

Self-consistent analysis of low temperature oxygen plasma and processes of its interaction with some polymer materials

V.V.Rybkin, A.B.Bessarab, E.V. Kuvaldina, A.I.Maximov, V.A.Titov

Ivanovo State Academy of Chemistry and Technology, Ivanovo, 153460, Russia

Abstract: Self-consistent model of glow discharge plasma in oxygen is discussed. The model is based on simultaneous solution of the Boltzmann equation, equations of charged and neutral particles balance, vibrational kinetics equations for $O_2(X^3\Sigma, V)$ molecules and heat-transfer equation. Model discussed allows to calculate intrinsic plasma properties on the base of its external parameters with acceptable accuracy. Results of experimental investigation of polymers plasmolysis are presented. Some aspects of oxygen plasma interaction with polymers are discussed on the base of experimental data and modelling results.

INTRODUCTION

Non-equilibrium oxygen containing plasmas are extensively used for polymers etching and modification. Their particular applications are connected with the processes of dry etching, testing materials stability under the Low Earth Orbits conditions, improvement of polymers adhesion and other properties. Recently, plasma chemical reactors were created for films and fabrics treatment on industrial scale and a problem of quantitative prediction of plasma intrinsic properties and chemical activity on the basis of its external parameters is of great importance today. It has to be noted that oxygen plasma reacting with polymers is a self-consistent system in which chemical composition and physical characteristics do not only control but are also dependent upon the rates of plasma species gas-phase and heterogeneous reactions. Analysis of such a system has to be based on the simultaneous solution of total set of combined equations describing plasma properties. It is evident that the simplest situation for correct plasma diagnostics and modelling is realised in the positive column of DC oxygen discharge with a negligibly small plasma perturbation by polymers etching reactions. This paper presents a summary of the investigations carried out by the authors in this field during the last years.

EXPERIMENTAL METHODS

Oxygen dc discharge was excited in flow type cylindrical glass reactor with 3 cm diameter under the pressure from 30 to 300 Pa, current density from 3 to 17 mA/cm² (deposit power from 0,05 to 2 W/cm) and gas flow rate from 10 to 100 cm/s.

Electric field strength, electron energy distribution function (EEDF), electron density and density of positive ions flux onto reactor wall were measured by electrostatic probes (1-4). Plasma emission spectroscopy and argon actinometry were used to determine concentrations of metastable $O_2(b^1\Sigma_g^+)$ molecules and oxygen atoms in ground and excited states (1, 3, 5, 6). Gas temperature was found from resolved rotational structure of $O_2(b^1\Sigma \rightarrow X^3\Sigma(0-0))$ emission band. Concentration and recombination probability of oxygen atoms on reactor wall in the plasma afterglow were determined by ESR spectrometry (7).

Kapton type polyimide (PI) films, poly(ethylene terephthalate) (PET) films and fabrics, poly(vinyl chloride) (PVC), poly(ethylene) (PE) and some other films were used in our experiments. Polymer samples were etched both in the discharge positive column under the floating potential and in the plasma afterglow.

Composition of polymers etching gaseous products and their evolution rates as well as the rate of oxygen consumption were measured by mass spectrometry method (8). Polymers mass alteration during plasma etching was measured by the periodical weighing of samples or by *in situ* weighing with the electromagnetic microbalances (8,9). Experimentally measured changing the samples temperature as function of time during etching process and after its interruption were used to calculate heat effects of active species interaction with polymers (9,10).

SELF-CONSISTENT ANALYSIS OF OXYGEN PLASMA

To analyse plasma properties it is convenient to consider complicated plasma system as a number of interconnected subsystems (models). We took into account the following models: electron gas kinetics model (EGKM), charged species balance model (CBM), neutral species reactions model (NRM), vibrational kinetics model (VKM) for $O_2(X^3\Sigma)$, heat sources model (HSM), heterogeneous reactions model (HRM). Testing the modelling results was accomplished by comparing the calculated plasma parameters with our experimental data and with the data from (11).

EGKM was based on solving Boltzmann equation, taking into account electron-electron collisions, electron collisions with $O_2(X^3\Sigma, V=0)$, $O(^3P)$, $O_2(a^1\Delta_g)$ and superelastic collisions with $O_2(X^3\Sigma, V)$ and $O_2(a^1\Delta_g)$. Comparison of calculation results with experimental data has shown the following (2,12-14). 1) Influence of e-e collisions and superelastic collisions on EEDF can be neglected. 2) EEDF middle part depends slightly on plasma particles composition and set of cross-sections for electron interactions with $O_2(X^3\Sigma)$ (15-17). 3) Electron collisions with $O(^3P)$ and $O_2(a^1\Delta_g)$ lead to increasing the relative part of high energy electrons in EEDF as compared to EEDF obtained taking into consideration the electron collisions with $O_2(X^3\Sigma)$ molecules only.

These conclusions are in a good agreement with data reported in (18).

VKM included 36 kinetic equations describing e-V, V-e, V-h energy exchange processes, V-T and V-V single-quantum exchange by O_2 molecules collisions, V-T multi-quantum exchange by $O_2(X^3\Sigma, V)$ collisions with $O(^3P)$. Vibrational temperature $T_v \leq 1000$ K has been obtained to be close to translation gas temperature owing to rapid V-T relaxation by collisions with $O(^3P)$ atoms. Consequently, vibrationally excited oxygen molecules in ground state can be neglected in electron-assistant reactions without sufficient loss of accuracy.

CBM equations were solved using the approach developed in (19) to calculate radial distribution of charged particles density and stationary values of reduced electric field. O_2^+ and O^+ ions were considered to be formed by the electron collisions with $O_2(X^3\Sigma)$, $O_2(a^1\Delta)$ and $O(^3P)$ while O^- by electron attachment to $O_2(X^3\Sigma)$ and $O_2(a^1\Delta)$. Charged particles loss processes included diffusion and wall recombination, ion-ion recombination, electron detachment by $O(^3P)$ and $O_2(a^1\Delta)$ and electrons.

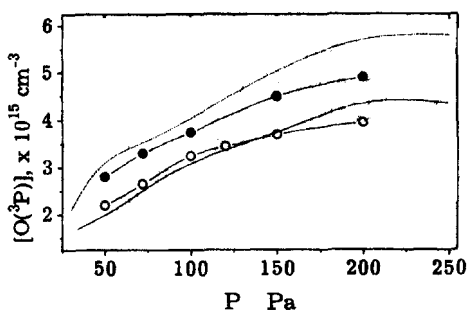


Fig.1 The calculated and measured $O(^3P)$ atom concentration versus pressure. Calculated data 50 mA (dashed line), 80 mA (solid line); experimental data- \circ 50 mA \bullet 80 mA

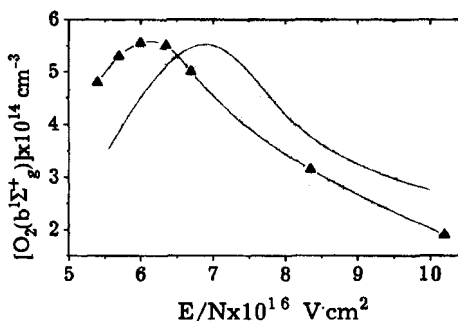
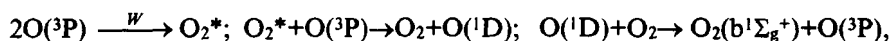


Fig.2 The calculated and measured $O_2(b^1\Sigma)$ molecules concentration versus the reduced field for 80 mA discharge current. Calculated data (solid line); experimental data- \blacktriangle

NRM kinetic equations described 47 reactions of formation and destruction for $O_2(X^3\Sigma, A^3\Sigma, a^1\Delta, b^1\Sigma)$ molecules, $O(^3P, ^1D, ^1S)$ atoms and O_3 . Comparison of experimentally measured $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ concentrations with the ones calculated in self-consistent manner has shown these molecules formation and destruction reactions proposed in (20) cannot correctly explain the experimental data. The same problem was noted in (1,11,15,21). To fit the modelling results to the experimental data we supposed the existence of additional reactions for $O_2(a^1\Delta_g)$ destruction and $O_2(b^1\Sigma_g^+)$ production along with the processes mentioned in (20). Our estimations show such a reaction for $O_2(a^1\Delta_g)$ can be the quenching in quasi-resonance interaction with $O_2(X^3\Sigma, V=6)$ which gives $O_2(X^3\Sigma, V=12)$. As concerning the $O_2(b^1\Sigma_g^+)$ molecules, a good fitting is attained by adding the processes described by the following scheme into the formation reactions:



where w means wall recombination, and O_2^* - O_2 excited state.

HSM was based on solving a heat-transfer equation combined with equations of EGKM, NRM and VKM. Relative part of electrons energy δ , which can provide experimentally measured values of gas temperature at the discharge axis and reactor wall temperature was calculated. Experimentally obtained δ value has been found to be equal to 0.5 independently on external plasma parameters. Calculation of heat evolution in gas-phase reactions described by NRM and VKM yielded $\delta=0.36$. A good agreement of modelling results with experimental data was attained supposing the additional gas heating source is wall deactivation of $O_2(b^1\Sigma_g^+)$ yielding $O_2(X^3\Sigma,V)$ followed by the vibration energy transfer to heat by V-T relaxation.

Some modelling results are shown in Fig.1-2. Oxygen plasma model developed allowed us to calculate fluxes of active particles to polymers surface under various external conditions.

OXYGEN PLASMA INTERACTION WITH POLYMERS

Various experimental data show plasma-polymers interaction process is multistage and multichannel. It is important that plasma particles reactions with polymer materials change both chemical composition of gas phase and composition and structure of polymer surface. As a result alteration of heterogeneous and gas-phase processes kinetics leads to nonlinearity of plasma-polymer system properties and can result in the instability of plasma uniform state and in qualitatively new behaviour. However, it is possible to create the conditions of small plasma perturbation by polymer etching reaction using the appropriate size of polymer sample and gas flow rate. Our experimental data were obtained under the such conditions.

A number of indirect experimental methods was used to determine contributions of different active species in process of polymers plasmolysis. First of all, our analysis was based on evident supposition that flux density of some active particles onto polymer surface cannot be less than formation rates of products resulting from the same particles action to polymer. Analysis of experimental results taking into account this consideration shows that $O(^3P)$ atoms and $O_2(b^1\Sigma, a^1\Delta_g)$ molecules can be the most possible etching agents for different types PI (22), PET films (23) and fabric (24), PE (27), PVC (28), polyacrylic acid and some other polymers. Measurements of PE, PI, PET, PVC etching rates (26,28,29) in flowing plasma afterglow where active particles concentration can be varied in controlling manner by the changing both plasma external parameters and distance from plasma to polymer sample showed the etching is caused by action of $O(^3P)$ atoms only (see Fig.3). Process is characterised by the first order rate constant depending on sample temperature. Apparent activation energies ΔE have been found to be equal to 48 ± 6 , 41 ± 3 , 46 ± 12 kJ/mol for PI, PET and PVC etching respectively. Mass spectral data showed O_2 is

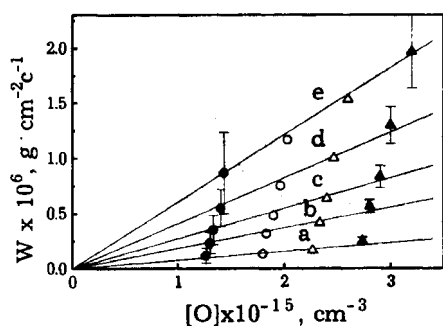


Fig.3 PI etching rate versus $O(^3P)$ atom concentrations. a, b, c, d, e correspond to temperatures 357, 385, 400, 417 and 435 K respectively. \blacktriangle -100 Pa, 80 mA; \bullet -85 Pa, 20 mA; \circ -85 Pa, 35 mA; Δ -92 Pa, 50 mA.

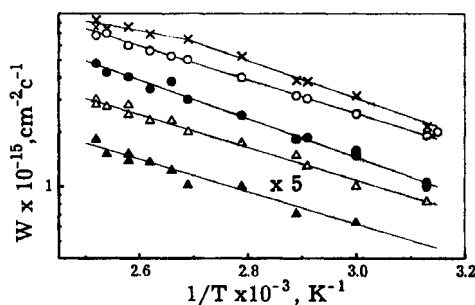


Fig.4 Gaseous products evolution rates and oxygen consumption rate versus substrate temperature under 50 Pa and 80 mA for PET etching. x, O, ●, Δ, ▲ correspond to oxygen, CO_2 , CO, H_2O and H_2 molecules respectively.

consumed in the reactions with PI and PET but CO, CO_2 , H_2O , H_2 are formed as products. The values of mass loss and oxygen consumption rates are controlled by these products formation only. At the same time PVC etching is accompanied by HCl molecules evolution along with the products mentioned above. Activation energies of the gaseous products formation, O_2 consumption and polymer mass loss processes are the same. Extrapolation of etching rates measured in afterglow to plasma region gives less rates than experimentally obtained in discharge positive column.

The PI and PET etching kinetics in positive column has the following features. 1. Activation energy values for processes of PI mass loss, gaseous products formation and O₂ consumption are the same but they depend on the sample temperature: $\Delta E = 40 \pm 5$ kJ/mol under $T > 378$ K and $\Delta E = 22 \pm 3$ kJ/mol under $T < 378$ K. Relative yields of gaseous products per one oxygen molecule reacting with PI are constant independently on temperature. PET films etching is characterised by the activation energies of processes mentioned above equal to 18 ± 3 kJ/mol under temperature less than 375 K. At $T > 375$ K ΔE value for CO₂, CO, H₂O and H₂ formation does not change while that of weight loss becomes equal to 35 ± 2 kJ/mol (see Fig.4). This result can be explained supposing the evolution of molecular O₂ as one of the etching products. 2. Rates of all processes discussed increase with discharge current growth but depend slightly on pressure while fluxes of O(³P) atoms and O₂(b¹Σ) molecules onto polymer surface increase in the both cases. Activation energies and relative yields of H₂O and H₂ molecules do not depend on current and pressure but that of CO₂ and CO molecules changes with these parameters. Under the small current and pressure this yield corresponds to that observed in afterglow experiments but current and pressure growth lead to the rising of CO₂ relatively CO yield.

Experimental results allow to propose the following hypotheses concerning the mechanisms of plasma oxidative destruction. 1. Multistage and multichannel plasma etching process has a common limiting stage. This stage, most likely, is reaction of atomic oxygen with polymer. 2. Rate constant of atoms interaction with polymers is a function of not only sample temperature but plasma parameters probably due to the interconnection of reactions channels. These channels can be connected with some active species in positive column which contribution to etching kinetics decrease with pressure growth. Alteration of etching products relative yields with plasma parameters also indicates the plasmolysis channels interconnection.

Positive ions and UV-photons are the active species which fluxes onto polymer surface decrease with oxygen pressure growth. We carried out the experiments on etching the PET fabric to determine the role of these active species in etching process (25,29). Fabric sample owing to its specific structure served as a kind of mask partially permeable for neutral active particles but eliminated the action of charged species and UV-photons on the back surface of sample. Comparison of PET film and PET fabric etching kinetics shows both positive ions and UV-photons can influence the plasmolysis process but we cannot separate their contributions in terms of our data or the data available from literature. So, Fracassi *et al.* (30) observed PI etching rate enhancement by ion bombardment, however this effect has a threshold energy about 20-30 V. Polymer samples floating potential was less than 5 V under our experimental conditions and positive ions flux onto polymer surface is about 100 times less than etching products formation rate. Oxidative etching of PI and poly(methyl methacrylate) under the action of UV-photons is known (31,32). However, results of photo-oxidation and plasma oxidation are different (32,33). Undoubtedly it can be considered that combined action of oxygen atoms, and UV-photons is not additive. It is confirmed by the results obtained in studies (34) when PE and PVC films were exposed to active particles in oxygen plasma afterglow, to UV-irradiation in inactivated oxygen under the same pressure and to all of these agents simultaneously. The combined action of UV-photons and neutral active particles was found to result in greater etching rates than the sum of rates obtained under the action of photons and neutrals taken separately.

Interaction of oxygen plasma with polymers is accompanied by heat evolution onto samples surface (8,9,10,35,36). This heat effect can lead to self-acceleration of oxidative destruction process and to unforeseen results under the conditions of limited heat-exchange. Instabilities of PI and photoresist plasma etching were observed by the authors of (8,35). Activation energy of heat evolution during PI etching in O₂ plasma has been found to be equal to 51 ± 2 kJ/mol under sample temperature $443 < T < 543$ K (36). This value is in a good agreement with ΔE value for atoms interaction with PI obtained in our experiments (27).

More complicated kinetic regularities are observed under conditions of large loading of reactor by polymer material (36). Size of PI sample influences the character of etching rate dependencies on external plasma parameters and relative yields of gaseous products. Etching products change the EEDF and rate constants of electron-assistant processes (5).

CONCLUSIONS

Non-equilibrium plasma and polymer under treatment must be considered as an indivisible self-consistent system. Understanding the mechanisms of polymers etching and modification demands the combined investigations both the reactions of active plasma agents formation and heterogeneous processes taking into account channels interaction.

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