

Influence the loading effect on modification of PET film and fiber by Argon Plasma

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Abstract. Poly(ethylene terephthalate) films and fabrics were modified by low-pressure argon plasma at different area of samples been treated. Contact angles for water and glycerol were measured and surface energy was calculated for film surface characterization. Height of water capillary rise was measured for fabric. The changes in chemical structure of surface layer were analyzed by ATR-FTIR method. Influence of sample area on non-homogeneity of plasma modification was shown. Some experiments were performed with polypropylene treatment in flowing plasma afterglow to confirm the reactions of oxygen active species originated from gas products of poly(ethylene terephthalate) etching in argon plasma.

1. Introduction

Plasma modification of polymers is widely used for improving their surface properties, such as wettability and dyeability, adhesion, biocompatibility etc. Treatment of polymer materials in low-pressure plasma of non-polymerized gases (O₂, N₂, NH₃, CO₂, air, Ar, He etc.) is accompanied by the formation of gaseous etching products, which alter plasma composition and properties [1, 2]. This phenomena is known as a so called “loading effect”. Molecular hydrogen is the main gaseous product at the treatment of polyethylene, polypropylene and some other polyolefins in plasma of noble gases, at the same time, oxygen, carbon monoxide and water molecules were observed in mass-spectra of argon plasma at the treatment of oxygen-containing polymers: polyvinyl alcohol, polyacrylic acid, poly(ethylene terephthalate) [1]. Moreover, atomic oxygen and hydrogen lines and OH radical bands were observed in emission spectra of argon plasma reacting with polyaramide fibers and poly(ethylene terephthalate) (PET) fabric [2]. It means the noble gas plasma contains the reactive oxygen species, which origin from the polymer etching products. As a result, it can be expected not only the changing of plasma composition and properties but changing the results of polymer modification due to gas products evolution. The aim of this work is experimental study of influence of gaseous etching products on surface modification of PET film and fabric in low-pressure argon plasma.

2. Experimental

PET film with the thickness of 60 μm and PET fabric with specific surface density of 187 g·m⁻² were used in our experiments. Area of samples was varied from 20 to 123 cm². Direct current discharge in argon was excited in cylindrical glass reactor with 3 cm inner diameter at argon pressure of was 50, 100 and 200 Pa, discharge current of 80 mA, and gas flow rate of 30 cm·s⁻¹. Polymer samples were



placed as cylinders on the reactor wall. Treatment time was 0.5, 1 and 5 min. Experimental setup and methods are described in detail elsewhere [4].

Surface modification of PET film was characterized by the contact angles (θ) for distilled water and glycerol, which were obtained using sessile drop image analysis (software ImageJ, “Drop-analysis”). The contact angles were used for calculation of polymer surface energy (γ), its polar (γ_p) and dispersive (γ_d) components by Owens-Wendt method. For fabric samples, height of water capillary rise was measured according to Russia State Standard 3816-81. The chemical changes induced by the action of plasma onto PET were studied by FTIR spectroscopy. The FTIR analysis was performed by a spectrometer (Avatar 360 FT-IR ESP, Nicolet) in an Attenuated Total Reflection mode with a ZnSe crystal.

3. Results and Discussion

Plasma treatment results in increase of hydrophilic properties of PET film and fabric (figure 1, tables 1, 2). Contact angles decreased, and surface energy increased due to increase of polar component. The polymer sample sizes slightly influence the result of PET film surface modification (table 1). Initial PET fabric has hydrophobic properties: water contact angle $\theta > 90^\circ$ (figure 1) and height of water capillary rise is only 2.66 cm after 3 min of wetting. Hydrophilicity was remarkably improved by plasma treatment: height of water capillary rise increased up to ~ 6 cm (table 2). It has to be noted that non-homogeneity of treatment results are observed for samples with large area ($S=123$ cm) as it is seen from Figure 2. The non-homogeneity is most pronounced at low treatment time and it reduces with the increase of treatment time.

To study the spatial uniformity of plasma etching, PET film samples were cut into three parts and placed in the reactor as shown in Figure 3a. The mass loss for each sample with the width of 4 cm was measured after plasma treatment and FTIR-spectra of samples were obtained. The experimental results show the sample placed in middle has minimum value of etching rate and maximum absorbance of C=O groups ($\nu=1710$ cm $^{-1}$) as compared to samples located at the edges (Figure 3b, c). These data indicates the spatial non-homogeneity of plasma properties and fluxes of active species onto sample surface at high loading of reactor with material under treatment. The non-homogeneity can be caused by fast consumption of active species in heterogeneous reactions or by influence of destruction products on kinetics of active species formation in plasma. Furthermore, formation of new active species as a result of excitation and dissociation of polymer destruction products can not be excluded.

To confirm the possible reactions of reactive oxygen species, special experiments were performed with the treatment of polypropylene (PP) films in flowing afterglow of argon plasma. PP films were placed 4 cm downstream of plasma and were treated in two regimes. In the first case, PP films were treated without PET sample loading in argon plasma. In the second case, PP films were treated with PET film loading in argon plasma. In both cases ATR-FTIR spectra of PP samples were recorded before and after treatment.

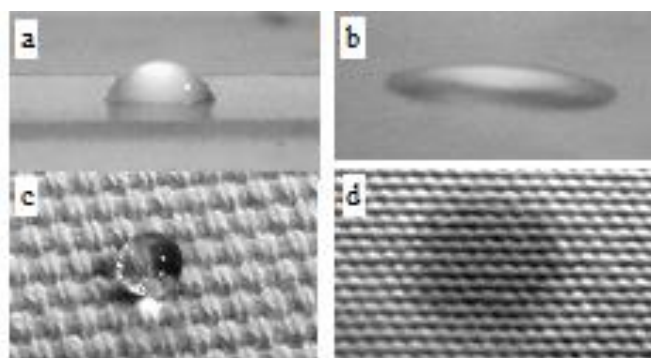


Figure 1. Images of water drops on the surface of PET film (a, b) and fabric (c, d) before (a, c) and after (c, d) plasma treatment at the $P=50$ Pa, $i=80$ mA, $t=5$ min.

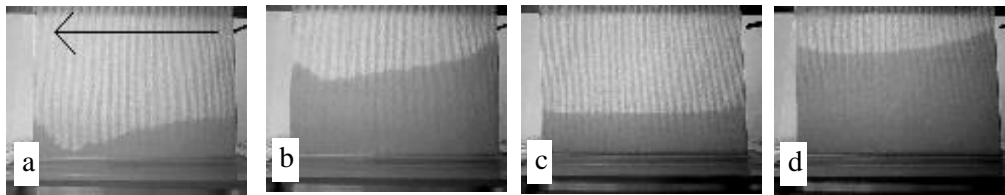


Figure 2. Influence the treatment time on the height of capillary rise: a, b – treatment time 0.5 min; c, d – treatment time 5 min; capillary rise time – 15 s (a, c) and 3 min (b, d). Arrow shows the direction of gas flow in plasma, width of fiber – 12 cm.

Table 1. Contact angle and surface energy of plasma treated PET films

Sample area (cm ²)	θ (degree)		Surface Energy (mJ·m ⁻²)		
	Water	Glycerol	γ_d	γ_p	γ
Untreated sample	78.2	64.5	25.5	10.2	35.7
20	25	28	20	46	66
41	26	26	22	44	66
82	26	25	23	44	67
123	23	24	22	46	68

Table 2. Height of capillary rise (h , cm) after plasma treatment of PET fabric for wetting time of 15 s and 3 min ^a.

Sample area, cm ²	Treatment time 0,5 min		Treatment time 1 min		Treatment time 5 min	
	15 s	3 min	15 s	3 min	15 s	3 min
20	2.20	5.58	2.14	6.40	2.70	7.36
41	2.23	5.80	1.97	5.67	2.60	7.23
82	2.15	5.68	2.21	6.12	2.59	7.12
123	2.01	5.96	2.31	5.92	2.51	6.85

^a $P=50$ Pa, $i=80$ mA. $h=0.6$ cm for untreated sample after 15 s wetting.

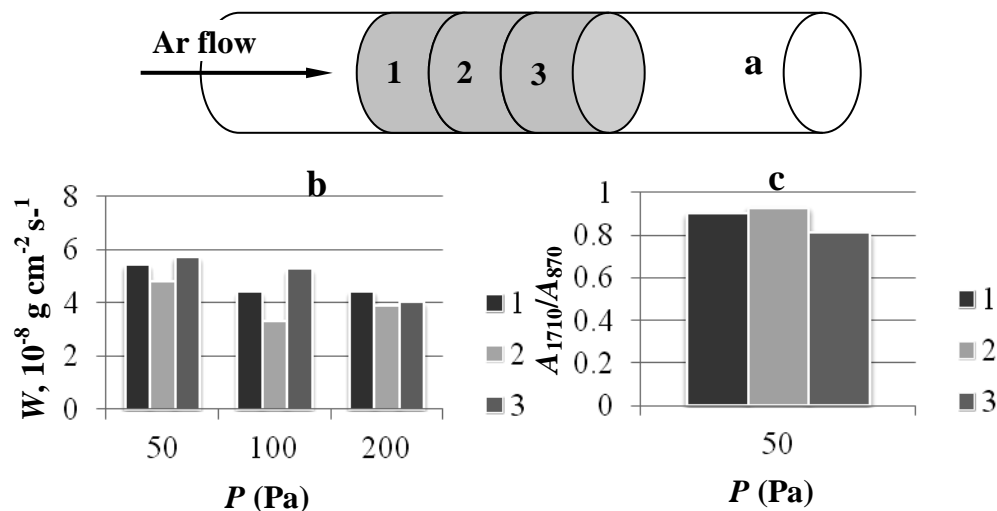


Figure 3. Scheme of sample placement in a reactor (a), etching rate (b) and reduced absorbance of C=O groups ($\nu=1710\text{ cm}^{-1}$) at the treatment of PET film in argon plasma. Discharge current – 80 mA, treatment time – 5 min.

Contact angles and surface energy of PP films after treatment are represented in table 3. ATR-FTIR spectra show an increase of absorbance at $\nu=1572\text{--}1809\text{ cm}^{-1}$ (C=O groups) after treatment of PP films in remote plasma. When PET film is placed in argon plasma the absorbance is higher (table 3). It can be due to oxidative reactions initiated by long-lived active species forming in plasma. These species (oxygen atoms and OH radicals) can be the products of dissociation of PET gaseous destruction products. Oxidation of PP surface leads to increase in hydrophilic properties: contact angles decrease and surface energy increase. It has to be noted that presence of PET in the plasma leads to higher values of PP surface energy.

Table 3. Integral absorption at $\nu=1573\text{--}1809\text{ cm}^{-1}$ ($S_{\text{C=O}}$), contact angles (θ) and surface energy of PP films fter treatment in remote argon plasma ^a

Sample area of PET film in plasma (cm^{20})	$A_{\text{C=O}}$ (relative units)	θ , degree		Surface Energy ($\text{mJ}\cdot\text{m}^{-2}$)		
		Water	Glycerol	γ_d	γ_p	γ
Untreated PP	1.0	88	83	11.7	10.3	22
0	1.9	67	62	17.2	20.4	37.6
20.4	1.9	60	59	14.2	27.2	41.4
40.8	2.1	59	61	12.3	29.3	41.6
81.6	2.0	55	61	9.8	34.5	44.3
122.4	2.2	61	56	19.1	23.8	42.9

^a Argon pressure 50 Pa, discharge current 80 mA, treatment time 5 min.

4. Conclusions

Treatment of PET films and fabrics results in increase of hydrophilic properties. Modification of samples with large area shows spatial non-homogeneity, which can be caused by the influence of gaseous etching products on plasma properties and kinetics of plasma active species formation. Experiments show the possible reactions of oxygen-containing active species originated from gas products of poly(ethylene terephthalate) etching in argon plasma

Acknowledgements

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5. References

- [1] Kutepov A M, Zakharov A G, Maximov A I 2004 *Vacuumno-plazmennoe i plazmenno-rastvornoe modifitsirovanie polimernikh materialov* M.: Nauka Publishers p 496 (In Russian)
- [2] Titov V A, Shikova T G, Smirnov S A, Ovtsyn A A, Kuzmicheva L A, Chlustova A V 2016 *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **7** 61 (In Russian)
- [3] Smirnov S A, Titov V A, Shikova T G, Ovtsyn A A, Kadnikov D V 2016 *Applied Physics* **4** 43 (In Russian)
- [4] Rybkin V V, Kuvaldina E V, Smirnov S A, Titov V A, Ivanov A N 1999 *High Energy Chemistry* **33** 409