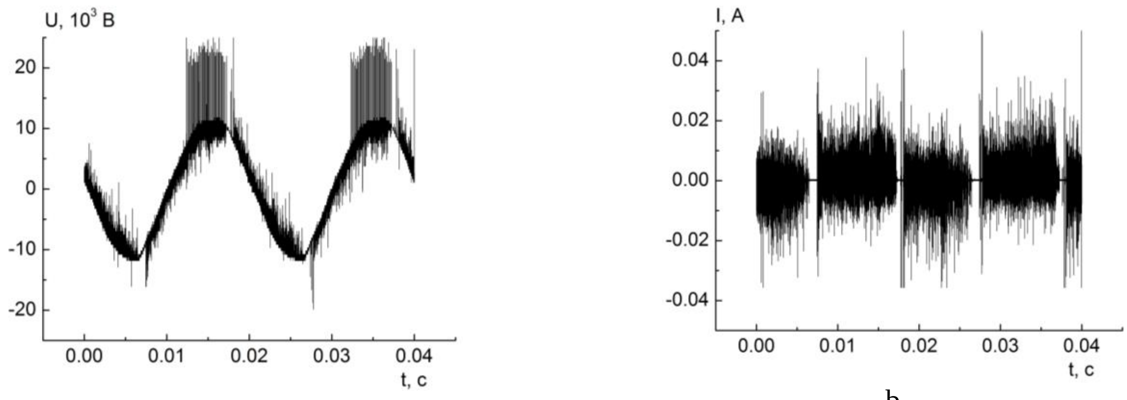


Fig. 1. The scheme of the experimental setup. 1 - step-up transformer, 2 – ballast resistance, 3 - current shunt, 4 – voltage divider, 5 – copper electrodes, 6 – substrate; 7 – glass dielectric; 8, 9 – He and C_2H_4 U-shaped pressure gauge; V_1, V_2 – current and voltage oscilloscope channels

Рис. 1. Схема установки: 1 – высоковольтный трансформатор, 2 – балластное сопротивление, 3 – токовый шунт, 4 – делитель напряжения, 5 – медные электроды, 6 – образец, 7 – диэлектрические барьеры, 8, 9 – U-образный манометр, 10 – капилляр, V_1 – первый канал осциллографа (измерение тока разряда), V_2 – второй канал осциллографа (измерение напряжения)



a b

Fig. 2. Oscillograms of voltages (a) and currents (b) during the deposition process

Рис. 2. Осциллограммы напряжений (а) и токов (b) горения разряда в процессе осаждения

Within 1 hour after the deposition process was completed, the contact angle of the test liquids on the deposited coatings was measured. The test liquids were deionized water (as a polar liquid), diiodomethane (as a strongly non-polar liquid), glycerol (as a weakly non-polar liquid), and VM-6 mineral oil. The angles were determined using the ImageJ add-on – Axisymmetric Drop Analysis

The surface morphology and elemental composition of the deposited film were studied using a TESCAN VEGA3 SBH scanning electron microscope (Czech Republic) with an Aztec EDS elemental energy dispersive analysis attachment (Oxford Instrumental, England). The surface was also studied using a Solver P-47 Pro scanning probe microscope (NT MDT, Russia).

MAIN RESULTS AND DISCUSSION

Fig. 2 shows the oscillograms of current and voltage during discharge combustion. As in the case of discharge in the He/HDMS mixture, studied in [22], the discharge is diffuse. The root-mean-square current of discharge combustion was 1.5-2 mA. The total power input into the discharge, at which the deposition process was carried out, was 16 VA. The power was determined by integrating over the period of the product of current and voltage.

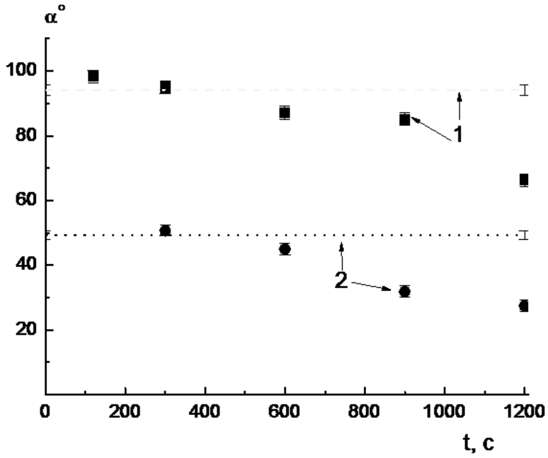


Fig. 3. Kinetics of water (1) and mineral oil (2) contact angles changes. Lines – the contact angle of original substrate
Рис. 3. Кинетика изменения краевого угла смачивания по воде (1) и маслу (2). Линии – величина угла смачивания исходной подложки

Fig. 3 and 4 show the results of measuring the contact angles of wetting of the substrate surface with deposited coatings depending on the deposition time. As can be seen from Fig. 3, deposition leads to a simultaneous increase in both the hydrophilicity and oleophilicity of the surface. Wettability with non-polar liquids (Fig. 4) also increases with increasing deposition tim.

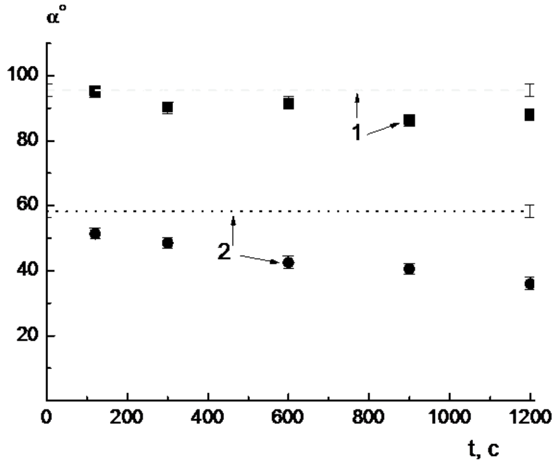


Fig. 4. Kinetics of glycerol (1) and diiodomethane (2) contact angles changes. Lines – the contact angle of original substrate
Рис. 4. Кинетика изменения краевого угла смачивания по глицерину (1) и дииодометану (2). Линии – величина угла смачивания исходной подложки

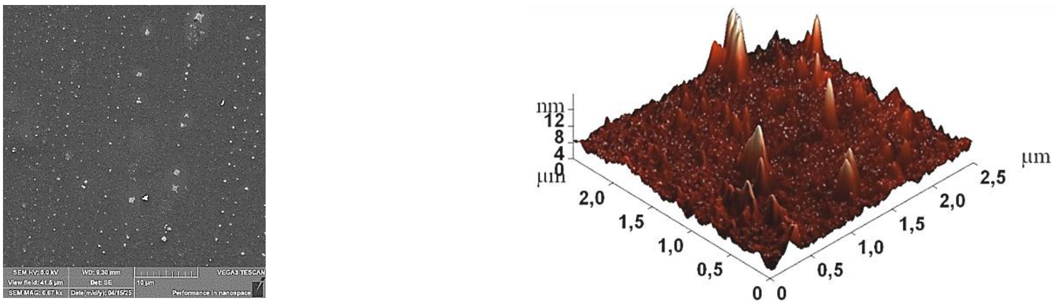
Using the measured wetting angles of the obtained coatings, the polar, dispersion and total surface energies were calculated. The total surface tensions of water and diiodomethane, their polar and dispersion components, and known relationships [23] were used for the calculation. The calculation results are given in Table. It can be noted that both the total energy and its components increase with increasing deposition time. At the same time, the dispersion component of energy, which is usually associated with surface roughness, tends to a quasi-stationary value.

Table

Surface energy calculation results for coatings

***Таблица*. Результаты расчета поверхностной энергии для покрытий**

Coating application time, s	Contact angle of H_2O, deg.	Contact angle of CH_2I_2, deg.	Polar component, mJ/m^2	Dispersion component, mJ/m^2	Total surface energy, mJ/m^2
0	94.1±1.8	58.3±1.9	1.7±0.3	27.9±0.5	29.6
600	87.1±2.1	42.5±2.0	2.5±0.2	36.3±2.1	38.3
1200	66.3±2.0	36.0±1.9	11±0.9	34.3±3.7	45.3



a b

Fig. 5. SEM (a) and AFM (b) images of coatings. Treatment time 5 min
Рис. 5. СЭМ- (a) и АСМ- (b) изображения полученного покрытия. Время осаждения 5 мин

Images of the coatings obtained using scanning electron and atomic force microscopes are shown in Fig. 5.

It should be noted that due to the small thickness of the coatings (~10 nm, Fig. 5) and the penetration depth of the probing electrons of ~1 μm, the elemental analysis showed the composition of the substrate rather than the coating.

The growth of a polymer film in low-temperature plasma consists of three stages: the formation of a uniform film repeating the surface relief, the growth of macromolecular cones on the surface of the already formed coating, and the destruction and etching of the film [24]. It can be assumed that the small light inclusions in this picture are those same macromolecular cones. These "islands" are evenly distributed over the surface, are located close to each other, and are almost the same size.

CONCLUSION

The paper demonstrates the possibility of depositing a polymer film in a planar dielectric barrier discharge of atmospheric pressure in a helium-ethylene medium. It has been established that the deposited coating leads to an increase in the wettability of the surface of the original substrate by both polar (distilled water) and non-polar (glycerin, diiodomethane, mineral oils) liquids.

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