Plasma modification of deep layers of polymer materials

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Abstract: The article presents a new approach to plasma processing of polymers, based on the saturation of the intermolecular space of a polymer with high pressure gas and the ignition of a discharge in a polymer volume (in the resulting micro cavities) at the time of pressure relief. The process of plasma treatment of internal micro cavities inside a polyethylene film was studied. Using the example of Young's modulus, the possibility to influence the bulk characteristics of polymers by such processing is shown.

Keywords: Plasma treatment, polymer materials, polymer films modification, DBD discharge, Young's modulus

1. Introduction and target setting

Polymer materials treatment by plasma methods is a well-known efficient technology which has wide industrial utilization. Plasma modification is used for food packaging films modification, treatment of fabric and films for improving adhesion ability before painting or gluing and so on. But all these treatment methods treat the surface of plastic materials because in all existing systems plasma can be created only in gas surrounding polymer material [1,2]. Under normal conditions, the occurrence of electrical breakdown within the polymer material causes melting and irreversible damage to the material. Surface treatment can change only a thin surface layer of the polymer, but the inner layers of the material are not affected. Sometimes this is acceptable but in many cases modification of internal volume of polymer material can be extremely helpful. For example, surface painting of a material has lower wear resistance in comparison with painting technologies when paint saturates the internal space of a material. Treatment of internal layers of materials can also be useful for the modification of fundamental mechanical properties of polymers [3], modification of gas and water separation membranes etc.

This work is devoted to the study of the possibility of generating microplasma discharges in micro cavities in the bulk of a polymer without significant destruction of the polymer material itself. To stimulate the formation of plasma inside the polymer material, polymer films are first placed in a discharge chamber (between two flat metal electrodes separated by a glass barrier) and saturated with gas under the pressure up to 150 bar. Then the pressure dropped for a certain time and during this time high voltage pulses were applied to the electrodes. When the pressure dropped enough for an electric breakdown, DBD ignited on the film surface and inside microcavities because residual pressure inside them provided the necessary gas concentration and made ionization length smaller than microcavities dimension. When the pressure dropped to atmospheric, part of microcavities collapsed and in this way polymer can be treated directly inside the internal layers of a material.

2. Experimental setup

Experimental setup consists of a cylindrical discharge chamber, with a window for optical measurements and a high voltage electrode system and power supply. The drawing of the discharge chamber is presented in Fig.1.

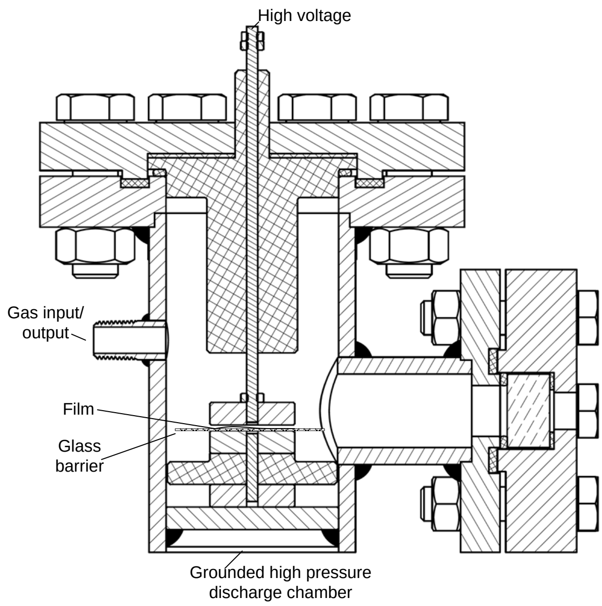

Fig.1 High pressure discharge chamber drawing

The treated film was placed on the surface of a flat grounded electrode covered with a glass barrier 1 mm thick. The discharge gap between the glass and the high voltage electrode varied from 0.5 mm to 1.5 mm. High voltage pulse power supply outputs were connected with the high voltage electrode and the grounded high-pressure discharge chamber. The high voltage power supply generates high voltage pulses with rise time up to 1 μs, voltage amplitude up to 25 kV and frequency from 10 Hz to 5 kHz for ignition of special transient form of pulse DBD with controllable strimmer parameters [4].

Gas input of the discharge chamber was connected with a gas system consisting of gas cylinders with hydrogen, oxygen, helium and argon, a pressure control system, a pressure drop valve and a pressure sensor.

3. Electric discharge parameters

Typical wave form of pulse current and voltage was presented for two different residual pressures on Fig.2.

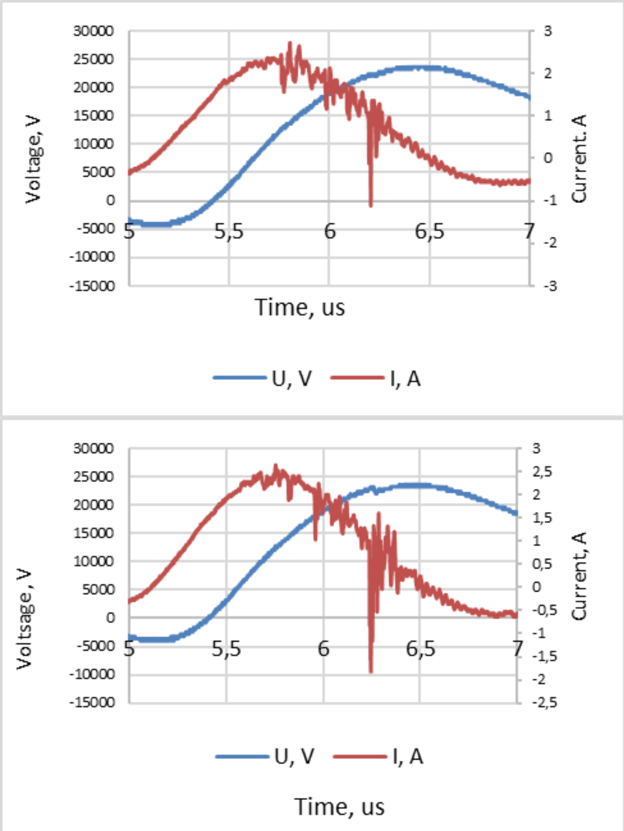

Fig.2. Current and voltage waveform for pressure 18 Bar (bottom) and 6.5 Bar (top).

The moment of ignition of the DBD discharge can be seen on the current oscillogram as the beginning of successive short current peaks. Voltage corresponding with this DBD ignition moment is presented on Fig. 3 as a function of the pressure.

Voltage and current waveforms give us the possibility to estimate the input DBD power corresponding to certain pressure and pulse repetition frequency. Using this data and the measured dependence of the pressure on time (during a pressure drop), the absorbed energy of the DBD discharge in each experiment (1-10 J for our case) can be estimated.

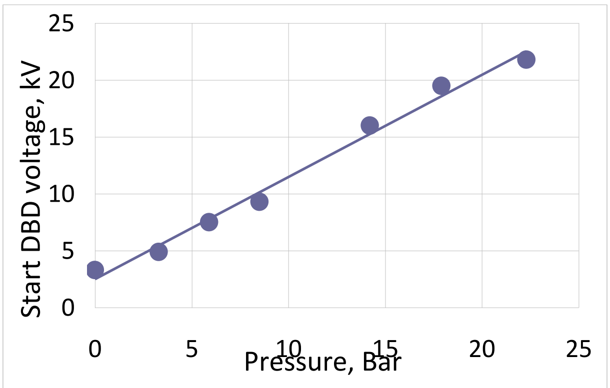

Fig.3. Dependence of DBD ignition voltage on pressure

The surface condition and internal micro cavities of the treated films were observed with an optical microscope by adjusting the focus to a desirable depth (Fig.4, Fig.5).

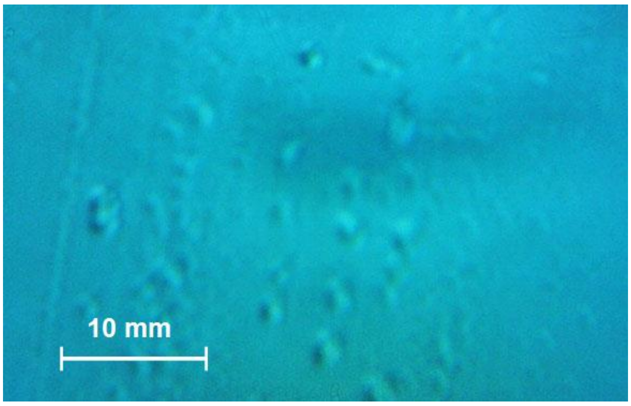

Fig. 4. Surface of treated polyethylene film

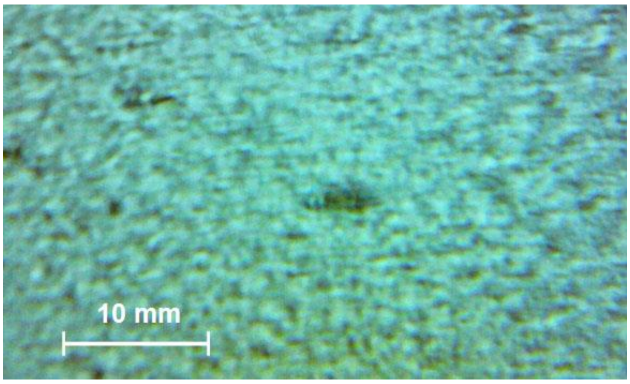

Fig.5. Internal micro cavities of treated polyethylene film

Micro cavities with different sizes can be observed on Fig.5 with dimensions up to 5 μm.

4. Experiments description

In experiments samples of high density polyethylene film with a thickness 15 μm was used. The samples were placed in the discharge chamber, which was filled with hydrogen, oxygen or helium to a pressure of 100-150 bar, and kept at this pressure from 15 to 60 minutes. Then pressure was dropped for a controllable time from 10 to 60 s. During the pressure drop time high voltage pulses were applied to electrodes of the discharge chamber. The frequency of the DBD varied in the experiments from 0 (power off) to 1500 Hz. Then the film samples were taken out of the discharge chamber and Young's modulus of the samples was measured by measuring the elastic forth which was applied for a 5% stretching.

5. Experimental results

Typical dependence of Young’s modulus on the frequency of the DBD is presented on Fig.6. The pulse repetition rate determines the discharge power at a certain pressure and, therefore, the energy absorbed by the plasma during the time of the pressure drop.

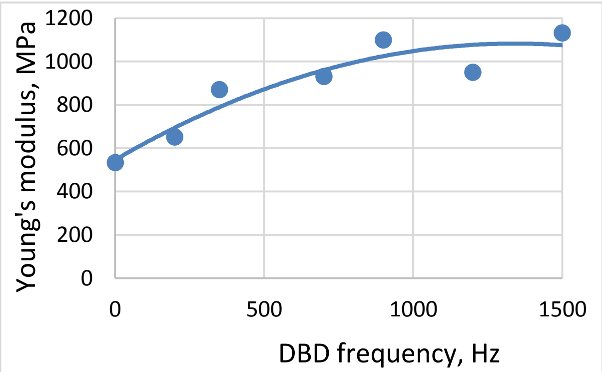

Fig. 6. Dependence of Young’s modulus of 15 μm polyethylene film on the frequency of DBD. Ambient gas- hydrogen, pressure 120 Bar, pressure drop time 60 sec.

6. Experiments results discussion and theoretic modelling

A theory of investigated phenomena has been developed, based on experimental results.

In particular a theoretical model of the processes of gas saturation and relief of polymer and breakdown conditions in micro cavities was developed.

A theoretical model of modifications of mechanical properties of polymer by electric discharge inside micro cavities was proposed.

The theoretical model of processes of gas diffusion and electric breakdown in cavities of polymer was used to analyse experimental results. For the electric breakdown processes the continual model was used since electron free mean path in this condition (1.7-3.4)*10^{-5} cm is much less than the size of the cavity d=5*10^{-4} cm.

Conditions of avalanche development were found from modelling of the initial stage of discharge propagation in the framework of a 1D spherical model. EEDF was calculated at different values of E/P. The processes of ionization, excitation, diffusion, recombination and attachment were taken into consideration. The dependence of critical values of E/P_{cr} on pressure and gap length (Paschen's type curve) was obtained. In particular, critical value E/P_{cr}=16.5 V/cm/Torr for Pd=7.6 Torr*cm (P=20 atm) and E/P_{cr}=21.5 V/cm/Torr for Pd=3.8 Torr*cm (P=10 atm). Reduced field strength in the experiment, assuming the form of the cavity inside the dielectric (ε=2.2) is spherical, was about 20 V/cm/Torr and 40 V/cm/Torr for pressures P = 20 and 10 atm respectively. One can see that these high values of the field provide a breakdown condition in the cavity.

Modelling results of the breakdown condition have a good correlation with the experiments conducted.

7. Conclusion

In the work, the process of internal processing of polymeric materials was studied using a DBD discharge, ignited during a pressure drop after the material was saturated with gas at high pressure.

The possibility of plasma treatment of the internal polymer layers without damaging or melting the material has been demonstrated.

The efficiency of the reversible treatment of the internal space of a polymer has been studied by creating microplasma discharges inside micro cavities.

Using the example of Young's modulus, the possibility of effectively modifying the mechanical properties of a polymer by this method has been demonstrated.

8. References

[1] V.G.Nazarov, Surface modification of polymers, Moscow, Moscow State University of Press (2008).

[2] M. Holc, M. Resnik et al, Surface engineering of polymers using neutral reactive gaseous species, 23st International Symposium on Plasma Chemistry, #584 (2017).

[3] A.L.Volynskii, N.F.Bakeev, Solvent Crazing of Polymers Volume 13 of Studies in Polymer Science, Newnes (2012)

[4] D. Medvedev, V. Petyaev, S. Korobtsev and B. Potapkin, Experimental study of transient forms of dielectric barrier discharge, 21st International Symposium on Plasma Chemistry, #525 (2013).