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Argon ion beam interaction on polyethylene terephthalate surface by a 4 kJ plasma focus device

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Abstract. Polyethylene terephthalate (PET) has a wide variety of applications ranging from making regular bottles to biosensors. However, for many of these applications, surface treatment is needed to improve its surface characteristics such as adhesion to other materials. In this study, we focussed on treating PET foils by dense Ar pulsed plasma produced by a 4.5 kJ Mather-type plasma focus device (20 kV, 40 μf, 115 nH) to examine its ability to make the PET surface hydrophilic. The most common method to examine this characteristic is measuring the water contact angle on a polymer surface. The results show that while the energy and density of plasma in our device are higher compared to other devices, as the exposure time is very low, the device can enhance the wettability of PET film surfaces.

Keywords. Polyethylene terephthalate surface treatment; Amirkabir plasma focus; plasma focus device; water contact angle measurement.

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1. Introduction

The plasma focus devices having energy from a few kJ to MJ are able to generate energetic ions with energy ranging from a few hundreds of keV to tens of MeV [1,2]. This device can generate short-lived (10–100 ns) but high-temperature (0.1–2.0 keV) and high-density (10^{18}–10^{20} cm^3) plasma. In recent years, the ion beams generated by plasma focus devices have been used for material processing [3,4], thin film deposition, semiconductor doping and ion-assisted coating [5], ion implantation and thermal surface treatment [6].

Polyethylene terephthalate (PET) is widely used in different industrial and biomedical applications for e.g., as bioabsorbable polymers, for biocompatibility enhancement, in devices used for bone fixation, in diagnostic biosensors etc., [7] because of its desirable bulk properties like transparency, high strength-to-weight ratio and good thermal resistance [8]. However, for many of these applications it is necessary to improve its surface characteristics such as wettability, dyeability, biocompatibility, adhesion to other materials and

surface conductivity [9,10]. For these purposes, many techniques such as flame treatment, washing, using abrasives, electric arc processing, graft copolymerization, corona discharge treatment and laser irradiation are used. For the past 15 years, plasma polymer treatment is considered as an effective method, especially in biomedical applications to improve adhesion because it is friendlier to the environment and does not affect the bulk properties of the polymer. This type of treatment specially makes the polymer surface hydrophilic and water contact angle with the surface generally decreases depending upon the device set-up, the type of gas introduced as well as plasma density and ion energies.

Ions, electrons, free radicals and photons available in plasma are responsible for breaking chemical bonds and producing radicals leading to a series of chemical reactions on the polymer surface. Argon, nitrogen, oxygen, ammonia and hydrogen [11] are mainly used to change the hydrophobic surface of the PET to hydrophilic. The hydrophilic modification by the argon plasma is mainly due to the formation of oxygen functional groups on their surfaces, even though the argon plasma does not contain oxygen atoms. Oxidation reactions occur at the carbon radicals after irradiation of the argon plasma with nearby oxygen atoms or a residual of oxygen in the surrounding media. In fact as argon plasma interacts with the PET surface, five main modifications may occur [7]: (1) Surface activation: where the interaction of plasma with the polymer involves both gas and surface reaction mechanisms. The gas-phase reactions in the discharge volume lead to the production of atoms, molecules, free radicals, ions, excited species in different electronic, vibrational and rotational states, electrons and photons. Depending on the energy and the reactivity of the plasma-created species with respect to each other and with respect to the surface, recombination/deposition processes on the surface or etching or ablation of the polymer takes place. (2) Functionalization (grafting) reactions: where carbon free radicals can react with the molecular and atomic species. (3) Crosslinking reactions: predominantly take place by the interaction of radicals formed on the polymer chains in plasmas. (4) Surface etching (ablation) reactions: where in plasma treatments, tough conditions such as high power density, low pressure and long treatment times give rise to decarboxylation which can dramatically affect the mechanical properties of the assembly at the interface and has a drawback on surface wettability. (5) Plasma cleaning/etching effect: one can take advantage of this ablation effect of plasmas to eliminate the contamination layers present on the surface of polymers. These layers are due to polymer processing aids and functional additives such as antistatic agents. This is caused by physical sputtering and/or etching by active species resulting from the decomposition of residual air.

Several reactions may take place or radicals may be produced because of Ar PET surface bombardment. Figure 1 shows some of these reactions [12].

Although several constituents are available in plasma, many investigations have shown that ions are the most efficient species in plasma which can modify the polymer surface [10]. In recent years, radio frequency (RF) generators and dielectric barrier discharge (DBDs) were the main candidates for producing plasma for treating polymer surfaces. There is a question about how much time the plasma – especially ions – need to start the reactions. Some researchers have also investigated the influence of pulsed plasma on polymers and compared it with continuous plasma generation. Inagaki *et al* [11] modified the surface of ethylene-co-tetrafluoroethylene films by H_2 and Ar remote plasmas operated at a radio frequency (RF) power of 100 W at 13.56 MHz frequency for 120 s. They

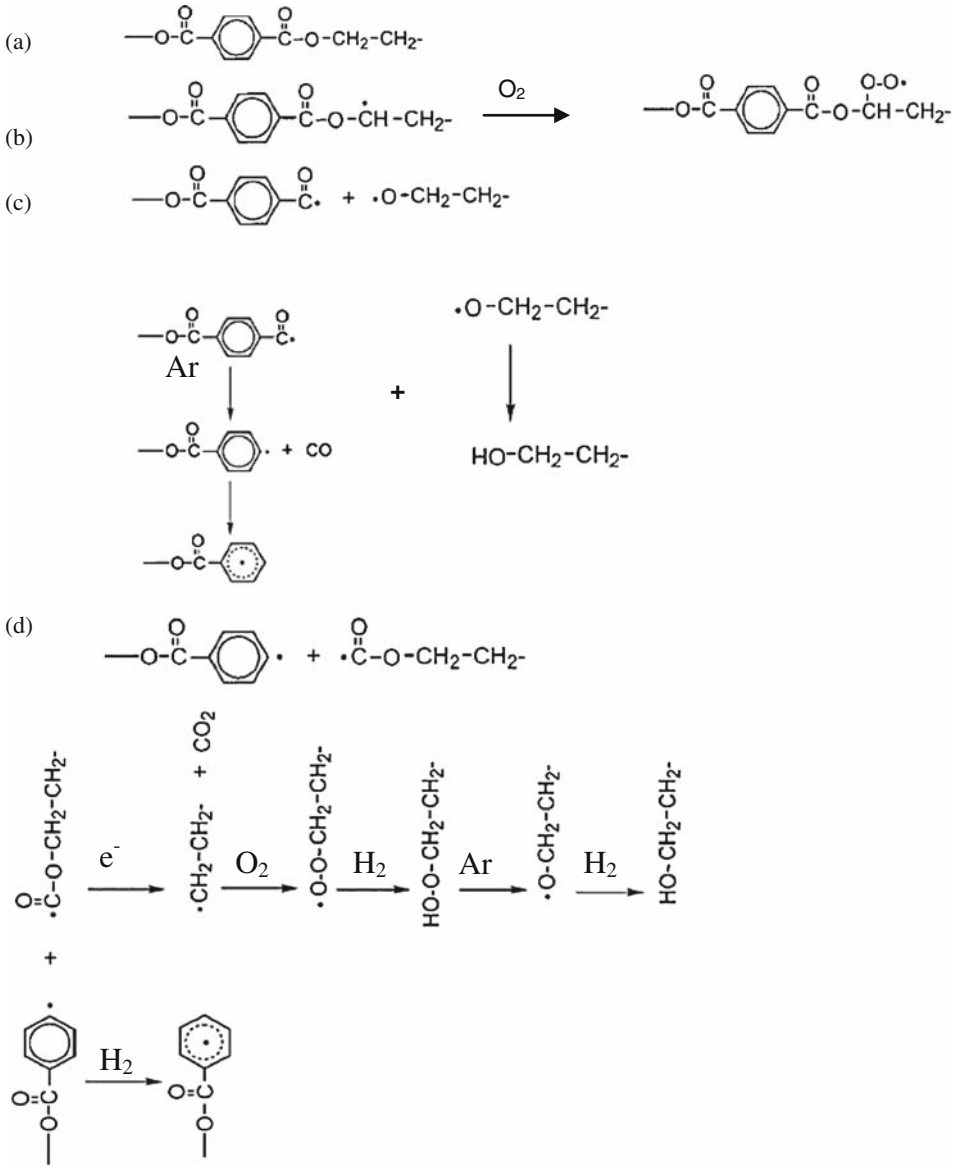

Figure 1. (**a**) PET monomer, (**b**) monomer irritated by argon and its reaction with oxygen, (**c**) scission of C–O bond and its corresponding radical reactions with hydrogen on the polymer surface and irradiation of other radicals by Ar and (**d**) scission of the C–C bond and its corresponding radical reactions with hydrogen or irradiation by Ar.

also studied aromatic groups in polymer chains on the plasma surface using argon, and oxygen plasmas were operated at RF powers of 25–100 W at 13.56 MHz frequency and a system pressure of 13.3 Pa for 0.2 s [12]. De Geyter *et al* [8] investigated the characterization of polymer films with a dielectric barrier discharge (DBD) in air, helium and argon at medium pressure for 42 s.

The objective of this research was to find the ability of the pulsed dense plasma in a plasma focus device to improve the hydrophilicity of PET. Water contact angle measurement is used to quantify this ability in a period of one month after plasma exposure.

2. Experiments

The APF device was energized by a 40 μf capacitor charged up to 15 kV. The measured total external inductance was 115 nH. The inner electrode was a hollow copper cylinder with 20 mm diameter and 148 mm length. The outer electrode was composed of six copper rods forming the shape of a squirrel cage with an inner diameter of 44 mm. The anode and cathode were separated by a Pyrex tube of 48 mm length. The vacuum system, consisting of a rotary and a diffusion pump, evacuated the chamber up to 10^{-5} torr before puffing neon gas. As the impurities affect the output radiation significantly, the chamber was evacuated to a pressure of 10^{-3} torr after five shots. Then, it is refilled with fresh neon gas. A parallel plate spark gap with a swinging cascade configuration was used as the high voltage switch. The gap was triggered via an isolating capacitor using HV SCR via a TV transformer. The dense plasma produced by the APF device and the experimental set-up are shown in figure 2.

PET samples were ordinary chemical products which were cut into 50 mm $*$ 50 mm pieces and stored in a 70% ethanol bath for 10 min and then washed and dried in standard air conditions. Purity of Ar was 99.99 and was used without further purification.

Regarding the previous work [13], in order to have a good characteristic of ions, the foils were mounted on a holder, 10 cm away from the central anode. As we would like to know only the influence of plasma ions an inert gas was needed to prevent the chemical reaction of gas with the available radicals on the PET surface. Among He, Ne and Ar, argon was selected because of the higher momentum of Ar ions compared to other inert gases.

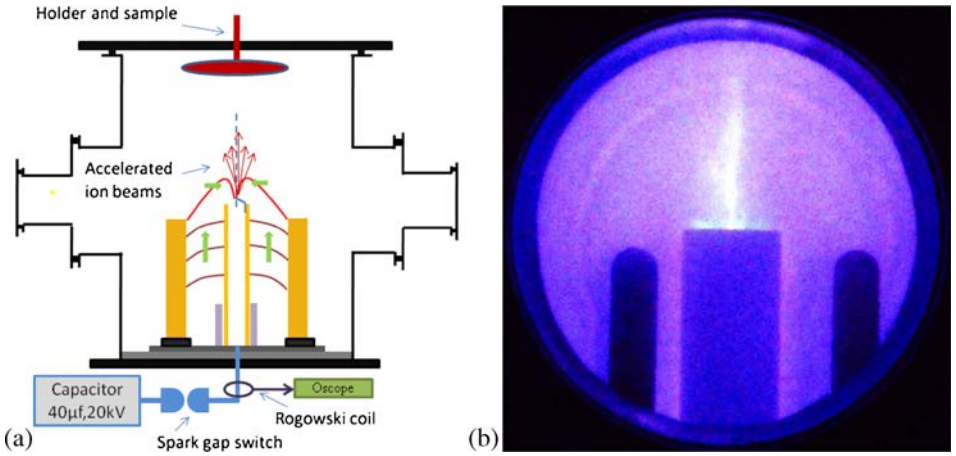

Figure 2. (**a**) A scheme of the APF plasma focus device as an ion beam accelerator and (**b**) a picture of the dense plasma column produced by the APF plasma focus device.

The average working pressure of the device was 3 mbar and before the start of each experiment, its conditions were optimized in order to have Ar ions in every plasma discharge.

Water contact angle with treated PET foils was measured by using the Dataphysics OCA-20 device with the sessile drop method [14] at room temperature of 18°C. For each experiment, there were two foils and water contact angle was measured at three points on the PET surface with an experimental error of $\pm 5^{\circ}$.

3. Results and discussion

In order to measure the influence of Ar plasma in the APF device [15] on the PET foil surface, we intially need to introduce a condition that plasma pinch will be available in every single shot. On the other hand, because the density and energy of ions in our device are higher than the generally used plasma generators [13], we should start from lower voltages and pressures to reduce the potential drawback of high-energy ion bombardment. The PET foils were exposed to plasma in three different steps: (a) 3 mbar air pressure, 10 kV capacitor voltage, 10 shots, (b) 3 mbar Ar pressure, 12.5 kV capacitor voltage, 10 shots and (c) the conditions were similar to step b but the number of shots were doubled to investigate the influence of higher plasma exposure time on surface wettability improvement. Figure 3 shows the typical characteristics of a plasma pinch in steps (a) and (b).

In fact, by increasing the voltage we would know the influence of higher energy ions on improving hydrophilicity. Table 1 shows the water contact angle of PET foils just after plasma exposure for all the three steps in comparison with the water contact angle of untreated PET foil.

As shown for steps (a) and (b), the water contact angle was decreased. While hydrophilicity improvement is less in step (a), its improvement in step (b) is comparable with earlier studies using other devices. Figure 4 shows a visual improvement of wettability using the APF device. Table 2 shows a comparison of the reduced water contact angle in this study with previous studies using Ar.

As a matter of fact, plasma treatment modifies the surface energy of PET films. Contact angle measurement is a simple and convenient method to determine the surface wettability. Contact angles are not only influenced by the interfacial tensions but also by other phenomena, such as roughness, chemical heterogeneity and molecular orientation [16].

The interaction between the liquid and the polymer surface is described by the surface energy of the polymer and the liquid. The shape of the liquid drop without any external interactions is spherical. The volume of the drop must be small enough to exclude the influence of gravity on its shape. Mainly, surface energy of the polymers is lower than that of metals [17]. In contact with the solid surface, the drop deforms depending on surface tension which can be described by different kinds of intermolecular interactions between the molecules of polymers and liquids [18]. Measurement of the contact angle is the usual method of quantifying the change in a processed plastic part. Finding the relationship between the contact angle and the surface energy is a widely accepted method for characterizing local surface changes in response to treatment of the parts [19].

Regarding tables 1 and 2, it is suggested that for an average pressure of 3 mbar and a capacitor voltage of 10 kV, the angle reduces from 88 to 72. Increasing the voltage

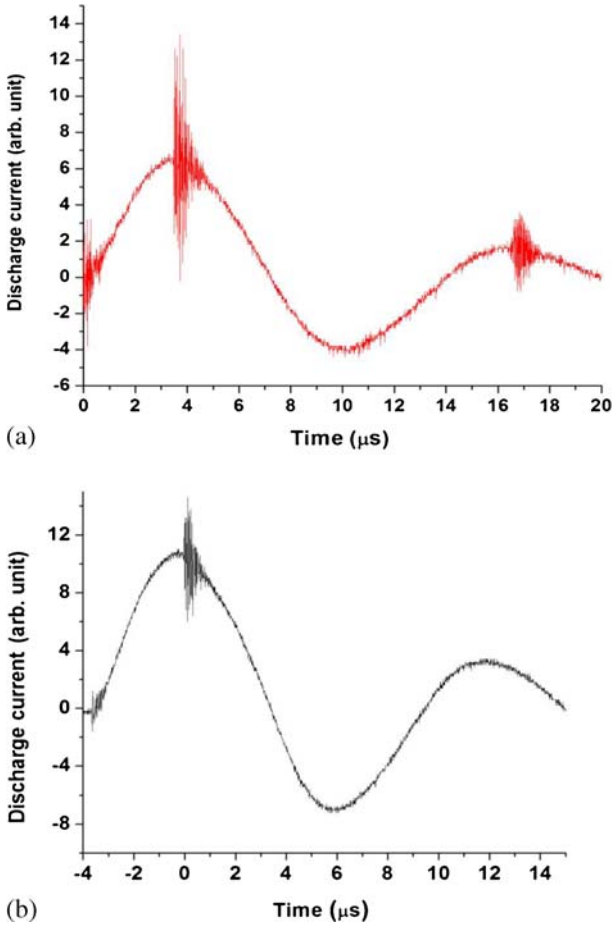

Figure 3. Diagram of a typical pinch voltage for (**a**) step (a) and (**b**) step (b).

has a good influence on reducing the angle from 88 to 51, which is not only comparable with other devices but also shows that – as reported in [12] – higher exposure time is not quite necessary to reduce water contact angle. This is because, for example in the APF device, each single-shot plasma – from beginning to disruption – lasts about 10^{-7} s. So for 10 shots the total exposure time is 10^{-6} s which is much lower than the reported exposure times. Therefore, ion characteristics play a more significant role in improving hydrophilicity than the exposure time.

Table 1. Water contact angle of PET foils for three steps just after plasma exposure.

Before exposure	Step (a)	Step (b)	Step (c)
88°	70.5°	51.2°	91°

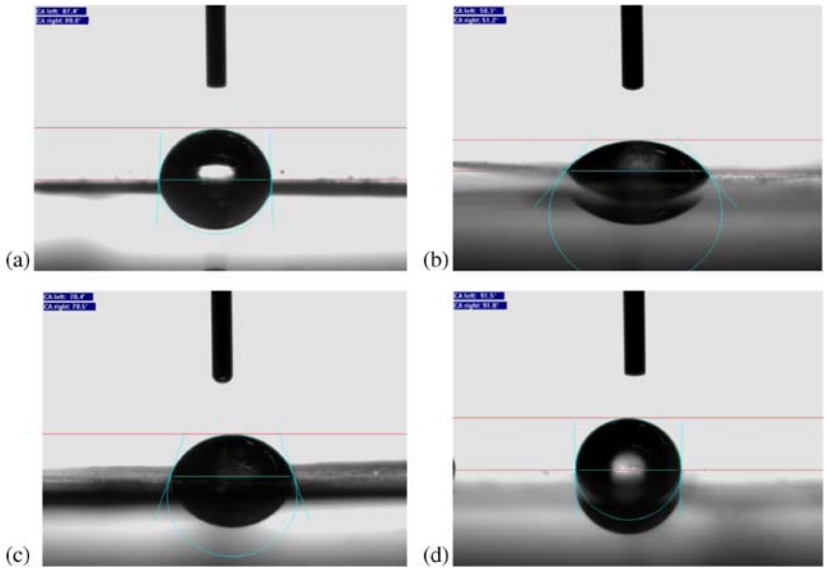

Figure 4. Visual comparison of the improvement in hydrophilicity: (**a**) before treatment, (**b**) for step (b), (**c**) for step (a) and (**d**) for step (c).

In step (c) however, it is shown that increasing the number of shots not only improves the hydrophilicity but also has a drawback as it increases the water contact angle from 88 to 92. This may suggest that higher ion bombardment time results in removing oxygen functional groups from the PET surface which is also reported in ref. [10].

Another important issue in improving polymer hydrophilicity is a phenomenon called aging effect. In this case, the wettability of plasma-treated polymer changes and the water contact angle usually increases up to its initial untreated surface value. Two main reasons are suggested for this phenomenon. (i) After plasma exposure, a high concentration of free radicals and unstable chemical groups with high polarity cause an increase

Table 2. Comparison of the improvement in hyrophilicity using Ar plasma in APF with two generally used devices.

Device	Set-up	Water contact angle before treatment	Water contact angle after treatment	Improvement in water contact angle (°)
RF generator	100 W for 120 s, continuous [11]	78	32	46
RF generator	30 W for a total exposure time of 0.2 s, pulsed [12]	78	45	32
DBD	Duration of 42 s, continuous [8]	75	29	46
APF device	12.5 kV, 3 mbar, total exposure time of 10^{-6} s, pulsed [15]	88	51	37

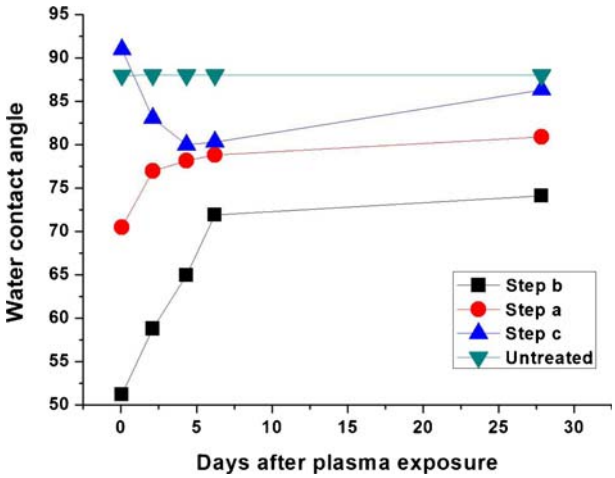

Figure 5. Water contact angle as a function of aging time after plasma treatment.

in surface energy which reduces water contact angle. With time, the chemical reactions with atmospheric constituents such as oxygen, water vapour and CO_2 reduce the surface energy and the water contact angle increases. (ii) On the other hand, higher surface energy in comparison with the surrounding medium or polymer interlayers results in a thermodynamically-driven reorientation of molecular chains and sometimes if the surface layer does not contain a sufficient carbonized structure, macromolecules tend to move inward and hence again surface energy reduces.

In figure 5, the aging effect for PET-treated films of each step is shown in a period of one month. For steps (a) and step (c), the water contact angle increases significantly till the seventh day and then it slowly increases till it becomes constant after 30 days. As it is shown, a 20° difference after exposure time reduces to 10° after one month for steps (a) and (b). Therefore, in many applications it is suggested that the adhesion takes place immediately after plasma exposure to prevent the aging effect. In step (c) however, there may be a challenge between the new reactions of the polymer surface with the surrounding medium and macromolecular movements after plasma treatment. One may suggest that because of higher bombardment time, the concentration of free radicals is higher on the surface for step (c) PET films compared to the two other experiments, i.e.,

Table 3. Water contact angle of PET films just after plasma exposure and after 30 days.

Device and set-up	Just after plasma exposure (°)	After 30 days (°)	Untreated (°)
APF step (a)	70.5	81	88
APF step (b)	51.2	74	88
APF step (c)	91	86	88
RF generator [11]	47	62	78

until the seventh day, reaction of free radicals with the surrounding medium like N_2 and O_2 are dominant and effective in reducing water contact angle [20]. But after the seventh day, reorientation of macromolecules becomes dominant as the number of free radicals decreases and the aging effect will behave similar to what was seen for steps (a) and (b). Table 3 shows a summary of the aging effect of water contact angles in this study and the reported aging effect in ref. [11] for Ar plasma.

4. Conclusions

The aim of this study was to examine the ability of the APF device to improve the hydrophilicity of PET samples. PET films were treated by pulsed Ar plasma. The effect of dense plasma exposure on the hydrophilicity improvement was investigated by measuring water contact angle. The results have shown that there exists an optimum device set-up which improves hydrophilicity of PET foils. Similar to previous studies, the aging effect occurs and results in hydrophobic recovery of samples. Higher exposure time does not necessarily improve hydrophilicity, i.e., there exists an optimum set-up to achieve the best wettability enhancement. In the near future, an extended characterization (XPS and AFM analyses) of the exposed polymer samples will be carried out to determine the key factor for altering hydrophilicity after plasma treatment (chemical modification or surface etching).

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