Effects of operating parameters on DC glow discharge plasma induced PET film surface.

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Abstract. A DC glow discharge plasma surface modification techniques are used to modify surface properties of polymeric materials such as adhesivity, hydrophobicity, hydrophilicity and biocompatibility. The plasma interaction with the surface produces modifications of its chemical structure and morphology. The objective of this study is to examine the effect of operating parameters such as discharge potential, pressure and exposure time on surface properties of polyethylene terephthalate (PET) film. The changes in hydrophilic properties of PET films were studied in detail using contact angle and surface energy measurements. The surface morphology and chemical composition of plasma modified film surfaces were studied by atomic force microscopy (AFM) and X-ray photo electron spectroscopy (XPS). It was found that the efficiency of the surface treatment increases with increasing discharge potential, pressure and exposure time. The AFM and XPS analysis showed changes in surface topography and formation of polar groups on the plasma modified PET surfaces.

1. Introduction:
Polyethylene terephthalate (PET) films are widely used in packaging and biomedical industries due to their superior mechanical, physical, and chemical properties and their relatively lower weight, high corrosion resistance, good electrical and thermal insulation [1]. However the surfaces of PET’s are generally characterized by a low surface energy and hence poor adhesive properties. In order to assure good adhesion between the polymer and coating, the surface of the polymer must be modified. Several surface modification methods are employed to modify the polymer surfaces, such as chemical treatments, thermal treatment, mechanical treatment, and electrical treatments (corona or glow discharge plasma treatment) [2]. Of the above-mentioned methods, low temperature glow discharge plasmas have been widely used to modify polymer surface properties without changing the bulk properties. Moreover, it is a dry treatment method, which is better suited for industrial applications [3]. Primarily, a glow discharge plasma treatment provides many possibilities to refine a polymer surface, enabled by the adjustment of parameters like gas flows, power, and pressure and treatment time. Depending on the gas composition and plasma conditions, ions, electrons, fast neutrals, radicals and UV-Vis radiation contribute to the polymer treatment, resulting in etching, activation and/or cross-
linking or, in many cases, combined effects can be obtained [4-6]. The glow discharge plasma can be generated with either a DC or RF power source. In the industry, RF glow discharge is generally employed for surface modification of polymers.

In the present investigation, a DC glow discharge plasma operating in air at low pressure is used to alter the surface properties of a polyethylene terephthalate (PET) film. Air plasma offers a variety of species contributing to surface processing, with the oxygen in the discharge providing the dominant species leading to chemical etching and surface modification. Oxygen moieties are also incorporated on to the polymer surface due to the post exposure of samples to atmosphere [3]. In this sense, an air plasma is very much similar to an oxygen plasma [7]. The paper mainly investigate, the influence of the main operating parameters, such as treatment time, discharge potential and pressure on the surface properties of PET film. The hydrophilicity of the PET films was analyzed by using contact angle and surface energy measurements. The surface morphology and chemical composition of the plasma modified film surfaces were studied by atomic force microscopy (AFM) and X-ray photo electron spectroscopy (XPS).

2. Experimental setup and methodology
Low pressure DC glow discharge was generated in a plasma chamber made of glass tube of length 29 cm and internal diameter 10 cm. The discharge chamber was first thoroughly cleaned and air tightened. Initially chamber was evacuated to a pressure of $10^{-3}$ mbar using a vacuum pump (EDWARDS: E2M5). Through an air inlet (fine control gas needle valve) the required low pressure was maintained and measured by a pirani gauge. Electrodes were made of aluminum. They were circular in shape with a diameter of 5cm. Electrodes were fixed inside the chamber axisymmetric and perpendicular to the axis and were separated by a distance of 3 cm. The polymer film was inserted with its surface perpendicular to the discharge axis between the parallel disc electrodes. A dc potential was applied between the two electrodes and adjusted till stable glow discharge plasma is generated. The samples were treated for different exposure time, discharge potential and pressure level. Typical operating parameters are shown in Table 1.

| Parameter              | Value          |
|------------------------|----------------|
| Discharge potential    | 250-400 V      |
| Pressure               | 0.09-0.2 mbar  |
| Exposure time          | 0-20 min       |
| Electrode separation   | 3 cm           |
| Plasma gas             | Air            |

2.1 Characterization of plasma modified PET films
The surface hydrophilicity of plasma modified PET films was investigated by contact angle measurements using the sessile drop method. Contact angle was measured with reference to two different liquids, namely, distilled water and glycerol of known polar ($\gamma_p$) and disperse ($\gamma_d$) components. At least 10 readings were taken at different places and an average value was determined. Contact angle measurements were done immediately after the plasma treatment to avoid ageing effect. There are various methods to calculate solid surface energy from contact angle measurements, but the break-up of surface energy in terms of its polar and dispersed components can be determined only by using Fowkes’ method [8]. The surface energy was calculated from contact angle measurement using Fowkes’ approximation as follows [9].

$$\frac{1 + \cos \theta}{2} \times \left[ \frac{\gamma_f}{\sqrt{\gamma_p \gamma_d}} \right] = \sqrt{\gamma_p} \times \sqrt{\gamma_d} + \sqrt{\gamma_p \gamma_d}$$
where $\theta$ is the angle of contact. $\gamma_l$ is the liquid surface tension. $\gamma_l^p$ and $\gamma_l^d$ are the polar and disperse components of the test liquids respectively. Finally, the total solid surface energy ($\gamma_s$) is expressed in terms of its polar and disperse components

$$\gamma_s = \gamma_s^p + \gamma_s^d \text{ (mJ/m}^2\text{)}$$

where $\gamma_s$ (mJ/m$^2$) is the total surface energy of the polymer film, and $\gamma_s^p$, $\gamma_s^d$ (mJ/m$^2$) are the polar and disperse components of surface energy of the polymer film.

The surface morphology of PET films were analysed using Seiko Instruments Scanning force microscopy (SFM, SPI3800N Probe station and SPA400 SPM Unit, SPM images were acquired in air with tapping mode) and the change in the chemical composition on the PET film surface and chemical binding state was examined using X-ray photo electron spectroscopy (Kratos Axis Ultra spectrometer, UK equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The concentration of each chemical component with C1s can be calculated by deconvolution using Gaussian–Lorentzian fit (XPSPEAK41 software).

### 3.0 Results and discussion

#### 3.1 Hydrophilic analysis: Contact angle and Surface energy results

Figure 1a shows the contact angle of PET film w.r.t. water as a function of exposure time for different discharge potentials while keeping working pressure constant at 0.2 mbar. It is seen that contact angle of the untreated surface is 86.2° for distilled water. The contact angle values decreased rapidly by 50% for even shorter exposure time (6 min). The contact angle of PET film decreased further with increasing the discharge potential and treatment time (Figure 1a). The values do not change significantly after longer exposure time due to saturation of plasma effect on the PET film. On increasing the discharge potentials the degree of ionization of plasma increases, producing high amount of active species which react immediately on the polymer surface. This leads to incorporation of oxygen-containing polar groups such as C=O, O-C=O and OH on the plasma treated film surface causing a decrease in contact angle [9-10].

Figure 1b illustrates the variation of contact angle of PET film w.r.t. water as a function of exposure time for different pressure levels; the discharge potential and electrode separation were kept constant at 400V and 3cm respectively. At a given pressure level, the angle of contact decreased significantly with increasing exposure time and reached the level of saturation. The decrease in contact angle of PET films proceeds faster when the operating pressure level is increased which may be due to the increase in concentration of reactive oxygen species with increase in pressure level.

The effect of plasma exposure time and discharge potential on the surface free energy and polar components of PET films are shown in Figures 2a and b respectively (Here in order to calculate surface energy we have measured angle of contact with respect to two different liquids namely water and glycerol. However contact angle data of glycerol is not given in the paper). The surface energy of plasma modified PET films increases on increasing the exposure time. It reached a maximum value at 15 min of exposure time, and thereafter tends to saturate. This may be due to lack of any change in the oxygen content incorporated onto the surface. Figure 2a, clearly exhibits that total surface energy of the PET film attained a higher value when the film was exposed to higher discharge potential compared with lower potentials. Similar kind of trend was observed in the increase in polar components as shown in Figure 2b.

Figure 3 a and b illustrates the variation in surface energy and polar components of the PET film surfaces as a function of plasma treatment time for different operating pressure levels. It has been observed that the total surface energy and polar component of surface energy of PET film increases with the time of exposure, which reaches maximum at 15 min, these values do not change significantly with longer exposure time which may be due to the effect of saturation. It was clearly noted that the total surface energy and polar components of PET film undergoes significantly higher change when the polymer is exposed at higher pressure levels which is mainly due to the incorporation of polar
groups like CO, COO, OH etc. [9]. However there is no appreciable change in dispersion components ($\gamma_s^{d}$) and therefore it is not shown here. Hence the increase in surface energy ($\gamma_s$) is due to the incorporation of polar groups onto the PET surface. Surface energy is a characteristic factor which affects the surface properties such as wettability, adhesion, printability, etc [11]. Since the surface energy increases with increase in time of treatment, PET film surface becomes hydrophilic after the plasma treatment.

**Figure 1** Variation of the contact angle of PET film w.r.t. water with time of exposure to DC glow discharge at (a) different potential and (b) pressure levels

**Figure 2** Variation of the (a) total surface energy and (b) polar components of PET film with time of exposure for DC glow discharge plasma treatment at different discharge potentials (d=3cm and P=0.2 mbar)
Variation of the (a) total surface energy and (b) polar components of PET film with time of exposure for DC glow discharge plasma treatment at different pressure levels (d=3cm and V=400 volts.)

3.2 Morphological and compositional analysis: AFM and XPS results

The change in morphology of PET films was studied by AFM analysis. Figure 4a shows the surface of the untreated PET film which is relatively smooth. After the plasma treatment, the surface of the PET film showed rough morphology (Figure 4b). In addition, the root mean square (RMS) roughness of untreated surface was 0.68 nm which got increased rapidly up to 14.13 nm when treated in air plasma. These morphological changes may be due to the removal of top few monolayers of the polymer film, caused by the bombardment of plasma particles on the surface of PET film [2, 12]. This resulted in an apparent increase in the surface roughness causing improvement in wettability and bonding strength.

The XPS spectrum of the untreated and plasma treated PET films is shown in Figures 5. It is seen that C1s and O1s are the major components. After plasma treatment, the intensity of O1s peak increases. The atomic concentration of C1s and O1s of the untreated PET film were 74.6 at.% and 25.1 at.% respectively. After the plasma treatment, C1s component decreased to 67.4 at.% and O1s component increased to 30 at%. These results suggest that the oxygen was incorporated on the
polymer film surface. The introduction of oxygen containing polar groups on the polymer surface may be the main reason for the hydrophilic improvement. Since PET films were treated in air plasma, it is obvious that some nitrogen–containing group will be incorporated onto the surface [2, 4, 9]. For untreated polymer films, there is no N1s peak but for plasma treated one, there appears to be a small N1s peak. The atomic concentration of N1s element increases from 0 to 1.0 at.% for plasma treated PET film surfaces.

Detailed high resolution spectra of carbon C1s peak for untreated and plasma treated PET are shown in Figures 6a and b. The spectra of untreated PET is composed of four main components at 285 eV (component C1), 286.43 eV (component C2), 288.95 eV (component C3) and 291.37eV (component C4) which may be attributed to C-C, C-O, O=C-O and π–π* shake-up satellite in phenyl groups respectively (Figure 6a) [13-15].

![Figure 5 XPS wide scan spectra of untreated and plasma treated PET film surfaces (V=400 volts, P=0.2mbar and t=20min)](image)

**Figure 5** XPS wide scan spectra of untreated and plasma treated PET film surfaces (V=400 volts, P=0.2mbar and t=20min)

![Figure 6. Deconvolution of the high resolution C1s spectra of PET film (a) untreated (b) plasma treated (V=400, P=0.2mbar, d=3cm and t=20min)](image)

**Figure 6.** Deconvolution of the high resolution C1s spectra of PET film (a) untreated (b) plasma treated (V=400, P=0.2mbar, d=3cm and t=20min)

The spectra of plasma treated PET film (Figure 6b) also show the components C1, C2 and C3, and additional peaks at 286.76 (component C5), 288.10 eV (component C6) and 286.0 (component C7), which may be attributed to C-OH and/or C-O-O-H, -C=O and C-N groups [13]. Furthermore the component C4, due to π – π* shake-up satellite, has a negligible intensity. The C1s peak of plasma
treated spectra clearly exhibited that the relative intensity of first peak at 285 eV has decreased. The relative intensity of other components such as C-O, O=O C-OH and/or C-O-O-H, and C=O increased significantly which may be due to C-C/C-H bonds in polymer surface gets broken by the plasma treatment, and the broken C-C/C-H bonds recombine with oxygen atoms that are produced by oxygen-containing groups into the molecular chain PET surfaces. The results suggests that the oxygen containing polar groups play an important role in decreasing contact angle and improving the hydrophilicity on the polymer surfaces.

Conclusion
A DC glow discharge plasma was used to modify the surface of PET film in both morphology and chemical composition. Surface modification of PET film was carried out at different discharge potential, pressure and exposure time. The results showed that the decrease in contact angle and increase in surface energy is more efficient when increasing the discharge potential, pressure and exposure time due to the incorporation of oxygen-containing functional groups onto the PET film surfaces. Simultaneously, AFM results showed the vigorous increase of the surface roughness as a result of the successful plasma etching and the XPS results confirmed that the carbon content decreases and the oxygen content increases on the surface of PET films. Furthermore, the oxygen-containing functional groups such as C-O, O=O C=O and COOH were introduced into the PET film surfaces. For this reason, the effect will find attraction on industrial applications.

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