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Modification of PET surface properties using extremely non-equilibrium oxygen plasma

Abstract: Polyethylene terephthalate (PET) foils have been exposed to oxygen plasma and its afterglow in order to reveal compositional and structural modifications of the surface layer. Oxygen plasma was created by electrodeless RF discharge in a glass chamber so the O-atom density was close to 10^{22} m^{-3} although the density of charged particles was only about 1×10^{16} m^{-3}. Long-living reactive particles created in plasma were leaked into the afterglow chamber using a two-stage rotary pump of pumping speed 4.4×10^{-3} m^3 s^{-1}. The density of O-atoms in the afterglow as measured with a catalytic probe was 3×10^{21} m^{-3}, while the density of reactive oxygen molecules was estimated theoretically. The functionalization was accomplished even after a brief exposure to either plasma or afterglow since all samples were saturated with oxygen-rich functional groups as revealed by XPS. The water contact angle measurements, however, showed that only plasma treatment allowed for super-hydrophilicity, explained by rich surface morphology as detected by AFM. The differences in morphological properties between plasma and afterglow treated samples were explained by different interaction mechanisms between low and high energy particles impinging the polymer surface.

Keywords: polymer, plasma, afterglow, surface morphology, functionalization

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1 Introduction

Today polymer materials are widely used in a variety of industrial branches. The type of polymer used for manufacturing products is selected according to chemical, thermal and mechanical properties. The surface properties of a selected polymer, however, may not be always adequate so they should be modified. A variety of mechanical and wet chemical methods for modification of surface properties of polymer materials were invented decades ago. They all have advantages and disadvantages. The major disadvantage of wet chemical methods is ecological unsuitability; nowadays they are avoided whenever possible and are being gradually replaced by dry plasma treatments. A variety of plasmas have been applied to functional polymer surfaces with specific functional groups, and numerous discharges have been applied for plasma generation. Increased hydrophobicity of polymers is achieved by functionalization with non-polar functional groups (usually containing fluorine) and super-hydrophobicity is achieved by combined effects of fluorine-rich surface functional groups and rich surface morphology on the nano-scale [1-3].

Improved hydrophilicity of polymers, on the other hand, is obtained by treatment with plasma created in different gases such as air, oxygen, water vapour and carbon dioxide [4]. Gaseous molecules partially ionize, dissociate and excite in a gaseous discharge forming reactive particles which readily interact with polymer surface causing modification of surface properties. Numerous authors reported excellent results on improved hydrophylicity for several types of polymers [5] including polyethersulphone [6-7], polyphenylene sulphide [8], polystyrene [9-10], polyvinylchloride [11-13], polyethylene naphthalate [14], polymethyl methacrylate [15], cellulose [16-19]. The authors report a different behavior of polymers upon plasma treatment. Some polymers can be made super-hydrophilic while only a moderate increase of the water contact angle was reported for other polymers [20-24]. The improved wettability was always attributed to the formation of polar functional groups on surfaces of different polymers, but the type and concentration of functional groups depended on the type of polymer and processing parameters. Some authors have reported modification of surface morphology upon treatment with gaseous plasma, but the results vary significantly not only

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between different types of polymers but also between different discharges used for plasma generation [25-28]. Many authors monitored polymer etching upon plasma treatment, and different results were reported for different polymers and processing conditions [29-30]. Quantitative results are not reported frequently since qualitative techniques (often optical emission spectroscopy) are often applied to monitor etching phenomenon [31-32].

A polymer of particular interest is polyethylene terephthalate (PET). It is a polyester widely used nowadays in different industrial branches as well as in medicine. It is a moderately hydrophobic polymer with a melting point just above 500 K. It is a preferred polymer for scientific research especially since even un-treated material contains oxygen-rich functional groups; therefore, results of characterization by surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) are rather easy to interpret. The material is rapidly functionalized using oxygen-containing gaseous plasma created by different discharges. Although numerous authors have addressed the scientific issues on interaction of gaseous plasma with PET materials [33-37] the role of different reactive plasma particles in surface modification is still not well understood. A reason for a poor understanding of phenomena is that plasma contains a variety of particles capable of modification of PET surfaces and synergistic effects might play a dominant role. The main goal of our research was to separately study interaction with high and low energy particles created in oxygen plasma in order to better understand the interaction with the surface of the widely used PET polymer. For this purpose we performed treatment of PET materials directly in plasma and in afterglow regions of the same experimental system.

2 Experimental Procedure

Experiments were performed in the system presented schematically in Fig. 1. The system is made from borosilicate glass Schott 8250 suitable for joining with Kovar alloy. The discharge part of the system is separated from the afterglow with a narrow tube of outer and inner diameters of 9 and 6 mm, respectively, made from the same material as the main (wide) tube of diameters 40 and 36 mm, respectively. Molecular oxygen of industrial purity is leaked into the discharge component where it is transformed into the state of non-equilibrium plasma using an electrode-less RF discharge. The RF generator is coupled with an antenna as shown in Fig. 1. On the other side, the system is pumped with a two-stage rotary pump of a pumping speed 4.4×10^{-3} $m^3 s^{-1}$. Pressure is measured in the afterglow chamber with a baratron which is protected from O-atoms with a recombinator made from oxygen-free high conductivity (OFHC) copper grid. The pressure was set to 75 Pa. The plasma density is measured with a simple double electrical probe floating on the space potential in the center of the discharge tube. The ion density at the RF power of about 200 W is around 1×10^{16} m^{-3}. The neutral O-atom density is measured in the center of the afterglow tube above the sample and the value is around 3×10^{21} m^{-3}. The discharge part of the system is forced-air cooled so the outer surface of the tube remains at room temperature.

Commercially available PET foils of a 0.250 mm thickness supplied by DuPont Teijin Films (Maylar A) were cut into 20 mm x 10 mm pieces and briefly cleaned in ethanol. The PET foil used for our experiments had a melting temperature of 249°C, glass transition temperature of 75°C and the degree of crystallinity was 35.5%.

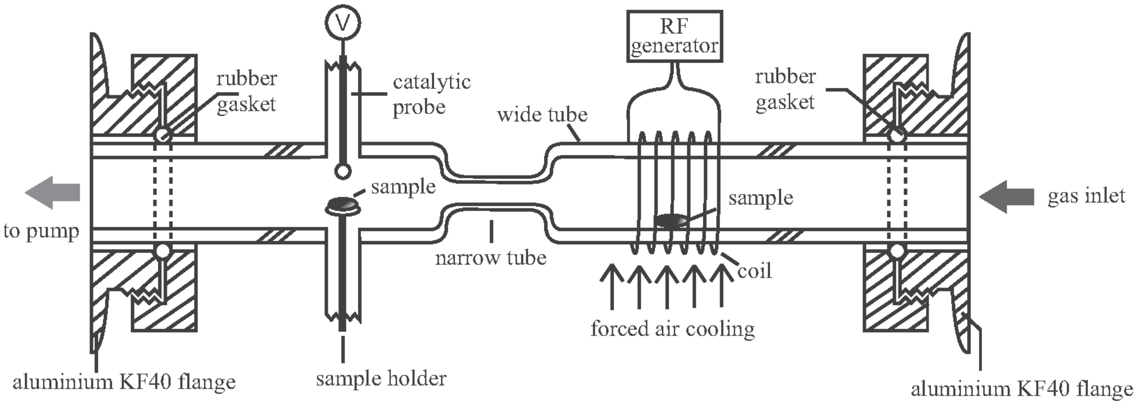

Figure 1: Shematic of the experimental setup. Not to scale.

According to the producer datasheet, the PET material was semi-crystalline with silica additives added in the polymer matrix. The samples were mounted either in the discharge or afterglow chamber. The treatment time was varied up to 120 s. Just after the treatment the samples were analyzed by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements (WCA) while atomic force measurements (AFM) were performed within a day after the treatment.

3 Results and Discussion

XPS survey spectra revealed an increase in the oxygen to carbon ratio in the surface film upon treatment of PET samples in both plasma and afterglow. The original O/C ratio was 0.26 (very close to the theoretical value) and even after the shortest treatment time of 3 s the ratio increased to 0.73 for both plasma and afterglow treatments. It remained fairly unchanged thereafter. The high resolution C1s peaks for untreated plasma and afterglow treated samples are represented in Fig. 2. The C1s peak of the PET sample consists of three peaks: a peak (C1) at a binding energy of 284.8 eV corresponding to C-C and C-H bonds in the phenyl ring, a peak (C2) at a binding energy of 286.6 eV corresponding to C-O bond and a peak (C3) at a binding energy of 288.9 eV corresponding to O=C-O bond. The spectra were taken after 10 s of treatment but very similar ones were obtained also after treatment for other periods. The C1 peak corresponds to C-C bonds. Since no significant difference between the plasma and afterglow treated sample were observed one can conclude that the surface saturates with functional groups irrespectively of the type of reactive particles used for treatment.

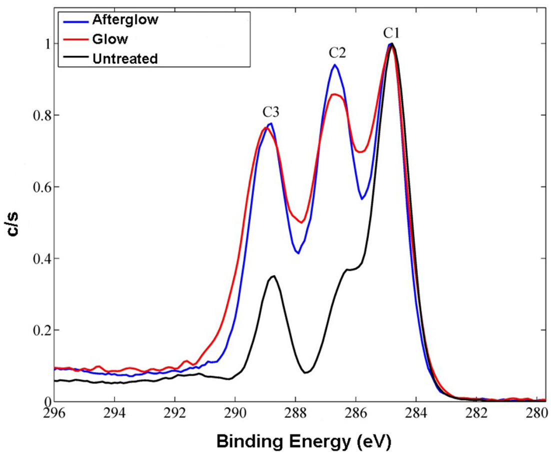

Figure 2: High resolution C1s peaks for an untreated sample and samples treated in plasma and afterglow for 10 s.

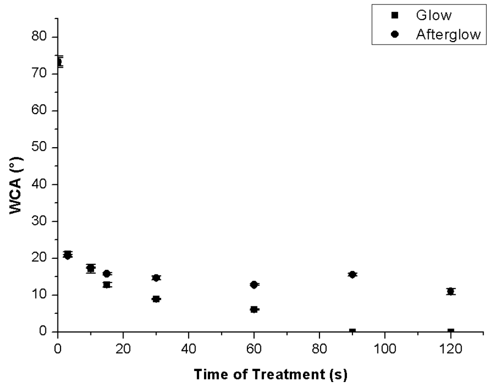

Figure 3: The water contact angle versus treatment time for samples treated in plasma (lower curve) and afterglow (upper curve).

Differences between samples treated with plasma and afterglow were observed using the WCA technique which determined the surface tension. Fig. 3 reveals the contact angles versus treatment time. The contact angle for untreated samples is about 74°. After the shortest treatment of 3 s the WCA dropped to about 22° and thereafter decreased with increasing treatment time. The contact angle became immeasurably small after about a minute of treatment for the plasma treatment, while it persisted at about 12° for samples treated in afterglow. The error bars in Fig. 3 represent statistical errors (measurements were repeated 5 times) and reveal high reproducibility of results. After ageing in air, the sample hydrophilicity changed due to reorientation of functional groups from the surface, to the more favorable state inside the surface. The PET foil which was treated for 3 s in plasma, showed that the water contact angle increased from 22° immediately after treatment to 35° after storage in air for 2 weeks and remains at this value after 4 weeks.

The differences in contact angles between plasma and afterglow treated samples are explained with different surface morphologies. Fig. 4 shows AFM images of samples treated in plasma and Fig. 5 represents corresponding images for the afterglow treatments. All images were taken on the surface area of 3 µm × 3 µm. The AFM technique allowed for determination of the average roughness. The values are summarized in Fig. 6. One observed huge differences between samples treated in plasma and afterglow. The average roughness of plasma treated samples increased over 10 nm while the roughness of afterglow treated samples remained below 2 nm. Furthermore, the lateral dimensions of nano-

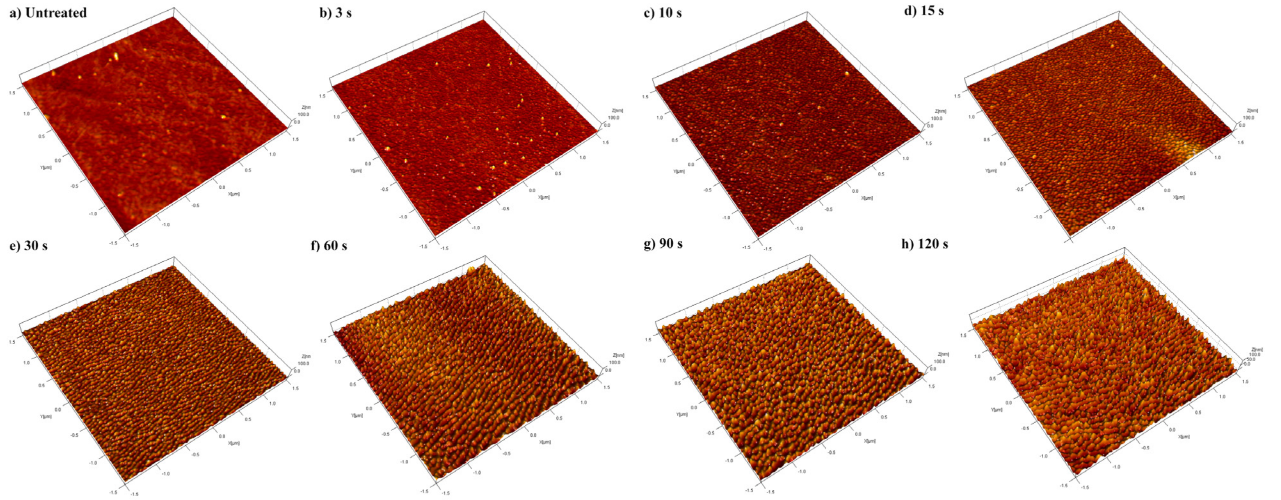

Figure 4: AFM images of samples treated in plasma.

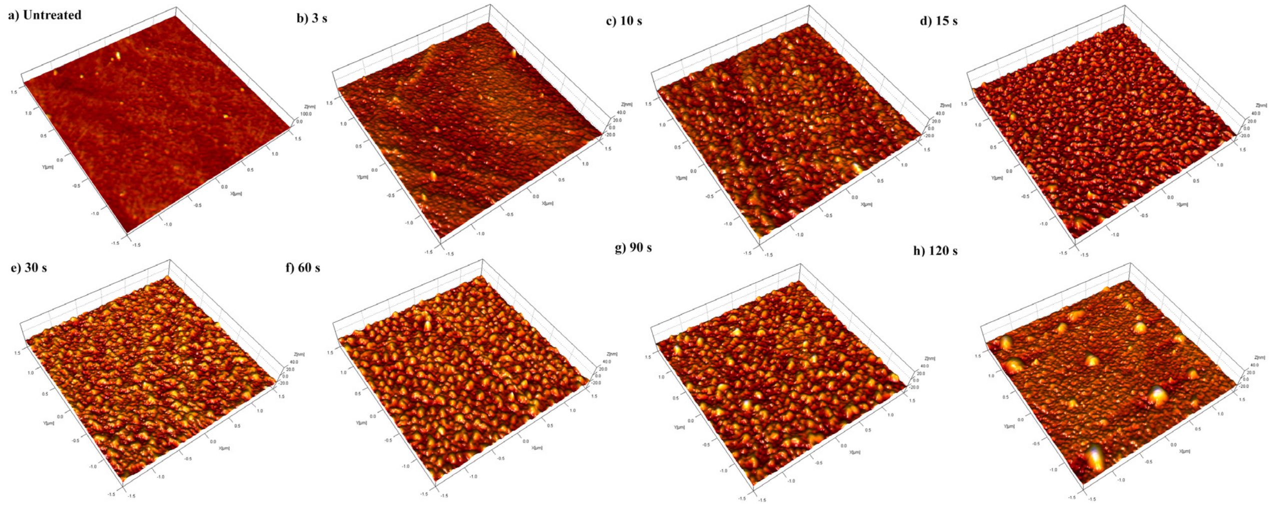

Figure 5: AFM images of samples treated in afterglow.

cones on plasma treated samples were much smaller than the afterglow treated samples. The combination of polar functional groups on the surface and rich surface morphology led to super-hydrophilicity of material most of the time. The necessary conditions for super-hydrophilicity of PET materials were reached in a minute of plasma treatment at our conditions, and the results are summarized in Fig. 6 indicating that super-hydrophilicity cannot be obtained in the afterglow.

Although the results do not allow for development of a detailed hypothesis on the interaction between reactive particles and PET material, they are worth discussing. Oxygen plasma afterglow is rich in neutral reactive particles of low potential energy, and any kinetic effects are neglected due to gas being maintained at room temperature. The estimated densities of particles in the afterglow are as follows: O-atoms in the ground state – 3×10^{21} m^{-3} (this value is also measured with the catalytic probe), O_2 molecules in the first metastable state (the "a" state) – 2×10^{21} m^{-3}, O_2 molecules in the second metastable state (the "b" state) – 1×10^{18} m^{-3}, O_3 molecules (ozone) – 2×10^{19} m^{-3}. [38] The density of molecules in the b state was too small to be taken into account in explanation of the rapid saturation of surface with oxygen groups, but all other particles could have been be involved in surface chemistry. Since the potential energy of O-atoms was the highest among the particles available in the afterglow, the functionalization was often attributed to these radicals. The atoms, together with O_2(a) as well as O_3 atoms cause etching of PET materials. Recent results obtained using

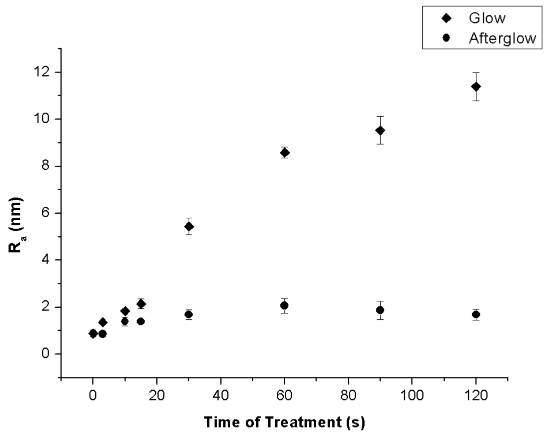

Figure 6: Roughness evolution of samples upon exposure to oxygen plasma and its afterglow.

quartz crystal microbalance showed that the etching rate at our conditions was around 10^{-2} nm s^{-1}. [36] The formation of nanostructures on PET samples treated in afterglow (Fig. 5) can be explained by easier etching of amorphous parts. Junkar et al. showed that amorphous PET was etched at a higher rate than semi-crystalline at the same conditions, so the formation of nanostructures of typical lateral dimension of almost 200 nm can be attributed to preferential etching of the amorphous phase. [33] These findings were confirmed also by DSC analysis, as plasma treated samples showed a higher crystalline content. Since the roughness did not increase substantially with increasing treatment time the etching selectivity using neutral particles found in the afterglow did not seem dramatic.

The density of atoms in plasma itself is somehow larger than in afterglow, but the difference is perhaps a factor 2, so the roughness evolution observed for the PET treated in glowing plasma (Fig. 4, 6) cannot be explained with O-atom effects. The density of ozone is lower in plasma than in afterglow, but the density of O_2 (b) molecules is about 2 orders of magnitude larger [38]. Furthermore, glowing plasma contains positively charged molecular ions and is a source of UV radiation at the energy of about 10 eV. Recent results show the etching rate of several nm/s in glowing oxygen plasma created in the same discharge tube [39]. The increasing roughness of samples treated in plasma is therefore explained with a rather strong etching. The explanation of the rich surface morphology shown in Fig. 4 is more complicated. The lateral dimension of the densely distributed nano-cones on plasma treated samples is about 70 nm, so roughly three times smaller than for the afterglow treatment. The existence of ions and UV radiation therefore facilitates formation of nanostructures of smaller lateral and higher vertical dimension. The ions impinge the surface at kinetic energy of roughly 15 eV since samples are kept at floating potential during treatment. The penetration depth of such ions is only a few nm, so they cannot cause substantial modification of the subsurface layer. Taking into account the low ion density (the measured value is 1×10^{16} m^{-3}) the ions themselves cannot cause etching at the observed rate (several nm s^{-1}), so synergistic effects of ions and neutral reactive particles should be responsible for a rather strong etching. The penetration depth of 10 eV photons in polymers is several 10 nm, so they are capable of modifying the subsurface layer [38]. The photons cause bond scission and thus structural changes of the polymer subsurface layer. This effect can explain differences in nano-structuring of PET between afterglow and plasma treatments. As mentioned earlier, small differences in the polymer structure are reflected in different etching rates resulting in the evolution of surface morphology as observed in Fig. 4.

4 Conclusions

Semi-crystalline PET samples were exposed to glowing oxygen plasma and its afterglow to study the evolution of surface properties due to interaction with reactive particles found in both types of highly non-equilibrium oxygen gas. The neutral particles of small kinetic energy were suitable for rapid surface functionalization resulting in improved surface wettability but super-hydrophilic properties could not be obtained due to lack of surface roughness. The addition of energetic particles such as UV photons and positively charged oxygen ions of energy around 10 eV did not influence the surface functionalization but caused increased surface roughness, formation of nanocones of sub-100 nm lateral and several 10 nm vertical dimensions and thus super – hydrophilicity of otherwise moderately hydrophobic material. The formation of such nano-cones which were even in dimension and covered the entire polymer surface had been explained by synergetic effects of UV radiation (which causes modification of several 10 nm thick subsurface layer) and oxygen ions which, together with chemisorbed oxygen atoms, caused extensive etching of less resistive component of the polymer.

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