Recombination of neutral oxygen atoms on polymer surfaces

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Abstract: Probability for heterogeneous surface recombination of neutral oxygen atoms on various polymer surfaces was measured by a catalytic probe. Experiments were performed in a flowing afterglow of a microwave plasma in a surfatron mode. Power was set to either 100 or 200 W. Pressure was varied in a range between 8-200 Pa, therefore the polymer samples were exposed to various fluences of neutral oxygen atoms. Recombination probabilities were of the order of 10^{-3}.

Keywords: surface atom loss probability, oxygen atom recombination, plasma, polymer.

1. Introduction

Oxygen plasmas are often used for tailoring surface properties of polymer materials. The most important reactive species formed in plasma are neutral oxygen atoms in the ground state. Their density strongly depends on discharge parameters such as power and gas pressure and also on the type of material used for construction of plasma systems. Recombination of oxygen atoms to a molecule $O+O \rightarrow O_2$ may occur only at a three body collision i.e. on surfaces of plasma chamber and on materials being treated in plasma. Therefore, plasma systems are often made of glass which has a very low probability for recombination. In literature, there are many reports about recombination probabilities for various materials (especially metals and ceramics), however, the results scatter significantly. Moreover, there is a lack of experimental data for polymer materials. Here we present measurements of probability for heterogeneous surface recombination of neutral oxygen atoms on various polymer surfaces by a catalytic probe.

2. Experimental

Experiments were performed in a flowing afterglow of oxygen plasma created by MW plasma at 100 and 200 W in a surfatron mode. Oxygen pressure was varied in the range between 8 and 200 Pa (flow between 40-2150 sccm). More details can be found in [1]. Cobalt catalytic probe was mounted in the afterglow to measure the density of oxygen atoms. A probe tip was heated because of catalytic recombination of oxygen atoms and the temperature was measured by a thermocouple. The O-atom density was calculated according to equation [1]:

$$n_{\mathrm{Co}} = \frac{8 m_{\mathrm{Co}} \cdot c_{\mathrm{p(Co)}}}{\gamma_{\mathrm{Co}} \cdot A_{\mathrm{Co}} \cdot W_{\mathrm{D}} \cdot \langle v \rangle} \cdot \left(\mathrm{d}T / \mathrm{d}t\right)_{\mathrm{Co}}, \qquad (1)$$

where m_{Co} is a mass of the cobalt probe tip, $c_{\mathrm{p(Co)}}$ is a thermal capacity of cobalt, $(\mathrm{d}T/\mathrm{d}t)_{\mathrm{Co}}$ is an absolute value of the temperature derivate of the cobalt probe after turning off plasma, $\langle v \rangle$ is the average thermal velocity of O atoms (630 m/s), γ_{Co} is the probability for atom recombination on the cobalt surface (0.12), W_{D} is a dissociation energy of neutral oxygen molecules (5.12 eV), and A_{Co} is the area of the cobalt probe tip. Calculated density for O atoms depended on pressure and the maximum was 6×10^{21} m^{-3}.

Another thermocouple was connected to a piece of a polymer (PET, PS or PTFE), which was folded and welded around the thermocouple. After ignition of plasma, the polymer probe was heated upon exposure to O atoms. This enabled calculation of recombination probability using similar equation as for cobalt:

$$\gamma = \frac{8 m \cdot c_{\mathrm{p}}}{\langle v \rangle \cdot W_{\mathrm{D}} \cdot A \cdot n_{\mathrm{Co}}} \cdot \left(\mathrm{d}T / \mathrm{d}t\right), \qquad (2)$$

where m is the mass of the polymer, c_{p} is the thermal capacity of the polymer, A is the area of the polymer probe tip, $\mathrm{d}T/\mathrm{d}t$ is the absolute value of the polymer temperature derivate after turning off the discharge, and n_{Co} is the O-atom density determined by the cobalt probe.

3. Results and discussion

Probability for recombination of O-atoms on various polymer surfaces was calculated using Eq. 2. This was done for various range of O-atom densities. It was found that recombination probabilities were somehow slightly higher at higher oxygen atom densities. This can be explained either with the temperature dependence of the recombination coefficient or the presence of the oxygen molecules in a metastable state. The average recombination probability is shown in Table 1.

Table 1.Recombination probabilities [1]

Polymer	Probability
PTFE	$(1.1 \pm 0.6) \times 10^{-3}$
PET	$(2.4 \pm 1.2) \times 10^{-3}$
PS	$(2.2 \pm 1.2) \times 10^{-3}$

4. References

[1] R. Zaplotnik, A. Vesel, M. Mozetic, Atomic oxygen and hydrogen loss coefficient on functionalized polyethylene terephthalate, polystyrene, and polytetrafluoroethylene polymers, Plasma Process. Polym. **15**, e1800021 (2018).