

## FEEDBACKS IN NON-EQUILIBRIUM OXIDATIVE PLASMA REACTING WITH POLYETHYLENE

KADNIKOV D. V. \*, OVTSYN A. A., S.A. SHIBAEV S. A., SMIRNOV S. A.

*Department of technology devices and materials for electronic equipment, Ivanovo State University of Chemistry and Technology, Sheremetevsky Avenue 7, 153000, Ivanovo, Russia*

\* [dkadnikov@rocketmail.com](mailto:dkadnikov@rocketmail.com)

**Abstract.** The experimental results on studies of loading effect at the action of a glow DC discharge in oxygen and air on polyethylene film are presented. At the increase in a polymer amount under a treatment the specific rates of etching and  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$  product formation rates are decreased. The gas temperature is changed slightly. The reduced electric field strength is increased in oxygen plasma and decreased in air plasma.

**Keywords:** air plasma, oxygen plasma, loading effect, gas temperature, reduced electric field strength, polyethylene.

### 1. Introduction

It is known that at plasma-chemical etching and modification of polymer materials the rates of plasma-chemical destruction are decreased at the increase in polymer amount. Given effect is usually named with loading effect. For the explanation of such effect it is assumed that the concentration of active species is decreased due to the increase in their consumption rates with the growth of material surface being treated at the fixed formation rates [1, 2]. But this explanation doesn't take into consideration that appearance in a gas phase of etching products has to influence the plasma-physical parameters and, as the result, has to influence the formation rates of active species. As far as we know nobody studied the given problem. For this reason the given article aims to study the effect of products of plasma-chemical destruction of polyethylene film (PE) on the parameters of DC glow discharges in oxygen and air.

### 2. Experimental

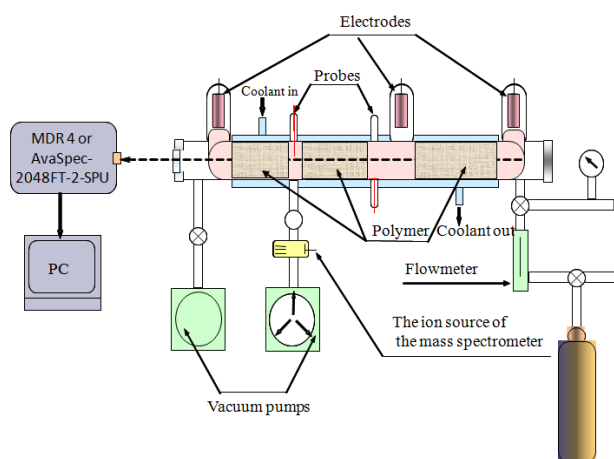


Figure 1. The sketch of experimental setup.

A DC glow discharge was excited in cylindrical flow reactor from glass. The diameter of inner reactor part was 3 cm. The pressure range was 50-300 Pa and discharge current was 20 - 110 mA (Figure 1). The linear velocity of gas flow was changed in the range of 10 - 50 cm/s at standard conditions. Samples of industrial films of PE of high pressure (RF State Standard 10354-82) of 110  $\mu\text{m}$  thickness were placed in a form of several cylinders on the thermostatically controlled reactor wall ( $T_w=310 \pm 5$  K) in a area of positive column. The polymer surface temperature was measured with the vitrified copper-constantan thermocouple. The total length of generatrix of several polymer cylinders was changed in the range of 1.5 - 13.5 cm. The position of extreme sample did not change and the part of inner reactor surface covered with polymer was increased from 4.7 to 42 %. The polymer mass loss was determined with the sample periodic weighting on analytic balance. The rate of oxygen consumption at reactions with polymer and the evolution rates of gaseous products of PE destruction were measured with mass-spectrometers MX-7304 and IPDO - 2A. The surface composition was analyzed by ATR - FTIR method (Avatar - 360). The positive ions flux density on the discharge wall (flat probe), electric field strength,  $E$ , concentration of  $\text{O}(^3\text{P})$  atoms, and  $\text{O}_2(\text{b}^1\Sigma_g^+)$  metastable molecules (emission spectroscopy, MDR - 24 and AvaSpec - 2048FT - 2 - SPU monochromators) was determined by the methods described in [3]. The rotational temperature was determined on distribution of relative intensities for  $\text{O}_2(\text{b}^1\Sigma_g^+, v=0 \rightarrow \text{X}^3\Sigma_g^-, v=0)$  band for  $\text{O}_2$  plasma, and for  $\text{N}_2(\text{C}^3\Pi_u^- \rightarrow \text{B}^3\Pi_u^+)$  band for air plasma. It was supposed that rotational temperature is equal to gas one. Using experimentally measured discharge parameters the electron energy function distribution (EEDF) was calculated by the methods described in studies [4–6]. At calculations the electron collisions both with molecules of plasma-forming gases and with

gaseous products of etching were taken into consideration. For  $O_2$ ,  $CO_2$ ,  $CO$ ,  $H_2O$ ,  $H_2$ ,  $N_2$ ,  $NO$  molecules the cross-section sets of studies [7–13] were used, respectively.

### 3. Results and discussion

The experiments showed that the stationary rates of films mass loss and evolution of products of plasma-chemical etching to gas phase are established after 5 min of plasma processing. These rates do not change until the 30 - 40% of initial polymer mass was removed [14]. After that time the process rate becomes slower. All data presented below refer to the stationary step of etching. Etching rate was increased with discharge current, linear velocity of gas flow and depended slightly on the gas pressure at other conditions being equal. The film which was situated at gas input had higher etching rate whereas samples situated lower on a gas flow were etched slower by 5 - 15%. The process apparent activation energy of plasma-chemical destruction of PE film determined on the temperature dependence of etching rate was  $39 \pm 2$  and  $40 \pm 3$  kJ/mol for oxygen plasma and air plasma, respectively. The activation energy did not depend on the reactor loading degree.

Figure 2 shows the average specific rates of mass loss of PE film ( $W_{et}$ ) at the treatment in air and oxygen plasmas. These rates depend on the loading degree (ratio of polymer surface being treated to total inner surface of reactor in plasma zone). At any discharge parameters the gaseous products of etching were the same. It was  $CO_2$ ,  $CO$ ,  $H_2O$  and  $H_2$  molecules. The oxygen only was consumed from gas phase (Figure 3). The given finding is also confirmed that mass loss rates determined on products rate formation are equal to mass loss rates after deduction of oxygen consume. The lack of carbon-containing compounds as a products shows that the destruction of main polymer chain without formation of gaseous products as a primary process, if it take place proceeds with very slowly.

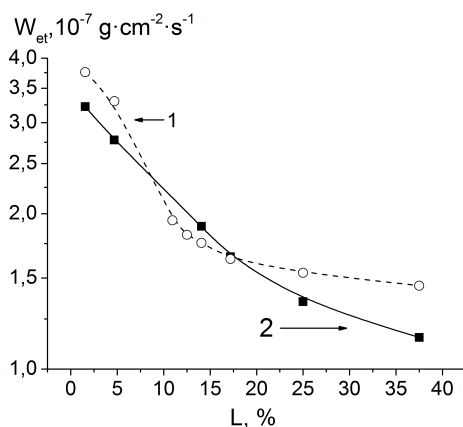


Figure 2. The dependence of etching rate of PE film in oxygen (1) and air (2) plasmas on the degree of reactor loading. The discharge current is 80 mA, the pressure is 100 Pa, the film temperature is  $310 \pm 5$  K.

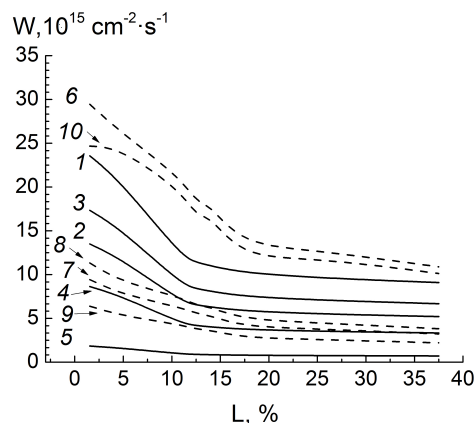


Figure 3. Averaged on sample square the rates of oxygen consumption (1, 2), and evolution rates of  $CO_2$  (2, 7),  $H_2O$  (3, 8),  $H_2$  (4, 9) and  $CO$  (5, 10) vs reactor loading degree at PE film etching in oxygen (1-5) and air (6-10) plasmas. The pressure is 100 Pa. The discharge current is 80 mA.

That is the destruction of oxidized molecules occurs along polymer chain on constituent their atoms with the different degree of oxidation. The total mole fraction of products in a gas phase reaches of 0.14 for oxygen plasma and 0.12 for plasma of air at the increase in the degree of reactor loading up to 37%. It is important to point out that the gaseous products yield per one consuming oxygen molecule was the same at the increase in amount of polymer treated though the yields are changed at the pressure growth for oxygen plasma. But it doesn't observe for air plasma.

The reduced electric strength measured experimentally for air plasma is decreased slightly at a low discharge current (Figure 4) but it is increased at higher current with PE surface growth. In oxygen plasma the electric field strength growth with reactor

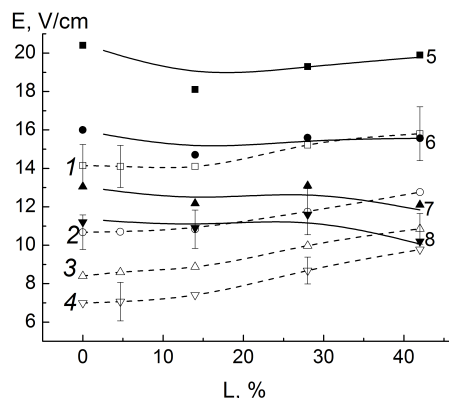


Figure 4. The dependence of electric field strength on reactor loading degree for oxygen plasma (dotted lines) and air (solid lines) at the discharge currents of 20 (1, 5), 50 (2, 6), 80 (3, 7), and 110 mA (4, 8). The gas pressure is 100 Pa.

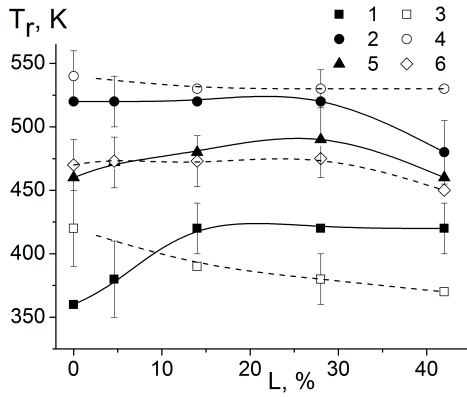


Figure 5. The dependence of rotational temperature of  $O_2(b^1\Sigma_g^+)$  in oxygen plasma (1, 2, 5) and rotational temperature of  $N_2(C^3\Pi_u^-)$  in air plasma (3, 4, 6) on loading degree. The discharge currents are 20 (1, 3), 110 (2, 4) and 80 mA (5,6). The pressure is 100 Pa.

loading degree with polymer (Figure 4). The similar changes can be explained by changes in balance of formation and loss of charges.

The increase in reactor loading degree with polymer results in a slight changes in rotational temperatures of  $N_2(C^3\Pi_u^-)$  and  $O_2(b^1\Sigma_g^+)$  in plasmas of air and oxygen, respectively (Figure 5).

Figure 6 shows the reduced electric field strength,  $E/N$ , at the discharges in oxygen and air depending on loading degree. The  $E/N$  values are decreased by 15-20% in air plasma. At the same time the  $E/N$  grows with the loading degree in oxygen discharge. Using experimental values of  $E/N$  and mole fraction of main components of gas phase ( $N_2$ ,  $O_2$ ,  $H_2O$ ,  $NO$ ,  $Ar$ ,  $CO$ ,  $CO_2$ ,  $H_2$ ) the EEDF calculation was carried out. Applying these EEDF the composition of plasma species was evaluated by means of common solution of equations of chemical kinetics and vibra-

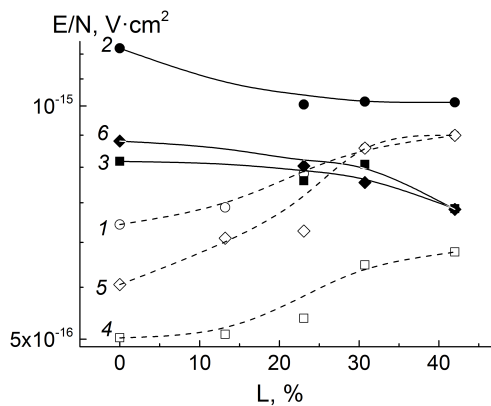


Figure 6. The dependence of reduced electric field strength on loading degree at the discharge in oxygen (1, 4, 5) and air (2, 3, 6). The discharge currents are 20 (1, 2), 110 (3, 4) and 80 mA (5, 6). The gas pressure is 100 Pa.

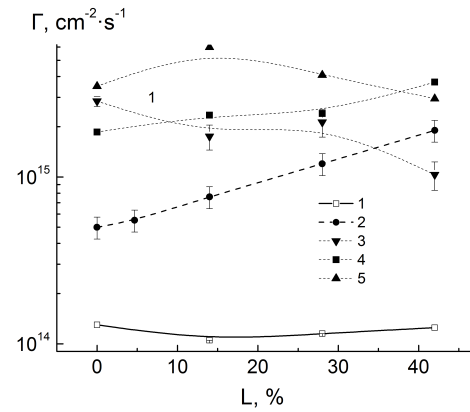


Figure 7. Flux density of positive ions (1, 2), UV-quanta (3), oxygen atoms (4), vibrational excited molecules (5) in air plasma (2-5) and in oxygen plasma (1) at different loading degree. The pressure is 100 Pa. The discharge current is 80 mA.

tional kinetics for ground states of molecules. The last kinetics includes the processes of single-quantum V-V and V-T exchange. It allows estimating the fluxes of active species of oxygen and air plasmas onto polymer surface (Figure 7).

It is necessary to point out the importance taking into consideration the second kind collisions of electrons with the vibrational excited nitrogen molecules and gaseous products of PE destruction. Calculations showed that the second kind collisions influence slightly the kinetic characteristic of electrons determining the EEDF "body". Thus, the difference of electron drift velocity does not exceed of 2%. The rate constants for processes with low threshold energies, for example, excitation of vibrational levels of

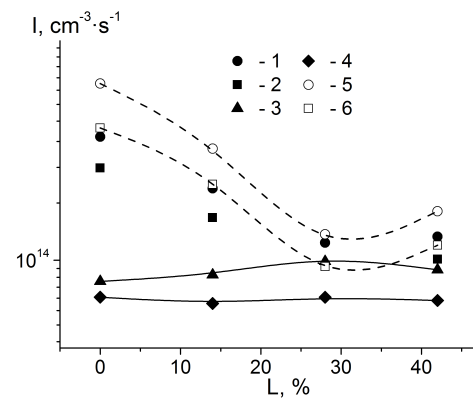


Figure 8. The dependence of emission intensities of lines for transitions  $O(3p^3P \rightarrow 3s^3S)$  (1, 5) and  $O(3p^5P \rightarrow 3s^5S)$  (2, 6), and bands of  $N_2(C^3\Pi_u^-, V' \rightarrow B^3\Pi_g, V'')$  for transitions  $V'=0 \rightarrow V''=3$  (3) and  $V'=4 \rightarrow V''=7$  (4) in air plasma (1-4) and oxygen plasma (5,6) on loading degree. Points are the experiment. Lines are calculations. The pressure is 100 Pa, the discharge current is 80 mA.

$N_2$  ( $X^1\Sigma_g^+$ ) and  $O_2$  ( $X^3\Sigma_g^-$ ) are slightly changed as well. The difference of rate constants of processes of electron impact than higher than  $E/N$  is lower and process threshold is higher [15]. For example, the rate constant of  $O(3p^3P)$  excitation with electron impact (threshold is 10.99 eV) differ by a factor of 1.5 - 4 depending on the discharge external parameters ( $E/N$  and mole fraction of gaseous products).

The adequacy of composition calculations were checked by comparison measured and calculated absolute intensities of atomic lines of oxygen and bands of molecular nitrogen (Figure 8).

Experimental data on kinetic regularities of polymer etching and parameters of non-equilibrium plasma at difference polymer square does not contradict to data of studies [16, 17].

## 4. Conclusions

Thereby, the loading effect was studied for plasmas of air and oxygen. Gaseous products of polymer etching influence strongly the electrical-physical parameters of discharge and kinetic regularities of plasma-chemical etching. This fact is necessary to take into consideration at further studies and development of new technological processes.

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (RFBR) (Project # 16-32-00404). The authors would like to thank Professor V.V. Rybkin and Smirnov S.A. from Ivanovo State University of Chemistry and Technology for helpful discussions and comments.

## References

- [1] B. Lamontagne, A.M. Wrobel, G. Jelbert, and M.P. Wertheimer. Large - area microwave plasma etching of polyimide. *J. Phys. D: Appl. Phys.*, 20(7):844–850, 1987.
- [2] D. Economau, E.S. Audit, and G. Barno. In situ monitoring of etching uniformity in plasma reactors. *Solid State Technology*, 34(4):107–111, 1991.
- [3] V.V. Rybkin and V.A. Titov. Kinetics and mechanisms of oxidative plasma interaction with polymers. In V.Ye. Fortov YU.A. Lebedev, N.A. Plate, editor, *Entsiklopediya nizkotemperaturnoi plazmy*, volume VIII-1. Chemistry of low-temperature plasma. of B, page 130. Moscow: Nauka, 2005.
- [4] A. M. Diamy, J. C. Legrand, V.V. Rybkin, and S.A. Smirnov. Experimental study and modelling of formation and decay of active species in an oxygen discharge. *Contrib. PlasmaPhys.*, 45(1):5–21, 2005.
- [5] S.A. Smirnov, V.V. Rybkin, A.N. Ivanov, and V.A. Titov. The simulation of the processes of formation and decay of neutral particles in dc discharge plasma in an argon-oxygen mixture. *High Temperature*, 45(3):291–297, 2007.
- [6] S.A. Smirnov, V.V. Rybkin, and I.V. Kholodkov. Simulation of the processes of formation and dissociation of neutral particles in air plasma: Vibration kinetics of ground states of  $n_2$ ,  $o_2$  and  $no$  molecules. *High Temperature*, 40(2):161–165, 2002.
- [7] Kajita S., Ushiroda S., and Kondo V. Influence of the dissociation process of oxygen on the electron's warm parameters in oxygen. *J. Appl. Phys.*, 67(9):4015, 1990.
- [8] Y. Itikawa. Cross section for electron collision with carbon dioxide. *J. Phys. Chem. Ref. Data*, 31(3):749, 2002.
- [9] J.E. Land. Electron scattering cross sections for momentum transfer and inelastic excitation in carbon monoxide. *Journal of Applied Physics*, 49:5716, 1978.
- [10] Rybkin V.V., Titov V.A., and Holodkov I.V. Kinetic characteristics and cross section for electron collision with water molecules. *J. Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Technol.*, 51(3):617, 2008.
- [11] Nishimura H. Yoshino M. Tawara H., Itikawa Y. Cross sections and related data for electron collisions with hydrogen molecules and molecular ions. *J. Phys. Chem. Ref. Data*, 19(3):617, 1990.
- [12] Gordiets B.F., Ferreira C.M., Guerra V.L., and et al. Kinetic model of a low-pressure  $n_2 - o_2$  flowing glow discharge. *IEEE Transactions on Plasma Science*, 23(4):750, 1995.
- [13] Rybkin V.V., Titov V.A., and Holodkov I.V. Kinetic characteristics and cross section for electron collision with  $no$ . *J. Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Technol.*, 52(12):3, 2009.
- [14] Kuvaldina E.V., Shutov D.A., Rybkin V.V., and Smirnov S.A. Kinetics of gaseous product formation in the surface treatment of polypropylene with nitrogen-oxygen plasmas. *High Energy Chemistry*, 38(3):200, 2004.
- [15] Rybkin V.V., Smirnov S.A., and Titov V.A. Populations of lower vibrational levels of  $n_2$  ( $x^1\sigma_g^+$ ) and their effect on some characteristics of electrons in air plasma. *High Energy Chemistry*, 31(5):352, 1997.
- [16] Titov V.A., Rybkin V.V., and Smirnov S.A. Physicochemical processes in the nonequilibrium plasma-polymer system. *High Energy Chemistry*, 43(3):172, 2009.
- [17] S.A. Smirnov, V.A. Titov, and V.V. Rybkin. Influence of heterogeneous physicochemical processes on the parameters of low-temperature plasma. *Russian Journal of General Chemistry*, 85(5):1260, 2015.