Surface free energy analysis for bipolar pulsed argon plasma treated polymer films

S Pelagade¹, N L Singh¹, Sejal Shah¹,², Anjum Qureshi¹,⁴, R S Rane², S Mukherjee², U P Deshpande³, V Ganesan³ and T Shripathi³

¹Department of Physics, M.S.University of Baroda, Vadodara – 390 002, India
²FCIPT, Institute for Plasma Research, Gandhinagar – 382 044, India
³UGC-DAE –CSR, University Campus, Khandawa Road, Indore-452017, India
⁴Department of Metallurgical and Material Science Engineering, Marmara University, Istanbul-81040, Turkey.

E-mail: singhnl_msu@yahoo.com

Abstract. The effect of low energy (300 eV) argon plasma treatment on the morphology of polycarbonate was studied by means of contact angle measurement, X-ray photoelectron spectroscopy (XPS), Vickers’ micro hardness indentation and atomic force microscopy (AFM). The surface free energy (SFE) changes from 38.5 mJ/m² to 74.9 mJ/m² on increasing the treatment time and the corresponding contact angle was changed from 63° to 17°, which shows the enhancement in surface adhesion. The XPS analysis shows the increase of the C-O and C=O functional groups upon treatment. The Vickers’ micro hardness was studied in the load range 10-500 gf. The micro hardness of the film increases with the treatment time. Atomic force microscopy (AFM) reveals that average surface roughness increases from 7.0 nm to 27.2 nm as treatment time increases.

1. Introduction
Polycarbonates (PCs) are synthetic polymers with a very vast field of applications due to their excellent breakage resistance, good transparency, low inflammability and good workability. Polymers have been applied successfully in the fields such as adhesion [1-3], biomaterials [4, 5], protective coatings, friction and wear-resistant composites, microelectronic devices [6] and thin film technology. Polymeric materials have been able to replace traditional engineering materials like metals and glass because of their high strength to weight ratio, resistance to corrosion, possibility of recycling and their relatively low cost. PCs can be used for plastic vessels, machine parts and optical grades can be used for compact discs (CDs, CDROMs and DVDs), optical fibres, etc. Many applications in industry, biology and medicine require improvement in surface properties without altering the bulk properties. Some of the techniques have been developed to modify the polymer surfaces for improved adhesion, wettability, printability and many other technologically important characteristics.

The surface modification techniques can be divided into three categories: (i) cleaning or etching by removal of material from the surface (ii) surface reactions producing functional groups and cross linking and (iii) deposition of thin films on the surface. An important objective of any such treatment is to remove loosely bonded surface contamination, thus providing intimate contact between interacting materials on the molecular scale. The common methods of surface modification include mechanical or chemical treatment and exposure to flames, photons, ion beams, and other types of
radiation. Among the various pre-treatment processes the plasma modification of the polymer surface wins a key position[7]. Reactions between plasma species and polymer surface make it possible to form polar groups on the polymer surface. Polar chemical groups like C-OH, C=O,CHO,COOH are reactive chemically, can form chemical bonds and therefore can cause an increase of the surface energy and wetting quality.

Over the years treatment of PC was performed by many research groups to modify polymer surfaces for improved wettability, adhesion, etc. Cho et. al.[8] investigated the effect of oxygen gas on polycarbonate surface irradiated with keV energy Ar⁺ ions and found that hydrophilic group formed by chemical reaction between unstable chain generated by ion irradiated and oxygen. Koh et. al.[9] studied the surface modification of polymers (PC, PET, and PMMA) by ion assisted reaction in reactive gases environment. The comparison between the conventional surface treatments and the ion assisted reactions are described in terms of physical bombardment, surface damage, functional group, and chain mobility in the polymer. Seidel et. al.[10] studied the adhesion property of Ar plasma treated Al-metallized polycarbonate. Hofrichter et.al.[11] studied the influence of N₂, H₂, and O₂ plasma treatment on pure and commercial grade polycarbonate in order to enhance the adhesion of plasma deposited silica films. Hegemann et. al.[12] studied the plasma treatment on PC for the improvement of wettability and adhesion as well as for the reduction of friction of polymer surfaces. Boldyryeva et. al.[13] investigated the possibility of nanoparticle formation in PC implanted with Ag⁺ and Cu⁺ ions and reported optical property and structure of PC. Kitova et. al.[14] studied the RF plasma treatment of polycarbonate substrates and found that all RF plasma treatments led to an increase in the polar component of PC due to an increased hydrogen bonding ability. Sira et. al.[15] investigated the surface modification of polycarbonate in homogeneous atmospheric pressure discharge burning in nitrogen and in a mixture of nitrogen and hydrogen. They found that treatment of polymers in the homogeneous discharge is spatially homogeneous and the surface roughness of the treated samples is smaller in comparison to that of filamentary discharge.

This paper discusses the surface modification of polycarbonate using low pressure bipolar pulsed argon plasma. The modified surface has been characterized by measuring the contact angles and thus calculating the surface free energy. The changes in chemical composition have been studied by means of X-ray photoelectron spectroscopy (XPS). The atomic force microscopy (AFM) is used to investigate the surface morphology of the material at the atomic scale. The change in mechanical strength of the PC films surface due to argon plasma treatment has been measured by using microhardness tester.

2. Experimental Detail
The Schematic of the experimental setup is shown in figure 1.

![Experimental set-up](image)

Figure 1: Experimental set-up.

The set up consists of 60 cm long cylindrical chamber of 30 cm diameter. It has two rectangular parallel plates of stainless steel of dimensions 16 cm x 7.5 cm, which works as electrodes. The inter
electrode gap was maintained 2 cm in all the experiments. Bipolar pulsed power source was used to generate the desired argon plasma. The applied voltage and current were measured with the help of high voltage probe (Tektronix P6015A, 1000X) and current transformer respectively. Tektronix (TDS 2024, 200MHz) digital oscilloscope was used to record the voltage and current waveforms (Figure 2). The Chamber was evacuated up to a pressure of 5x10⁻⁵ mbar and during the treatment it was filled with Ar gas for a pressure of 0.1 mbar. PC films of thickness 275 µm each of sizes 20 mm x 20 mm were cleaned in isopropyl alcohol and dried before inserting into the plasma chamber.

The surface morphology was studied by AFM (Digital Nanoscope IIIa Instrument Inc.) in contact mode. Digital Microhardness Tester (FM 700, Future-Tech Corporation, Kawasaki-Japan) was used to determine the Vicker’s hardness number (HV) by the indentation technique. Contact angle goniometer (NRL C.A. Goniometer, Model 100-00-230) was used to measure the contact angle. XPS measurements on the samples were carried out using VSW ESCA machine with AlKα radiation (1486.6 eV) [17] During the experiment, chamber vacuum was better than 10⁻⁹ torr. The electron take-off angle was 40° and the X-rays were operated at 10 KV and 10 mA emission current. No other signals apart from carbon and oxygen were found in XPS spectrum. To compensate for the charging effects, the carbon peak assumed to be lying at 285 eV. Curve fitting has been done using the Gaussian/Lorentzian curve fitting programme.

3. Results and Discussion

3.1 Determination of surface free energy

A good understanding of the surface properties of a solid may be obtained relatively inexpensively from the measurement of the surface free energy. Therefore, the contact angle measurement was done to study of surface free energy, wettability and adhesion of low surface energy materials. [15, 18]. The surface free energy of a solid is an important parameter, playing a vital role in the phenomena that occur at solid-liquid and solid-gas interfaces. Hence, knowledge of this parameter is useful in studies of adsorption and wettability processes, which play important role in many industrial applications of the material. Measurement of contact angle of liquid with the solid surface permits a rapid and qualitative evaluation of surface free energy of the polymers. In the present paper, analysis of the surface free energy of PCs has been made on the basis of dispersive and non-dispersive components. Surface free energy (γf) and its polar (γs,p) and dispersion (γs,d) components of the sample were determined from two sets of contact angles (water and glycerin) according to Owens-Wendt-Kaelble equation (Owens and Wendt 1969). [19]

\[ \gamma_f (1 + \cos \theta) = 2[\gamma_f^d \gamma_s^d]^{1/2} + 2[\gamma_f^p \gamma_s^p]^{1/2} \]
where, $\gamma_l$, $\gamma_l^p$ and $\gamma_l^d$ are the total surface free energy, the polar component and the dispersion component of the surface free energy of the liquid, respectively. The values of the surface free energy of the test liquids obtained from the literature are given in Table 1[7].

Table 1. Surface free energy and its polar and dispersion components of water and glycerine used to determine the surface free energy of PC.

| Liquid    | Total surface energy $\gamma_l$ (mJ/m$^2$) | Polar component $\gamma_l^p$ (mJ/m$^2$) | Dispersion component $\gamma_l^d$ (mJ/m$^2$) |
|-----------|--------------------------------------------|----------------------------------------|------------------------------------------|
| Water     | 72.8                                       | 51                                     | 21.8                                     |
| Glycerine | 63.4                                       | 29.7                                   | 33.6                                     |

The values of surface free energy and its components before and after the treatment in argon plasma are compared in figure 3. The surface free energy and its polar and dispersion components for PC are found to be on higher side (~10%) as compared to the previous data [7]. This change may be due to the change in plasma treatment conditions.

It reveals that all the three treatment times can produce significant increase in the surface free energy. Argon plasma treatment produces purely physical surface modification and no new functional groups are incorporated on the polymer surface. The direct and radiative energy transfer processes cause the surface modification in all types of inert gas plasma treatments. The direct energy transfer corresponds to the ion bombardment of the surface, which is particularly important in the case of the PC specimens placed on the capacitive-coupled electrode. Another important factor for the modification mechanism is the UV (VUV) radiation emitted by the plasma. The exposure of the sample to the argon discharge is sufficient to break chemical bonds (C-C, C-H), and leaves free radicals at or near the surface. These radicals can react only with other surface radicals or by chain transfer reactions. If the polymer chain is flexible, or if the radicals can migrate along it, then recombination, unsaturation, branching, or cross-linking can occur. Moreover, the plasma removes low molecular weight species or converts them to high molecular weight species by crosslinking reactions. In summation, the argon plasma treatment causes the crosslinking at the PC surface as well as the sputtering of the material.

For untreated PC, the values of polar and dispersion components of surface free energy are lower. There is a substantial increase in the polar component after treatments, whereas no significant change is observed in the dispersion component. The ratio of polar component to the total surface free energy
is also regarded as the polarity of the material. An important information obtained from the surface energy measurement is that the polar component increases, corresponding to the formation of covalent bonds. The increase in surface free energy is attributed to the functionalization of the polymer surface with hydrophilic groups (i.e. attract water).

3.2 Microhardness

The Vicker’s hardness number (Hv) was determined by the indentation technique performed with a microhardness tester in the load range 10 to 500 gf for a constant loading time of 20 s. Indentation was made with a Vickers’ diamond pyramidal indenter housing a square base and pyramidal angle of 136° between the opposite faces attached to an optical microscope using a pilar micrometer / image analyzer. The average of the two diagonals of indentation was used for the calculation of hardness value. The hardness number (Hv) was calculated using the relation:

\[ Hv = \frac{1854.4 \times P}{d^2} \text{ Kgf/mm}^2 \]

Where P is the indenter load in gf, d is the average of the two diagonal lengths in micrometers.

Several indentations were obtained at each load and the average hardness number was calculated. The variation of Hv with load ranging from 10 to 500 gf for both untreated and argon plasma treated PC films is illustrated in figure 4.

![Figure 4: Plot of hardness vs applied loads](image)

The Vicker’s hardness increases as load increases. However, on approaching a certain load value, the rate of increase of hardness slow down and then became constant. At higher loads, beyond 200 gf, the interior of the bulk specimen is devoid of surface effects. Hence hardness value at higher loads represents the true value of the bulk and is consequently independent of the load. The hardness is found to increase as treatment time increases. This may be attributed to cross-linking phenomenon at the polymer surface [20, 21]. It is also corroborated with XPS analysis.

3.3 XPS Analysis

The information about the changes induced by argon plasma treatment was obtained from the XPS measurements. The atomic compositions of the PC surface before and after the treatment are compared in Table 2.

**Table 2.** Atomic concentration of carbon and oxygen measured by XPS for untreated and argon plasma treated (10 mins) PC films.

| Treatment Condition       | C (%)  | O (%)  | O/C ratio |
|---------------------------|--------|--------|-----------|
| Untreated PC              | 83.36  | 16.63  | 0.19      |
| Argon Plasma treated      | 56.46  | 43.54  | 0.77      |
The treatment produced a decrease in the carbon concentration on the PC surface. On the other hand, the oxygen content increased. The structure of the PC with numbered bonds is shown in figure 5.

Figures 6(a) and 7(a) show the C 1s and O 1s peaks respectively of the high resolution XPS spectra of the untreated sample. The area of individual peaks is proportional to the amount of chemical bonds. The numbers in Fig.6 and Fig.7 represent different bonds according to structure shown in Figure 5 [15]. The binding energy and the area of the individual peaks are summarized in Table 3. The area of the peaks was normalized to the first peak, based on the assumption that the low temperature plasma is not able to break down the phenyl ring.

Figures 6(b) and 7(b) show the C 1s and O 1s peaks respectively of the PC sample treated with the argon plasma for 10 min. From the XPS data, O1s/C1s ratio is increased from 0.20 to 0.77 for untreated to argon plasma treated PC samples. This increase is due to the increase in C-(p.r)/C-C and C=O/C-C ratios. The ratio of oxygen to carbon concentration is increased considerably as a result of increase of the oxygen component after plasma treatment [22, 23].
3.4 AFM analysis

The AFM images of untreated and argon plasma treated samples on 5 x 5 μm² area are shown in figure 8.

The root mean square (RMS) roughness of the untreated and Ar-plasma treated (10 min) samples was found 7.0 nm and 15.7 nm respectively. The roughness of the PC sample increases with treatment time, hence improves the adhesion. It reveals that sputtering effects are not homogeneous from all over the surface [8].

4. Conclusion

Argon plasma treatment of PC surface has increased the surface hydrophilicity. The increase in the polar component of the surface free energy after plasma treatment suggests the formation of polar groups on the surface. The treatment leads to improve the adhesion to polymers via surface cleaning, cross-linking, or formation of chemical bonds. The increased adhesivity produced by argon plasma treatment is well supported by AFM results. The hardness of PC surface increases as treatment time
increases. The XPS analysis reveals an increase of O/C ratio due to plasma treatment i.e. surface contains hydrophilic functional groups.

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