Modification of Surface Properties of Ultrahigh-Molecular – Weight Polyethylene Films by DC Discharge

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Abstract. The methods of surface modification of ultrahigh-molecular-weight polyethylene (UHMPE) by the low-temperature plasma are considered. Installations for treatment of polymers with various types electric discharges as well as the methods for studying the changes occurring on the polymer surface are described. The experimental results are given concerning properties of 100 μm UHMWPE film before and after treatment by the low pressure air dc discharge. The film samples were placed at the anode. The measurements of the peel resistance (T-test according to ASTM 1876-01) of adhesion joint of modified UHMWPE with polyimide and polytetrafluoroethylene films were obtained using polyurethane adhesive.

1. Introduction
Ultrahigh-molecular-weight polyethylene (UHMWPE) (molecular weight of 1.5×10⁶ to 6×10⁶) is characterized by high mechanical properties, resistance to corrosive chemicals, a low water uptake, a low coefficient of friction, and high abrasion resistance. These properties determine the use of UHMWPE in many areas of technology and, since recently, in medicine and biology, including the manufacture of artificial joints and implants for surgery and orthodontics. Currently, UHMWPE is manufactured under various brand names: Polymín™ SK (BASF, Germany), Polystone M™ (Roechling, Germany), Tivar™ (Quadrant, Belgium), Tecafine PE10™ (Ensinger, Germany), Okulen 2000™ (SP-Plast, Finland), GUR™ (Ticona, Germany), Chirulen™ (Poly-Hi Solidur, Germany). UHMWPE is produced also by Goodfellow (United Kingdom) and Braskem (Brazilian Chemicals).

Note that the UHMWPE surface is hydrophobic and for many applications, for example, in lining, its contact and adhesive properties require a substantial improvement. It is known that low-temperature plasma treatment is currently one of the most technically promising and environmentally friendly methods for surface modification of polymer materials. This method makes it possible to alter the surface properties of a nanosized polymer layer without changing its bulk characteristics [1–6].

In this paper we consider some methods for modification the surface of UHMWPE films by low-temperature plasma and data of adhesion properties of the obtained films [5, 7, 8].

The goal of this study is also the examination of adhesion properties of UHMWPE films using the T-peel test for the contact of this film with PTFE and PI films and Polyurethane adhesive.

2. Methods of plasma modification of UHMWPE films
To modify UHMWPE films, low- or atmospheric-pressure discharge excited over a wide current frequency range, including the utility (50 or 60 Hz), medium (20–90 kHz), radio (RF, 13.56 MHz) and the microwave (MW, 2.45 GHz) frequencies and DC discharge are used [8]. The treatment is carried
out using both laboratory setups, and industrial units. The schematics of the most commonly used installations are shown in Figures 1 and 2.

As an example, Figure 1 shows a schematic of an experimental dielectric barrier discharge (DBD) setup with an industrial ac power supply [9]. Glass-coated copper electrodes (4, 6) are arranged in the working chamber (5) at a distance of 7 mm from each other. The upper electrode (4) is connected to a 50-Hz high-voltage power source (3), and the lower electrode (6) is grounded. A sample of UHMWPE film was placed on the lower electrode; Ar, He, N₂, or air was used as a plasma gas; and methyl methacrylate was the precursor for the thin film of another chemical nature deposited on the sample surface by plasma polymerization.

Figure 2 shows a schematic of an APC 2000 industrial unit (Sigma Technologies Int.) in which a process for modifying UHMWPE films by treatment in a 90-kHz discharge in air was studied [10]. The working gas was a mixture of He (3) and water vapor (1, 2) fed directly through hollow electrodes (4) in a certain ratio. A 1-mm thick sheet was mounted on a rotating electrode (6) with an Al₂O₃ dielectric coating and treated by DBD with an input power from 0.861 to 2.58 W/cm² for 0.4–40 s.

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**Figure 1.** Schematic of an ac DBD reactor: (1) process-gas cylinder, (2) metering valve, (3) high-voltage power supply (50 Hz), (4) upper electrode, (5) working chamber, (6) grounded lower electrode, (7) pressure gauge, (8) vacuum valve, and (9) backing pump [9].

**Figure 2.** Schematic of the commercial APC 2000 atmospheric pressure discharge plasma machine: (1) evaporator, (2) heaters, (3) He supply line, (4) grounded electrodes with He and water vapor supply, (5) discharge power source (90 kHz), (6) rotating grounded electrode, and (7) dielectric coating [10].
Oosterom et al. [11] used single lap-joint shear testing to determine the adhesive strength for UHMWPE sheets (thickness 1.4 mm). Samples of UHMWPE (Chirulen 1020, Germany) were modified by corona discharge (TIGRES CKG unit, 50 Hz, Germany) or by RF glow discharge (TNO Laboratories, 13.56 MHz, the Netherlands). To make measurements, two specimens of a 110 × 25 × 1.4 mm size were lap-jointed with the adhesive MA300 (ITW Plexus, United Kingdom) to have a contact length of 20 mm. After holding for 24 h, the joint was examined using a Zwick 20 kN testing machine (Germany) at room temperature and crosshead speeds of 3 and 6 mm/min. The shear strength was 0.3 MPa for the initial sheet and increased to 1.06 and 0.93 MPa for the samples modified by the corona and the RF glow discharge, respectively.

Rodriguez-Santiago et al. [10] investigated surface changes using the ASTM 1876-01 T-peel test. Goodfellow UHMWPE films (75 μm) were modified by helium–water vapor DBD discharge using a SigmaTechnologies model APC 2000 (90 kHz) atmospheric pressure plasma system. Two specimens of a 15.2 cm×30.5 cm×75 μm size were bonded with the DevThane 5 polyurethane adhesive (Devcon, the United States). The sample prepared in this manner was rolled down with a roller for leveling and held for 24 h at room temperature. For measurements, 30.5 cm×2.5 cm strips were cut, and tests were performed using an MTS Synergie electromechanical testing machine at a crosshead speed of 0.4 cm/s. For the film modified over 15 s, the peel resistance increased tenfold from 0.25 to 2.5 N/cm.

3. Adhesion properties of UHMWPE films modified by DC discharge

Samples of the UHMWPE film of 100 μm thickness (Russia) were used in the study. The procedure for film modification by DC discharge and the installation were detailed in [12].

The samples of 35×40 mm were placed at the anode and treated at a working plasma gas air, pressure of 5–45 Pa and a discharge current of 50 mA for 10–60 s. Filtered atmospheric air with humidity of 50% was used as a working gas. The diameter of the electrodes is 180 mm, so the area of the dielectric sample is approximately 5% of the electrode area. In this case there was not any difference between the glow discharge with sample or without one. The discharge in this case is homogeneous.

The adhesive strength of the polymers studied was evaluated using a T-peel testing configuration according to ASTM 1876-01 [5, 10, 13]. The T-peel test is a test designed to determine the peel resistance (A) of adhesive bonds between flexible adherends. Standard Test Method for Peel Resistance of Adhesives (T-Peel Test) according ASTM 1876-01 is shown in Figure 3.

![Figure 3. Standard Test Method for Peel Resistance of Adhesives (T-Peel Test) according ASTM 1876-01. Test Panel and Test Specimen [13].](image)
The test specimens consisted of two 15.2 cm×30.5 cm films bonded together with a urethane-based adhesive (PU). The PU adhesive is a solution of polyurethane rubber in acetone and ethyl acetate. The adhesive was applied to the adhesive surfaces of 2 films, dried at 90°C for 5 min, then these surfaces were combined and held under a press at a pressure of 3 kg/cm$^2$ and T = 100°C for 1 min. The cured specimens were then cut into strips (see Figure 3) and tested. The peel tests were conducted on a Hounsfield H1K tensile machine at a speed of 100 mm/min. The result of the measurements is averaging over 10 tests.

Adhesion between pairs of UHMWPE/PTFE and UHMWPE/PI films was also studied. Samples of the PTFE film (60 μm, “Plastpolymer”, Russia) and PI (50 μm, PM-1, GOST-6-10-121-85, Russia) were used in the study.

The experimental values of the T-peel resistance (A) measured immediately after the plasma treatment according ASTM 1876-01 are given in the table 1.

**Table 1.** Experimental data on the peel strength (A)

| Sample                  | Adhesive | A, N/m |
|-------------------------|----------|--------|
|                         | Initial sample | Plasma treated |
| UHMWPE/ UHMWPE          | PU       | 12 ± 1 | 470 ± 30 |
| UHMWPE/PI               |          | 12 ± 1 | 457 ± 31 |
| UHMWPE/PTFE             |          | 10 ± 1 | 280 ± 24 |

From the data given, it can be seen that the initial films have very low adhesion. Processing by DC discharge at the anode leads to a multiple increase in the adhesion of the film pairs indicated in the table. The A value increases approximately 40 times for pairs of UHMWPE/UHMWPE and UHMWPE/PI, and 30 times for the UHMWPE/PTFE pair.

According to the data of X-ray photoelectron spectroscopy data [9,10] the processes of modifying UHMWPE films by oxygen and air plasmas results in formation in the surface layer of oxygen-containing functional groups. Apparently, increase in adhesion strength A (table 1) is due to the interaction of these polar groups (hydroxylic, carboxylic, fluoroanhydride and others) with the active groups of adhesive.

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**4. Conclusion**

Thus, in present paper on the basis of experiments conducted, we have demonstrated that the treatment of UHMWPE by the low temperature plasma, and more specifically, by the low pressure dc discharge is technologically effective and environmentally friendly method to improve its adhesion properties.

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