Modification of polypropylene in the afterglow of the atmospheric pressure discharges in air and argon

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Abstract. Polypropylene films were modified in the flowing afterglow of the atmospheric pressure DC discharge in argon and in air. The modification was carried out at a discharge current of 15 mA, a gas flow rate of 24 and 105 m/s and a treatment time of 3 - 30 s. Polymer samples were placed on the distance of 5 - 15 mm downstream the plasma. Contact angles for water and ATR-FTIR spectra were used for the film surface characterization. Concentrations of oxygen containing groups in modified polymer layer were estimated on the base of ATR-FTIR data. Modification in the both plasma forming gases results in the decrease of the contact angles and in the formation of oxygen containing groups in polypropylene. Dependencies of contact angles on treatment time, gas flow rate and plasma - polymer distance were obtained. Increasing the treatment time and the gas flow rate results in a higher oxidation degree of the PP. Treatment in the afterglow of the argon plasma has been shown to give the less water contact angles and more densities of oxygen containing groups in polypropylene at the gas flow rate of 105 m/s and the treatment time of 30 s.

1. Introduction
Plasma modification of polymer materials is a promising tool for improving their properties: surface energy, wettability, adhesion to coatings etc. To improve these properties, atmospheric pressure discharges in different gases are used: in air [1-4], argon [5-7], helium [8], mixtures of oxygen and argon [9], oxygen and helium [8], nitrogen and argon [10]. Regardless of polymer and the plasma forming gas, the similar qualitative changes in the surface properties were observed: a decrease of the contact angles, an increase in the concentration of oxygen containing groups and in the surface roughness. However, it is difficult to compare the effectiveness of the modification depending on the plasma gas nature and on the polymer type, since the treatment conditions are strongly different in various studies. These conditions include not only the plasma gas but discharge type, dissipated power, treatment time, gas flow rate and polymer location.

The aim of this study was to compare the results of modifying polypropylene films in the flowing afterglow of the atmospheric pressure direct current discharges in air and in argon.

2. Experimental
Simplified scheme of the experimental setup is shown in figure 1. Direct current (DC) discharge was excited between the nozzle anode with the inner diameter of 470 µm, through which the plasma forming gas was supplied, and a stainless steel plate with the thickness of 1 mm, which was used as a
cathode. Interelectrode gap was 1 mm, discharge current was 15 mA. The gas flow rate was 24 and 105 m/s in different experiments.

Polypropylene (PP) films with the 20 µm thickness (TU RB 00204079.164-97, Mogilevkhimvolokno Ltd) were used in our experiments. The polymer samples with the sizes of 1,5×5 cm² were placed on the distance of 5, 7, 10, 12 and 15 mm downstream the plasma. To characterize modification results, water contact angles measurements and ATR-FTIR spectroscopy (Avatar 360 FT-IR ESP) were used. Elemental analysis of the sample was performed on a scanning electron microscope (Tescan VEGA 3 SBH) with an X-ray energy dispersive microanalysis system (Oxford Instruments X-act).

3. Results and discussion
Dependences of the PP film contact angle on the treatment time are shown in figure 2. Treatment in the flowing afterglow of the discharges in argon and in air leads to an improvement in the surface wetting: the water contact angles decrease from 89° for the original sample to 58° and 44° for the samples treated with the discharges in air and argon, respectively. The most pronounced changes occur in the first 10-20 seconds of treatment, a further increase in treatment time does not lead to a noticeable change in the contact angle.

Water contact angles obtained at the treatment of PP films with the discharges in air and argon are listed in table 1. These data show that for a fixed exposure time the surface wetting increases with increasing gas flow rate and with decreasing distance between sample and plasma where the active species are generated. The results obtained at the treatment in both gases are similar at the flow rate of V = 24 m/s but are different at V = 105 m/s: treatment in argon plasma leads to lower contact angles.
Table 1. Water contact angles for the PP films treated in the flowing afterglow of the air and argon discharges at the treatment time of 30 s.

| Gas flow rate (m/s) | Plasma - polymer distance (mm) | Water contact angle (degree) |
|---------------------|--------------------------------|------------------------------|
|                     |                                | Air  | Argon |
| 24                  | 5                              | 51   | 57    |
|                     | 7                              | 78   | 78    |
|                     | 10                             | 76   | 83    |
|                     | 12                             | 85   | 84    |
|                     | 15                             | 85   | 86    |
| 105                 | 5                              | 58   | 44    |
|                     | 7                              | 64   | 49    |
|                     | 10                             | 79   | 58    |
|                     | 12                             | 75   | 57    |
|                     | 15                             | 84   | 66    |

ATR-FTIR spectra showed the formation of oxygen containing groups in the polymer surface layer (figure 3). Treatment in the both gases results in the increase of absorption in the region of stretching vibrations of the C=O bond (1590-1820 cm\(^{-1}\)). When argon plasma is used, there is also an increase in the absorption of stretching O-H bonds (3000-3600 cm\(^{-1}\)). Increasing the treatment time and the gas flow rate results in a higher oxidation degree of the PP. It is more pronounced for a discharge in argon (table 2). The relative concentration of oxygen containing groups decrease with the increasing the plasma - polymer distance.

Concentrations of carbonyl and hydroxyl groups in modified layer of PP can be estimated as 
\[ c = \Delta A / (\varepsilon \lambda / l) \]
where \( \Delta A \) is the difference between the absorbance in the treated and initial samples, \( \varepsilon \) - the extinction coefficient and \( l \) is the penetration depth of the IR radiation into the sample. The penetration depth was estimated using the formula:
\[ l = \lambda_1 / [2 \pi (\sin^2 \Theta - n_21^2)]^{1/2} \]
where \( \lambda_1 \) is the radiation wavelength in an optically denser medium, \( \Theta \) is the angle of incidence, \( n_21 \) is the relative refractive index. The extinction coefficients from references [11-13] were used for the calculation.

Figure 3. ATR-FTIR spectra of PP films: 1 - initial untreated sample, 2 - sample after the treatment with the argon plasma, 3 - sample after the treatment with the air plasma. Treatment conditions: gas flow rate 105 m/s, treatment time 30 s, plasma - polymer distance 7 mm.
Table 2. Relative absorbance for CO and OH groups normalized to the values for untreated sample.

| Treatment conditions | $A_{3283}/A_{2838}$ | $A_{1722}/A_{2838}$ | $A_{1633}/A_{2838}$ |
|----------------------|----------------------|----------------------|----------------------|
| Untreated sample     | 1,00                 | 1,00                 | 1,00                 |
| Argon, 24 m/s        | 1,03                 | 1,20                 | 0,99                 |
|                      | 1,21                 | 1,41                 | 1,24                 |
|                      | 1,59                 | 1,77                 | 1,43                 |
| Argon, 105 m/s       | 0,90                 | 1,81                 | 1,39                 |
|                      | 1,25                 | 2,28                 | 1,44                 |
|                      | 1,71                 | 2,66                 | 1,58                 |
| Air, 24 m/s          | 1,04                 | 2,09                 | 1,50                 |
|                      | 1,06                 | 2,48                 | 2,04                 |
|                      | 0,89                 | 2,32                 | 1,85                 |
| Air, 105 m/s         | 0,95                 | 1,92                 | 1,59                 |
|                      | 1,07                 | 2,76                 | 2,00                 |
|                      | 0,97                 | 2,44                 | 1,72                 |

Note: $A_{2838}$ - the absorbance at the maximum of the band for the C-H in CH₂; $A_{1722}$ - the absorbance at the maximum of the band for the C=O in the carboxyl group, ketones and aldehydes; $A_{1633}$ - the absorbance at the maximum of the band for the C=O in the enolic diketones and unsaturated oxyketones.

The results of estimating the concentrations of oxygen containing groups are listed in table 3. These data agree with the results of the X-ray energy-dispersion analysis, which also showed a higher oxygen content in the PP treated with argon discharge at a gas flow rate of 105 m/s (table 4). Data of table 3 shows the values of concentrations for oxygen containing groups to be higher than those obtained at the thermo- and photooxidation of polypropylene [13, 14]. The total concentration of carbonyl groups after thermal oxidation of PP at a temperature of 138 °C for two hours was 0.128 mole/l [13], and for photo-oxidation for 335 hours - 84 mole/l [14].

Table 3. Concentration of oxygen containing groups after the treatment of PP films in the flowing afterglow of the DC discharges in air and argon.

| Gas and flow rate | Treatment time (s) | Concentration of groups (mole/L) | Total concentration (mole/L) |
|------------------|--------------------|----------------------------------|-----------------------------|
|                  |                    | OH | C=O (1722 cm⁻¹) | C=O (1633 cm⁻¹) |                      |
| Argon, 24 m/s    | 20                 | 0,165 | 0,031 | 0,044 | 0,240 |
|                  | 30                 | 0,495 | 0,062 | 0,088 | 0,645 |
|                  |                    |    |        |       |                   |
| Air, 24 m/s      | 20                 | -   | 0,109 | 0,206 | 0,315 |
|                  | 30                 | -   | 0,109 | 0,162 | 0,271 |
| Argon, 105 m/s   | 20                 | 0,165 | 0,093 | 0,088 | 0,346 |
|                  | 30                 | 0,660 | 0,124 | 0,118 | 0,902 |
| Air, 105 m/s     | 20                 | -   | 0,140 | 0,191 | 0,331 |
|                  | 30                 | -   | 0,109 | 0,132 | 0,241 |

Table 4. Concentration of oxygen atoms in the modified PP films.

| Plasma treatment | [C] (mass %) | [O] (mass %) |
|-----------------|--------------|--------------|
| Untreated sample| 97,20        | 2,80         |
| Air plasma      | 96,76        | 3,24         |
| Argon plasma    | 96,37        | 3,63         |
4. Conclusions
The comparative study of the polypropylene film surface modification in the flowing afterglow of the atmospheric pressure DC discharge in argon and air has shown the following. Modification in the both plasma forming gases results in the decrease of the contact angles and in the formation of oxygen containing groups in the polymer surface layer. The contact angles depends on the gas flow rate and on a plasma - polymer distance at the fixed treatment time. Increasing the treatment time and the gas flow rate results in a better wettability and a higher oxidation degree of the PP surface. Treatment in the afterglow of the argon plasma has been shown to give the less water contact angles and more densities of oxygen containing groups in polypropylene at the gas flow rate of 105 m/s and the treatment time of 30 s.

Acknowledgments
The study was supported by the Russian Foundation for Basic Research and the Government of Ivanovo Region through the grant No. 15-42-03124.

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