Chapter 3

Spectroscopic studies of polymer surfaces

Abstract

This chapter deals with the spectroscopic studies of polymeric surfaces using XPS and ATR-FTIR analysis. Effect of bipolar argon plasma on electronic and chemical structure of PC, PET, PTFE and PES polymers was studied with different treatment times. The results obtained from spectroscopic techniques show that plasma treatment has lead to the significant modifications in the chemical structure of the polymer at the surface.

3.0 Introduction

The exposure of polymers to plasma is an important method for the purpose of etching, surface modification and deposition in a wide range of different fields. Plasmas can affect a polymer in many ways depending on the composition of the gas discharge. There are many interactions that can occur when a polymer is exposed to a argon plasma. The various plasma constituents that can affect the polymer include positive ions, excited neutrals, electrons and UV/VUV photons. These ion bombardments can cause drastic changes to a polymer exposed to a plasma. Plasma ions accelerated toward the polymer surface induce physical sputtering of material from the surface and collision cascades within the material. Depending on the type of chemical bonds the sample material contains, there can be a preferential bond breaking and selective removal of one species over another. This can cause depletion and changing of chemical composition within the penetration depth of the ions.

Polymers have been observed to undergo various types of radiation driven degradation mechanisms under a plasma environment. Degradation mechanisms include chain cross-linking, main-chain scission, and side chain removal. The degradation mechanism is highly dependent on the polymer structure. We have investigated the effect of bipolar argon plasma treatment on electronic and chemical structure of thermoplastic polymers such as PC [110-111], PET [112], PTFE [113] and PES [114] using XPS and ATR-FTIR and the results are discussed for pristine and 10 min treated samples.

The thermoplastic polymers used in this study are discussed in **section 2.1** of **Chapter 2**. These samples were treated with bipolar argon plasma at

Facilitation Centre for Industrial Plasma Technologies (FCIPT), Gandhinagar, Gujarat,India (Unit of Institute for Plasma Research, Gandhinagar).

3.1 XPS Analysis

3.1.0 Introduction

XPS counts electrons ejected from a sample surface when irradiated by X-rays. A spectrum representing the number of electrons recorded at a sequence of energies includes both a contribution from a background signal and also resonance peaks characteristic of the bound states of the electrons in the surface atoms. The resonance peaks above the background are the significant features in the XPS spectrum.

XPS spectra are quantified in terms of peak intensities and peak positions. The peak intensities measure how much of a material is at the surface, while the peak positions indicate the elemental and chemical composition. Other values, such as the full width at half maximum (FWHM) are useful indicators of chemical state changes and physical influences. That is, broadening of a peak may indicate a change in the number of chemical bonds contributing to a peak shape, a change in the sample condition (X-ray damage) and/or differential charging of the surface (localized differences in the charge-state of the surface).

The underlying assumption when quantifying XPS spectra, is that the number of electrons recorded is proportional to the number of atoms in a given state. The basic tool for measuring the number of electrons recorded for an atomic state is the quantification region. The primary objectives of the quantification region are to define the range of energies over which the signal can be attributed to the transition of interest and to specify the type of approximation appropriate for the removal of background signal not belonging to the peak.

Samples Comparison:

A direct comparison of peak areas is not a recommended means of comparing samples for the following reasons. An XPS spectrum is a combination of the number of electrons leaving the sample surface and the ability of the instrumentation to record these electrons; not all the electrons emitted from the sample are recorded by the instrument. Further, the efficiency with which emitted electrons are recorded depends on the kinetic energy of the electrons, which in turn depends on the operating mode of the instrument. As a result, the best way to compare XPS intensities is via, so called, percentage atomic concentrations. The key feature of these percentage atomic concentrations is the representation of the intensities as a percentage, that is, the ratio of the intensity to the total intensity of electrons in the measurement.

Relative Intensity of Peaks:

Each element has a range of electronic states open to excitation by the X-rays. The rule for selecting a transition is to choose the transition for a given element for which the peak area, and therefore in principle the relative sensitivity factors (RSF), is the largest, subject to the peak being free from other interfering peaks. Transitions from different electronic states from the same element vary in peak area. A set of relative sensitivity factors are necessary for transitions within an element and also for all elements, where the sensitivity factors are designed to scale the measured areas so that meaningful atomic concentrations can be obtained, regardless of the peak chosen.

Overlapping Peaks:

The subject of peak-fitting data is complex. A model is typically created from a set of Gaussian/Lorentzian line-shapes. Without careful model construction involving additional parameter constraints, the resulting fit, regardless of how accurate a representation of the data, may be of no significance from a physical perspective.

Peak Positions:

In principle, the peak positions in terms of binding energy provide information about the chemical state for a material. The ability to calibrate the energy scale is dependent on the success of the charge compensation for the sample and the availability of a peak at known binding energy to provide a reference for shifting the energy scale.

Charge Compensation:

The XPS technique relies on electrons leaving the sample. Unless these emitted electrons are replaced, the sample will charge relative to the instrument causing a retarding electric field at the sample surface. For conducting samples electrically connected to the instrument, the charge balance is easily restored; however, for insulating materials electrons must be replaced via an external source. Insulating samples are normally electrically isolated from the instrument and low energy electrons and/or ions are introduced at the sample surface. The objective is to replace the photoelectrons to provide a steady state electrical environment from which the energy of the photoelectrons can be measured.

Without effective charge compensation, the measured energy for a photoelectric line may change as a function of kinetic energy of the electrons. Charge compensation does not necessarily mean neutralization of the sample surface. The objective is to stabilize the sample surface to ensure the best peak shape, whilst also ensuring peak separation between transitions is independent of the energy at which the electrons are measured. Achieving a correct binding energy for a known transition is not necessarily the best indicator of good charge compensation. A properly charge compensated experiment typically requires shifting in binding energy, but the peak shapes are good and the relative peak positions are stable.

The atomic concentrations of different elements present in the polymer provide only general information about the surface chemical structure. In order to gain a better understanding about the type of functional group formed, peak fittings are required. The carbon C 1s line is the most informative peak which is sensible to all changes in the polymer and therefore details of the incorporated species can be obtained. Peak fitting was done using the Gaussian/Lorentzian curve fitting programme in order to determine the formation of new functional groups and the loss or rearrangements of the ones originally present as explained in **section 2.3.3.3** of **Chapter 2.**

3.1.1 XPS analysis of PC

The information about the changes induced by argon plasma treatment was obtained from the XPS measurements. The structure of the PC with numbered bonds is shown in **Figure 3.1.**

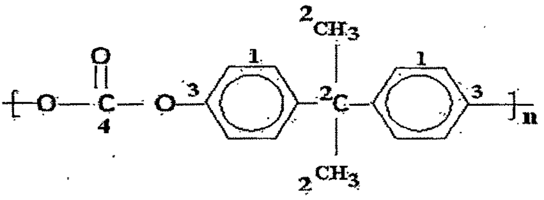

Figure 3.1: *The structure of the PC bisphenol-A with numbered carbon bonds: 1-phenyl ring (p.r), 2-C-C, C-H, 3-C-(phenyl ring), 4-O-(C=O)-O*

Figure 3.2a and **3.2c** show the C 1s and O 1s peaks of the high resolution XPS spectra of the untreated sample. The area of individual peak is proportional to the amount of chemical bonds. The numbers in **Figure 3.2** are corresponding to different bonds according to structure shown in **Figure 3.1** [55]. The peak 1 belongs to Phenyl Ring (p.r) at 284.0 eV, 2 belong to C-C, C-H (285 eV), 3 belongs to –C- (p.r) (286.2 eV) and C=O (288.4 eV).

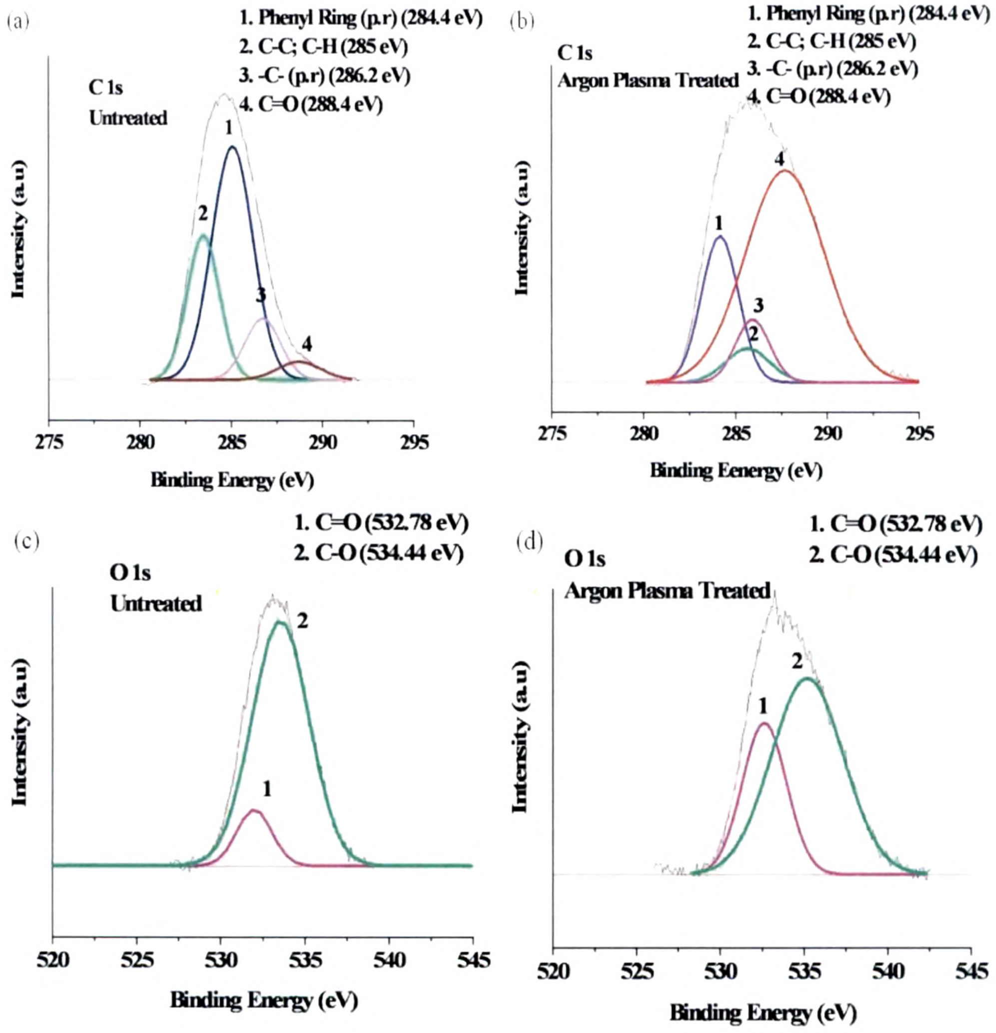

Figure 3.2: *XPS spectra of (a) C 1s peak of untreated PC sample; (b) C 1s peak of Ar Plasma treated PC sample;(c) O 1s peak of untreated PC sample; (d) O 1s peak of Ar Plasma treated PC sample. The number corresponds to bond according to Figure 3.1*

The binding energy and the area of the individual peaks are summarized in **Table 3.1**. The areas of the peaks were normalized to the first peak, based on the assumption that the low temperature plasma is not able to break down the phenyl ring.

Peak No.	1	2	3	4
Bond	Phenyl Ring (p.r)	C-C;C-H	-C-(p.r)	-C = O
BE (eV)	284.5	285	286.2	290.4
Untreated PC	1	0.487	0.226	0.079
Ar Plasma treated	1	0.276	0.405	3.1168

Table 3.1: *Binding energy and the relative areas of individual peaks numbered according to Figure 3.1. The areas were normalized to the first peak area*

Figures 3.2b, and **3.2d** show the C 1s and O 1s peaks of the PC sample treated with the argon plasma respectively. From the XPS data **(Table 3.2)**, O1s/C1s ratio is increased from 0.19 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 oxygen component after plasma treatment [115, 116].

The atomic compositions of the PC surface before and after the treatment are compared in **Table 3.2**.

The treatments produced a decrease in the carbon concentration on the PC surface. On the other hand the oxygen content increased.

Treatment Condition	C (%)	O (%)	O/C ratio
Untreated PC	83.36	16.63	0.19
Argon Plasma treated	56.46	43.54	0.77

Table 3.2: *Atomic concentration of carbon and oxygen measured by XPS for untreated and argon plasma treated (10 min) PC*

Summary

The XPS survey scans and C 1s and O1s peaks of the pristine and Ar-plasma treated PC are shown in **Figure 3.2** and **Table 3.1**. The main peaks are located at 284.4 eV and 532.8eV respectively (**Figure 3.2**). The C1s peak of PC after deconvolution is composed of four peaks and O1s is composed of two peaks. For PC treated by argon plasma dominating feature of the survey scan is sharp C 1s peak at 284.4 eV and an O1s peak at 532.8 eV, which significantly increases due to the surface oxidation from 16.63 % to 43.54 % after plasma treatment, while the concentration of carbon decreased from 83.36 % to 56.46 %. The O/C ratio of pristine PC is obtained as 0.19 and treated for 10 min by Ar-plasma is obtained as 0.77. Higher value of O/C ratio was observed for treated film. The reason for the remarkable increase of O/C ratio is due to the change of surface from hydrophobic to hydrophilic ie. the plasma treated PC film consists of formation of oxygen containing groups on the surface in the form of C-O and O-C=O.

3.1.2 XPS analysis of PET

The structure of the PET with numbered A, B and C bonds is shown in **Figure 3.3.**

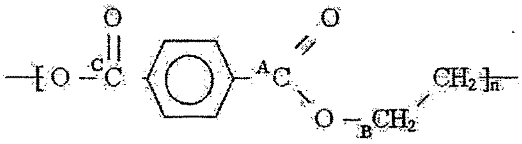

Figure 3.3: *The structure of PET: A: C-C bonds in phenyl ring; B: C-O; C: O=C-O*

In order to study the chemical composition of untreated and treated surfaces of PET, XPS was performed. The several curves were fitted into the C 1s spectra to get the information about the presence of different functional groups. The curve fitting of C 1s peak reveals the existence of carbon in three states, peak A belongs to C-C and C-H bonds (284.8 eV), peak B belongs to C-O (286.4 eV) and peak C belongs to O=C-O (288.8 eV) bond [115]. The peak A decreased upon plasma treatment whereas peak B and C increased slightly as shown in **Figure 3.4b**. The O 1s spectrum of PET film shows two chemical states corresponding to O=C (531.9 eV) and C-O (533.5 eV).

Figure 3.4a and **Figure 3.4c** show C 1s peaks and O 1s peaks of untreated sample. After the plasma treatment the C 1s peaks (**Figure 3.4b**) and O 1s peaks (**Figure 3.4d**) considerably changed. It is observed that O 1s spectra have considerably increased of C=O peak intensity due to plasma treatment. The intensities of higher binding energy side of the peak C 1s components, C-O and O=C-O became stronger as a consequence of the increase in treatment time. This is due to oxidation at the surface.

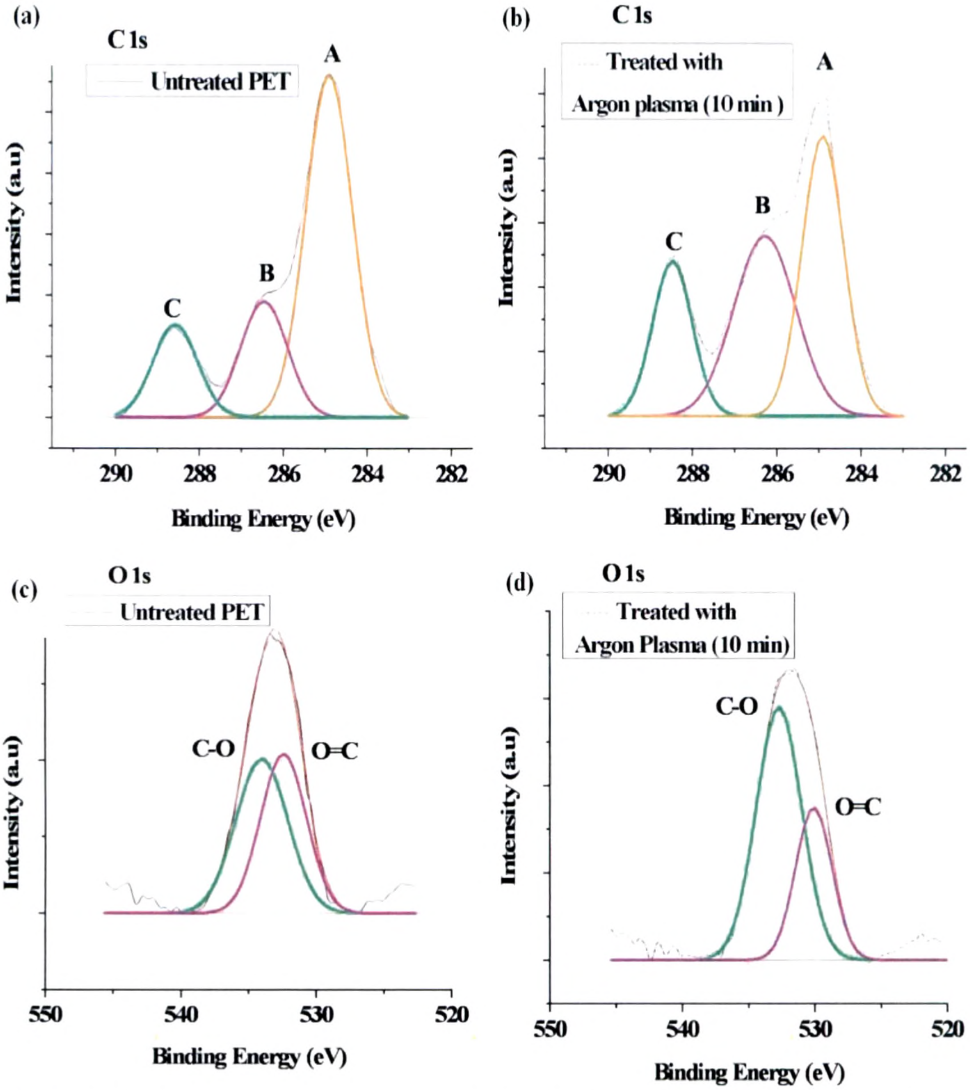

Figure 3.4: *XPS spectra of (a) C 1s peak of untreated PET sample; (b) C 1s peak of Ar Plasma treated PET sample;(c) O 1s peak of untreated PET sample; (d) O 1s peak of Ar Plasma treated PET sample. The alphabets A, B and C corresponds to bond according to* ***Figure 3.3***

The binding energy and the area of the individual peaks are summarized in **Table 3.3**. The areas of the peaks were normalized to the first peak, based on the assumption that the low temperature plasma is not able to break down the phenyl ring.

Peak No.	1	2	3
Bond	Phenyl Ring (p.r)	C-C;C-H	-C = O
BE (eV)	284.5	284.8	288.8
Untreated PET	1	0.98	0.64
Ar Plasma treated	1	0.68	1.01

Table 3.3: *Binding energy and the relative areas of individual peaks numbered according to Figure 3.4. The areas were normalized to the first peak area*

The relative concentrations can be calculated from area under the peak. The ratio (O 1s/C 1s), where O 1s and C 1s are the sum of the relative concentrations of oxygen component and carbon component respectively, was calculated at the surface. The surface composition of PET is shown in **Table 3.4**. The ratio of oxygen to carbon concentration is increased considerably as a result of increase of oxygen component after plasma treatment. [115, 116]

Sample	C (%)	O (%)	O/C
Untreated	76.4	23.59	0.31
Treated in argon (10 min)	63.63	36.37	0.57

Table 3.4: *Atomic concentration of carbon and oxygen measured by XPS for untreated and plasma treated (10 min) sample*

Summary

The XPS survey scans and C 1s and O1s peaks of the pristine and Ar-plasma treated PET are shown in **Figure 3.4** and **Table 3.3**. The main peaks are located at 284.8 eV and 531.9 eV respectively (**Figure 3.4**). The C1s peak of PET after deconvolution is composed of three peaks and O1s is composed of two peaks. For PET treated by Ar-plasma, the dominating feature of the survey scan is sharp C 1s peak at 284.8 eV and an O1s peak at 531.9 eV, which significantly increased due to the surface oxidation from 23.59 % to 36.37% after plasma treatment, while the concentration of carbon decreased from 76.4% to 63.63% (Table3.4).

The O/C ratio of pristine and 10 min treated PET is obtained as 0.31 and 0.57 respectively. Higher value of O/C ratio was observed for treated film. The reason for the remarkable increase of O/C ratio is due to the change of surface from hydrophobic to hydrophilic ie. the plasma treated PC film consists of formation of oxygen containing groups on the surface in the form of C-O and O-C=O.

3.1.3 XPS analysis of PTFE

A suitable method for the determination of type of functional groups on a polymer surfaces is X-ray photoelectron spectroscopy (XPS). For detailed analysis of chemical changes induced by plasma treatment on PTFE surfaces,a high resolution XPS spectra were recorded and is shown in **Figure 3.5 (a-f)**.

A basic problem in polymer analysis is surface charging due to the loss of surface electrons by X-ray irradiation. In common practice manual shifting of un functionalized C 1s peak (C-C) to 284.8 eV is performed. From the recorded spectra, it can be noticed that there is little change in shape of the curve of untreated and treated samples.

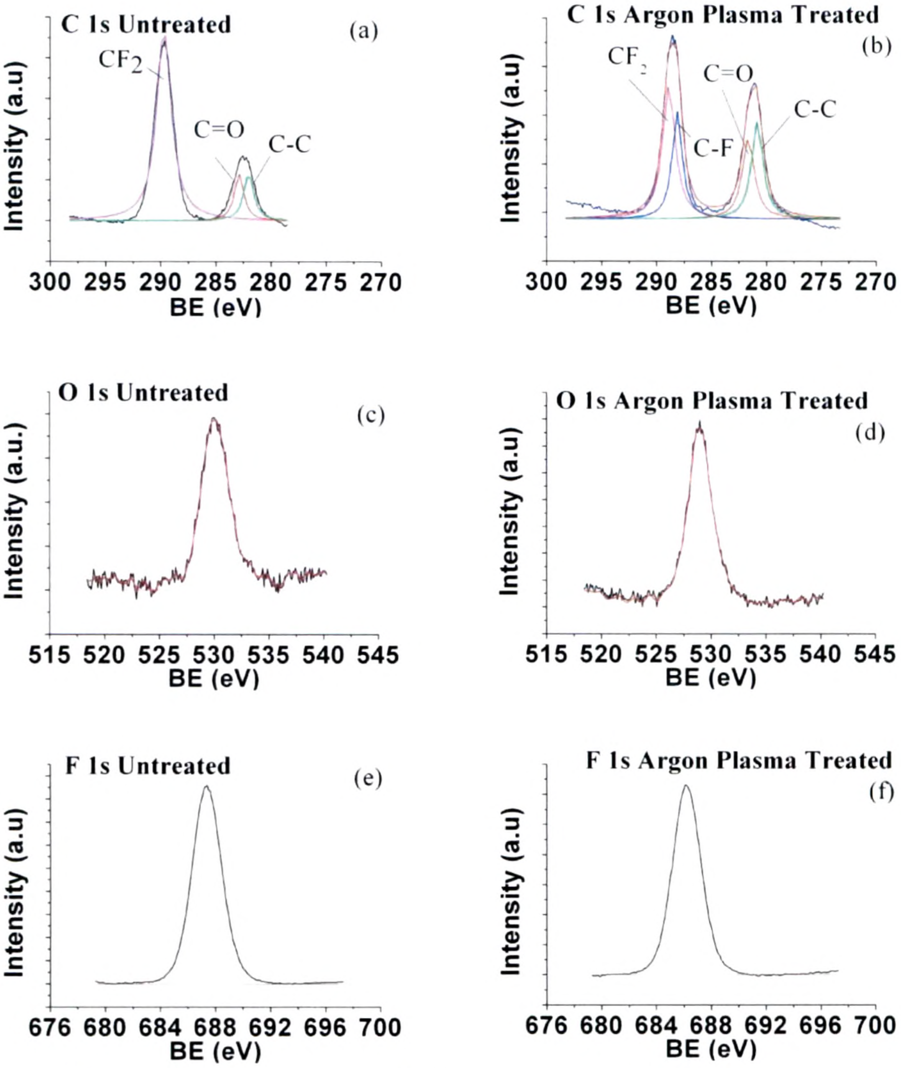

Figure 3.5: *XPS spectra of (a): C 1s untreated; (b): C 1s argon plasma treated; (c): O 1s untreated; (d): O 1s argon plasma treated; (e): F 1s Untreated; (f): F 1s argon plasma treated*

Figure 3.5a shows the XPS spectra of C 1s peaks for the untreated PTFE sample. In this figure, the peak for -CF_2- (a difluoromethylene group), which is the origin of the hydrophobicity, is detected at 294.5 eV. **Figure 3.5b** shows the XPS spectrum of C1s peaks for the PTFE sample treated by argon plasma . The peaks for –C=O (carbonyl group), -C-O- and –C-C- are detected at 288.8 eV, 286 eV and 284.8 eV respectively. When functional groups such as –C-O- and –

C=O are incorporated into a polymer surface, the surface became hydrophilic and the surface adhesion is improved.

The C 1s peak for treated and untreated samples shows variation in area under the peaks as shown in **Table 3.5**. Although the peak assigned the CF_2 group in the C1s XPS spectrum of the plasma treated PTFE is smaller than that of untreated PTFE. This result was assumed the de-fluorinated layer due to the plasma treatment. The intensities of higher binding energy side of the peak C 1s components, C-O and C=O became stronger as a consequence of the increase in treatment time. This is due to oxidation at the surface.

Peak No.	1	2	3
Bond	$-CF_2-$	C-C;C-H	-C = O
BE (eV)	294.5	284.8	288.8
Untreated PTFE	788.59	454.08	409.57
Ar Plasma treated	432.09	1179.18	666.53

Table 3.5: *Binding energy and the area of individual peaks*

The C 1s peak for treated sample shows a variation of about 18% to that of untreated sample, whereas the peak assigned as the CF_2 group in the C 1s spectrum of treated PTFE has reduced to about 14% compared to that of untreated. The result is attributed to defluorination of layer of the plasma treated PTFE. The surface composition of PTFE before and after the plasma treatment is tabulated in **Table 3.6.**

Sample	C	F	O	F/C	O/C
Untreated	34.52	62.22	3.26	1.8	0.094
Treated in argon (10 min)	40.68	53.27	6.05	1.3	0.148

Table 3.6: *The surface composition of PTFE before and after the plasma treatment*

Summary

The XPS survey scans and C 1s, F 1s and O1s peaks of the pristine and Ar-plasma treated PTFE are shown in **Figure 3.5** and **Table 3.5**. The main peaks are located at 284.5 eV, 294.5 eV and 532.8eV respectively **(Figure 3.5)**. The C1s peak of PTFE after deconvolution is composed of three peaks, F1s is composed of one peak and O1s is composed of one peak. For PTFE treated by Ar-plasma, the dominating feature of the survey scan is sharp C 1s peak at 284.5 eV, F1s peak at 294.5 eV and an O1s peak at 532.8 eV, which significantly increases due to the surface oxidation from 3.26 % to 6.05% after plasma treatment and the concentration of carbon increased from 34.52% to 40.68%, while the concentration of fluorine decreased from 62.22 % to 53.27 %.

The F/C ratio of pristine and 10 min Ar-plasma treated PTFE is 1.8 and 1.3 respectively. This decrease is due to the de-fluorination. The O/C ratio of pristine and 10 min treated PTFE is 0.094 and 0.148 respectively. Higher value of O/C ratio was observed for treated film. The reason for the remarkable increase of O/C ratio is due to the change of surface from hydrophobic to hydrophilic ie. the plasma treated PC film consists of formation of oxygen containing groups on the surface in the form of C-O and O-C=O.

3.1.4 XPS analysis of PES

The analysis of chemical changes induced by low energy argon plasma treatment on PES surfaces, the high resolution XPS spectra were recorded and is shown in **Figure 3.6**. It is observed that there is a overlap of the peaks due to C-C bond at a binding energy of 284.8 eV and C-S bond at a binding energy of 285.3 eV. [69] A basic problem in polymer analysis is surface charging due to a loss of surface electrons by X-ray irradiation. In common practice manual shifting of unfunctionalised C 1s peak (C-C) to 284.8 eV is performed. Carbon peak of untreated PES consists of two peaks; one, A at 284.8 eV corresponds to C-C bonds and the other, B at 286.5 eV corresponds to C-O bonds.

The C 1s peak for treated and untreated samples show variation in area under the peak as shown in **Table 3.7**.

Peak No.	1	2
Bond	C-C;C-H	-C - O
BE (eV)	284.8	286.5
Untreated PES	9291.69	175.11
Ar Plasma treated	9165.55	4709.70

Table 3.7: *Binding energy and the area of individual peaks*

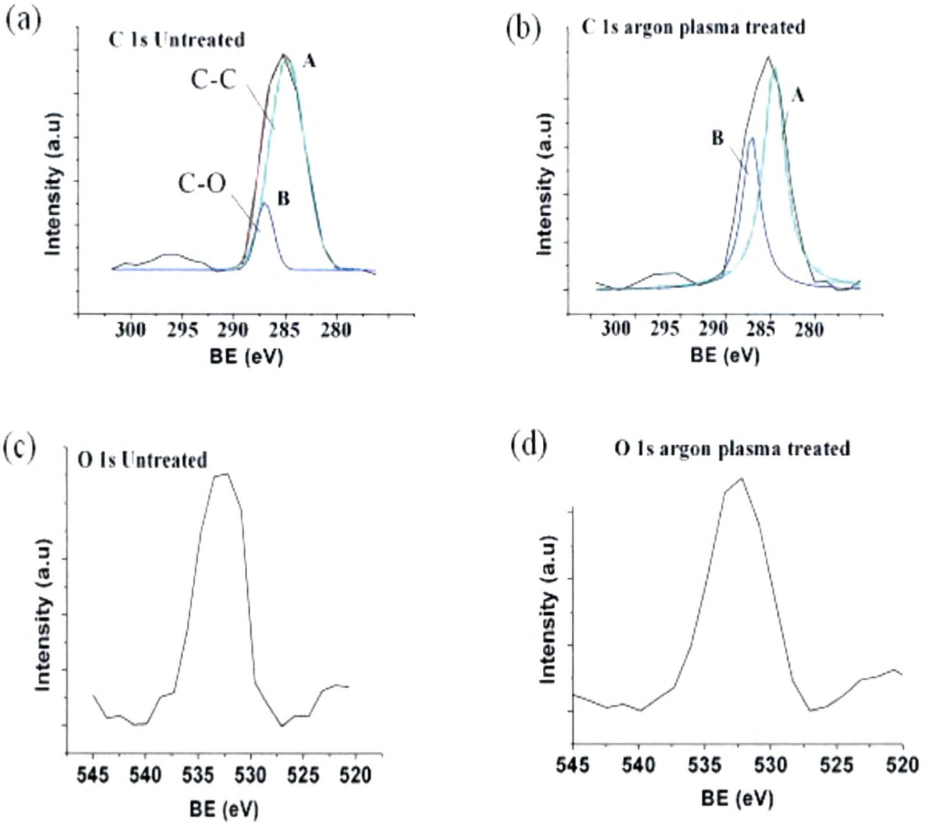

Figure 3.6: *C 1s peak of the XPS spectra of (a) untreated and (b) Ar plasma treated samples; O 1s peak of the XPS spectra of (c) untreated and (d) Ar plasma treated samples*

The surface composition of PES before and after the plasma treatment is tabulated in **Table 3.8**.

Sample	C	O	O/C
Untreated	84.9	15.09	0.177
Treated in argon (10 min)	78.26	21.74	0.277

Table 3.8: *The surface composition of PES before and after the plasma treatment*

Summary

The XPS survey scans and C 1s and O1s peaks of the pristine and Ar-plasma treated PES are shown in Fig. 3.6 and Table 3.7.The main peaks are located at 284.8 eV and 532.8eV respectively (Fig.3.6).The C1s peak of PES after deconvolution is composed of two peaks, and O1s is composed of one peak (s). For PES treated by Ar-plasma, the dominating feature of the survey scan is sharp C 1s peak at 284.8 eV , and O1s peak at 532.8 eV, which significantly increased due to the surface oxidation from 15.09 % to 21.74% after plasma treatment, while the concentration of carbon decreased from 84.9% to 78.26%. The O/C ratio of pristine and 10 min treated PES is 0.177 and 0.277 respectively. The higher value of O/C ratio was observed for treated film. The reason for the remarkable increase of O/C ratio is due to the change of surface from hydrophobic to hydrophilic ie. the plasma treated PC film consists of formation of oxygen containing groups on the surface in the form of C-O and O-C=O.

3.1.5 Conclusions

XPS analysis showed that the very first changes under plasma treatment occur in the outer most surface layer. Different features were fitted to the carbon C 1s and O 1s peaks to analyze the formation of functional group on the surfaces of the polymers. It is observed that the functional groups are formed on the surfaces. Following conclusions can be drawn,

- XPS analysis reveals an increase in O/C ratio due to plasma treatment i.e surface contains hydrophilic functional group. The results are compared in **Table 3.9** for different polymers.

- Treatment with argon plasma does not introduce additional functionalities as the plasma treatment was performed under high vacuum condition. Modified samples when taken to air, the oxygen content increased drastically.

Composition	PC		PET		PTFE		PES	
	Untreated	Treated (10 min)	Untreated	Treated (10 min)	Untreated	Treated (10 min)	Untreated	Treated (10 min)
C	83.36	56.46	76.4	63.63	34.52	40.68	84.9	78.26
O	16.63	43.54	23.59	36.37	3.26	6.05	15.09	21.74
O/C	0.19	0.77	0.31	0.57	0.094	0.148	0.177	0.277
% rise (O/C)	305.3		83.9		57.4		56.5	

Table 3.9: *Surface composition before and after the plasma treatment*

3.2 ATR-FTIR Analysis

3.2.0 Introduction

Infrared (IR) spectroscopy is one of the most common spectroscopic technique used for functional group characterization. Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves. Infrared is broken into three categories: far (4 – 400 cm^{-1}), mid (400 - 4,000 cm^{-1}), and near-infrared (4,000 - 14,000 cm^{-1}). Near-infrared refers to the part of the infrared spectrum which is closer to visible light, while far-infrared refers to the part that is closer to the microwave region. Mid-infrared is the region between these two regions which is the most useful part of the electromagnetic spectrum useful for measuring organic compounds. The basic concept behind this spectroscopic technique is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam to determine the chemical functional groups in the sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wave number range regardless of the structure of the rest of the molecule. An IR spectrum is produced by absorption of energy (400 - 4000 cm^{-1}) due to vibrations of polar covalent bonds.

Fourier Transform Infrared Spectroscopy provides specific information about chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. FTIR is an improved technique to make the IR measurements easier and faster, in which the IR beam is guided through an interferometer. A FTIR spectrum is obtained from performing a mathematical Fourier Transform on the interferogram.

ATR-FTIR is a method for analyzing solid samples using infrared spectroscopy. It is also suitable for characterization of materials which are either too thick or too strongly absorbing to be analyzed by transmission spectroscopy. The basis of this method is that an infrared beam is reflected off the sample, with the absorption measured from the reflected beam. Unfortunately the reflected radiation has a very low intensity. To get around this limitation, the infrared beam is bounced through a crystal such as ZnSe or Ge at an angle such that the beam is totally internally reflected. The solid sample sits on the crystal, and the result is that the beam will be reflected off the sample as shown in **Figure 2.14** of **Section 2.3.5.1 (Chapter 2).**

ATR-FTIR analysis is performed in the following subsections and the results are compared with the XPS analysis.

3.2.1 ATR-FTIR analysis of PC

The ATR-FTIR spectra of the pristine and irradiated samples of PC are shown in **Figure 3.7.**

The absorption bands as obtained from the pristine spectrum are identified as: (A) 765 cm^{-1}: out of phase skeletal vibration of C-H deformation; (B) 1030 cm^{-1}: C-O stretching vibration; (C) 1080 cm^{-1} : -C-C bending vibration; (D) 1505 cm^{-1} : ring -C-C stretching vibration (E) 1775 cm^{-1} : C=O stretching vibration; (F) 2359 cm^{-1}: the release of CO_2. [117 - 119].

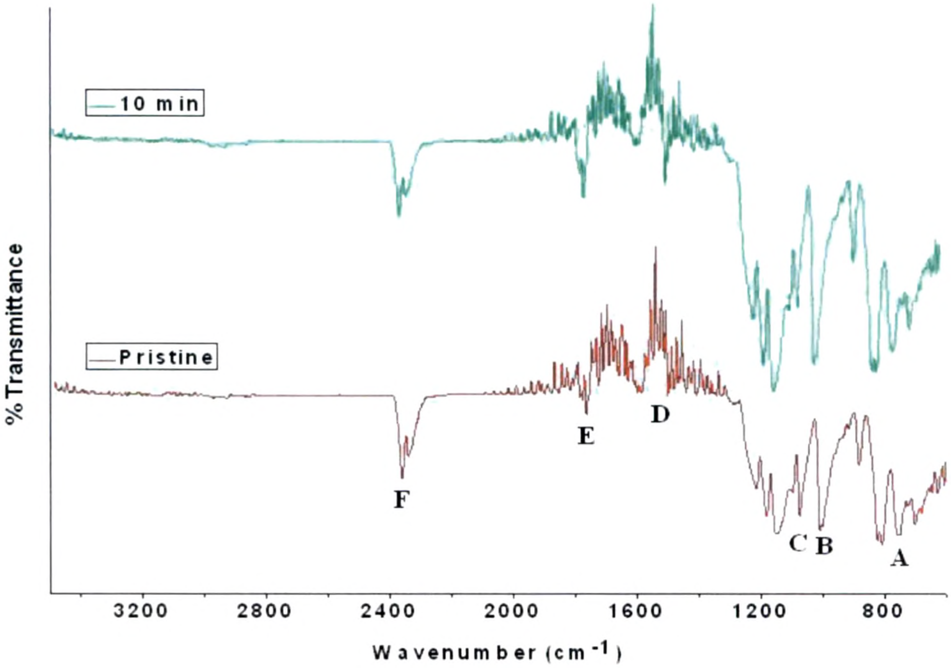

Figure 3.7: *ATR-FTIR spectra for pristine and argon plasma treated PC samples*

It is observed that there is no change in overall structure of the polymer but minor changes in intensities were observed for all the treatment times. For the sake of comparison with XPS analysis, we have shown only spectrum of pristine and 10 min treated samples. The minor changes in the peaks of the irradiated/treated samples may be due to the breakage of few bonds in the ladder structure, but this will not change the overall structure of the polymer.

At a glance it is apparent that the plasma treatment has not caused any changes to take place other than the increase/ decrease in the intensity of the peaks. From the spectra (**Figure 3.7**), it is noticed that the intensity of –C-C peak is decreased, whereas the –C=O peak intensity is increased after argon plasma treatment. This simply tells us that there are more carbonyl bonds available at the sample surface to absorb IR light. This result is also corroborated with XPS analysis [**Chapter 3, Table 3.1**].

3.2.2 ATR-FTIR analysis of PET

The chemical changes in surface layer of plasma treated polymer are analyzed using ATR-FTIR spectroscopy. The ATR-FTIR spectra of the pristine and the argon plasma treated PET samples are shown in **Figure 3.8**.

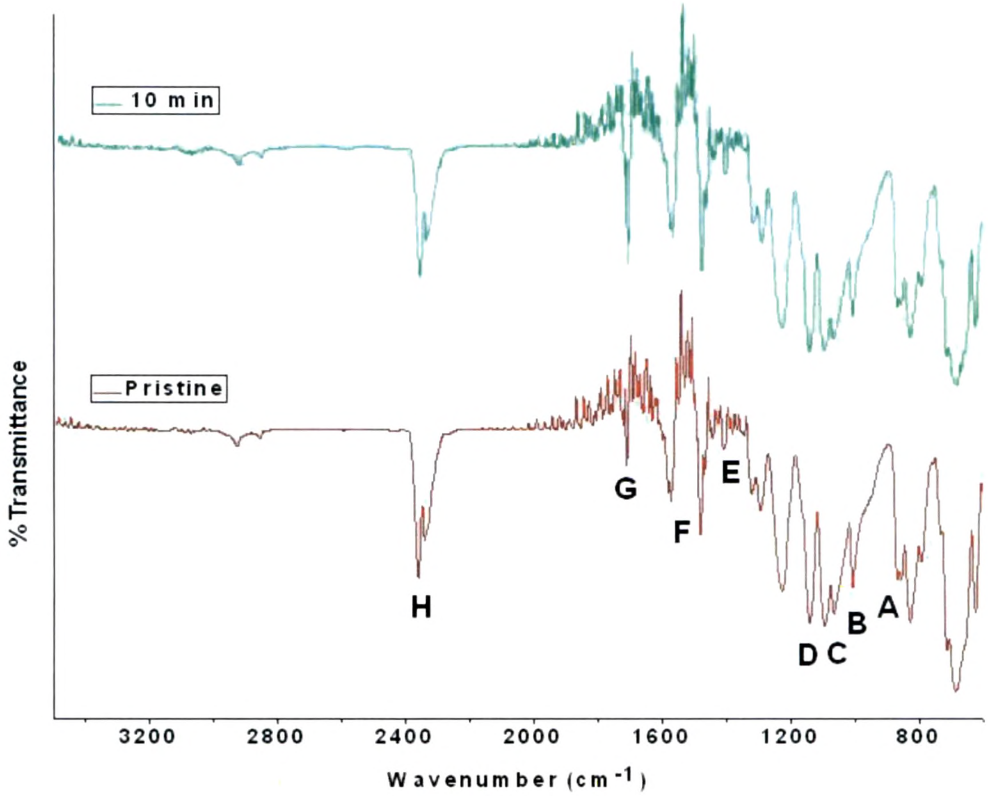

Figure 3.8: *ATR-FTIR spectra for pristine and argon plasma treated PET samples*

The absorption bands obtained from the pristine spectrum are as: (A) 1410, 1018, 872 cm^{-1}: vibration of aromatic ring; (B) 1244 and 964 cm^{-1}: stretching vibrations of C-O bonds; (C) –C-C- stretching vibration bands appears near 1037 cm^{-1}; [120, 121] (D) 1124 and 1100 cm^{-1}: stretching vibration of C-O bonds due to amorphous and crystalline structure of PET [118] (E) 1340 and 1177 cm^{-1}: bending vibration of CH_2 group; (F) benzene ring –C-C- stretching vibrations at 1505 cm^{-1} [122]; (G) 1712 cm^{-1}: C=O stretching vibration; (H)

2359 cm^{-1}: the release of CO_2. It is observed that there is no change in overall structure of the polymer but a minor change in intensities have been observed for Ar-plasma treated sample. This might be due to the breakage of a few bonds in the structure. It may be concluded that PET is resistant to radiation. [65]

The two regions of the spectra (C-C and C=O) correspond to fundamental vibrations associated with the bonds of the carbon. The intensity of peak for C-C bond is decreased, whereas for C=O bond, it is increased as observed in **Figure 3.8.** At a glance, it is apparent that the plasma treatment has not caused any changes to take place other than an increase/decrease in the intensity of the peak of some functional groups. This simply tells us that there are more carbonyl bonds available at the sample surface to absorb IR light. This result is also corroborated with XPS analysis [**Chapter 3, Table 3.3**].

3.2.3 ATR-FTIR analysis of PTFE

Figure 3.9 shows the ATR-FTIR spectra of untreated and plasma treated PTFE samples. Compared to the untreated PTFE, the absorption intensity of C–F bonds of treated PTFE (from 1100 to 1300 cm^{-1}) became weak and some new absorption peaks appeared. Timmons et al [123] used XPS spectrum to investigate the surface variation of PTFE before and after treatment and found that the treatment process will induce a defluorinated reaction and the concentration of carbon and oxygen on PTFE surface significantly increased. As a result, the modified fluorocarbon surface is expected to have more improvement in adhesion, bonding ability and wetting property. [124]

The ATR IR spectrum of the pristine PTFE contains no absorption band in the range of 2800–4000 cm^{-1} [125, 126]. For the argon plasma-treated PTFE film, the spectrum consists of two strong broad absorption peaks at (A) 1202 cm^{-1}, (B) 1146 cm^{-1} are assigned to C-F bonds and (C) 2359 cm^{-1}: the release of CO_2 as shown in **Figure 3.9**. The surface wettability of PTFE can be improved significantly by argon plasma treatment, as reflected by the significant decrease of water contact angle and the remarkable increase of the adhesion strength with an adhesive. This is due to the defluorination, the introduction of oxygen and the formation of the hydrophilic species, as confirmed by XPS [**Chapter 3, Table 3.5**] and ATR FTIR spectra. The area of C-F peak for 10 min argon plasma treated decreased, which resulted in the increase of hydophilicity.

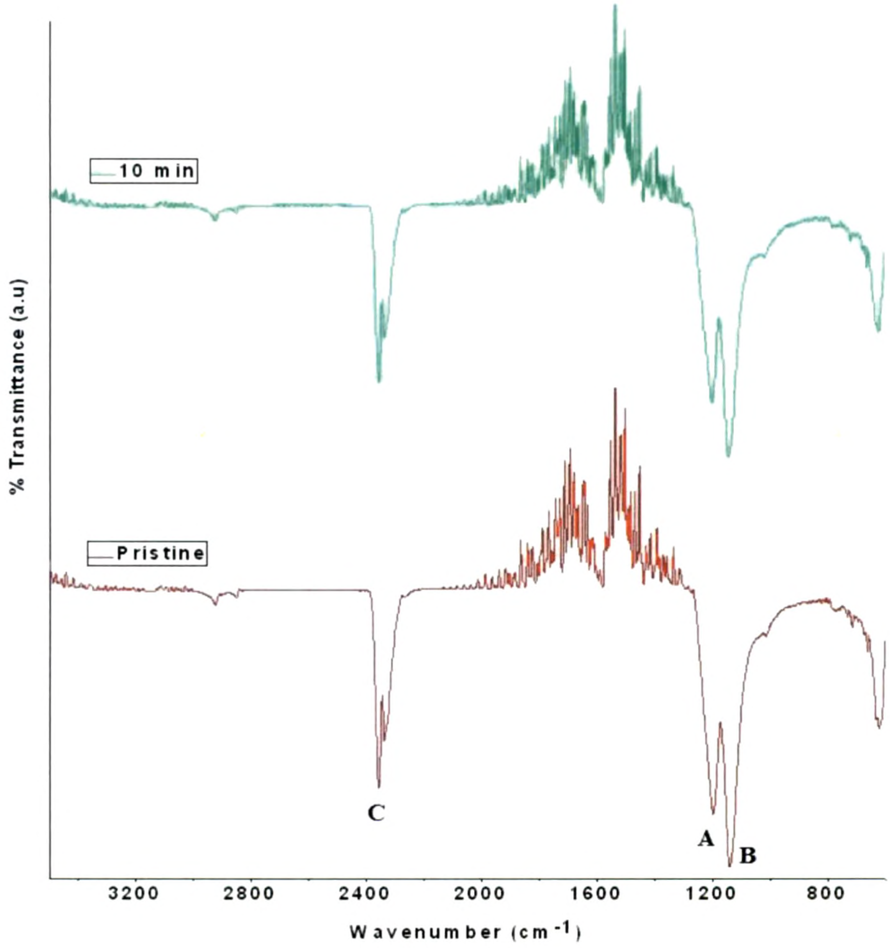

Figure 3.9: *ATR-FTIR spectra for pristine and argon plasma treated PTFE samples*

3.2.4 ATR-FTIR analysis of PES

Figure 3.10 shows, the spectra of pristine and the plasma irradiated PES samples. The absorption bands as obtained from the pristine spectrum are identified as (A) 720 cm^{-1}: CH_2 absorption bands; (B) 890 cm^{-1}: C-H bending vibration; (C) 1080 cm^{-1}: C=S stretching vibration; (D) 1241 cm^{-1}: C-O streching vibration; (E) 1712 cm^{-1}: C=O stretching vibration; (F) 2359 cm^{-1}: the release of CO_2; (G) 3000 cm^{-1}: C-H stretching vibration. It is observed that there is no change in overall structure of the polymer but a minor change in intensities has been observed for treated sample. This might be due to the breakage of few bonds in the structure as well as formation of unsaturated structure. It may be concluded that PES is resistant to radiation.

The intensity of the peak at 1080 cm^{-1}, attributed to C-S vibration, is reduced in the plasma treated PES sample than that of pristine one, which indicates the weakening of the C-S bond.[127]. The area of C-S peak for 10 min argon plasma treated is decreased, while -C-O and the group (C=O and C-O) areas increased for treated PES sample as observed from the analysis of ATR-FTIR. The increase in area of –C-O group for treated PES is also observed using XPS analysis [**Chapter 3, Table 3.7**].

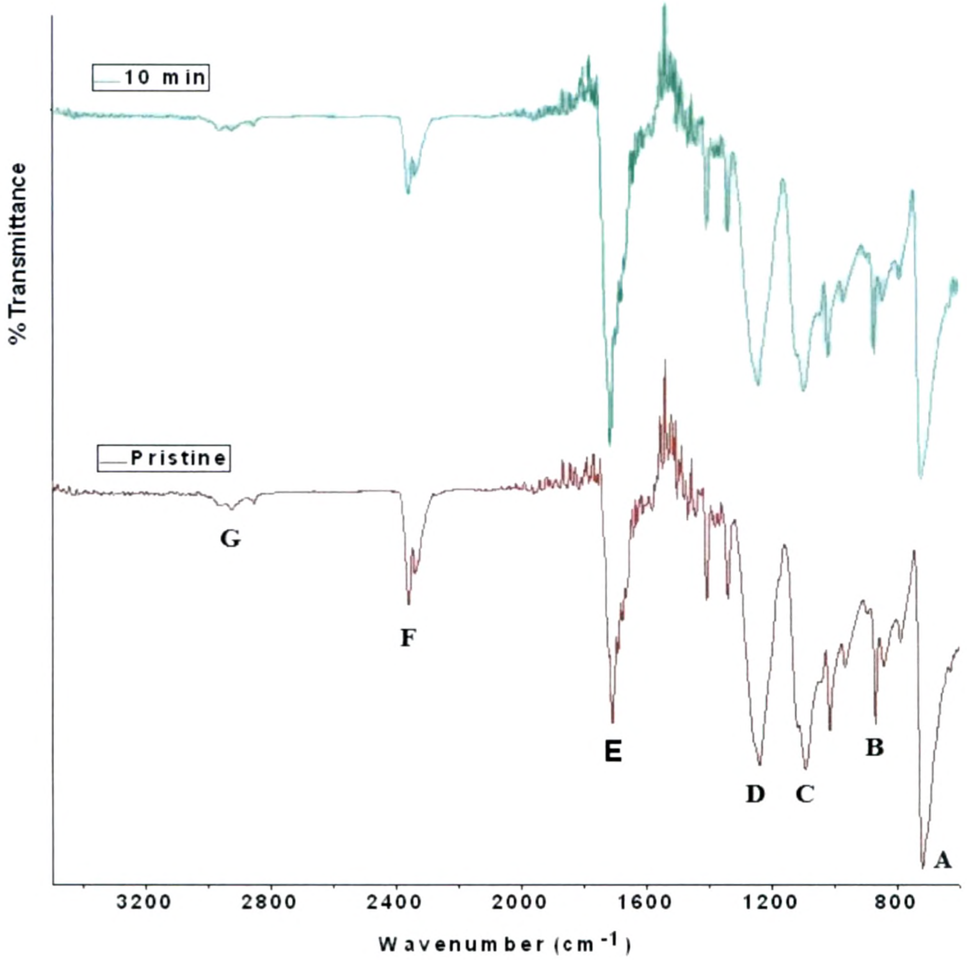

Figure 3.10: *ATR-FTIR spectra for pristine and irradiated PES samples*

3.2.5 Conclusion

The variation of transmittance (%) for the pristine and Ar-plasma treated polymers were compared and the peak analysis was done to study the disappearance of some existing bonds, emergence of new ones and structural changes which includes the alteration in position and intensity of the characteristic bands.

It is observed from the comparison of pristine and plasma treated FTIR spectra of all polymers that no significant change has been observed in the overall structure of the polymer. The minor changes observed in the intensity of the treated sample as compared to the pristine one, it may be due to the breakage of only few bonds in the structure. The most of the peak positions were found unshifted. Only the transmittance value of particular functional groups changed. This might be due to the breakage of few bands in the structure. The results obtained are supported by XPS results.