Chapter 4

Surface free energy, micro hardness and surface morphology studies of polymer surfaces

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Abstract

In this chapter the effect of argon plasma on physical properties of polymeric surfaces of PC, PET, PTFE and PES are discussed with different treatment times.The surface properties of the pristine and plasma treated samples was studied by means of surface free energy, Vickers' microhardness indentation and atomic force microscopy (AFM). The results of all the characterisations have been correlated to give a better and apparent view of chemical, mechanical and surface morphology.

4.0 Introduction

Argon plasma is a partially ionized gas generated by applying an electrical field to a gas under a vacuum. In case of surface treatment of polymers, argon is one of the common gases used. The modification consists of oxidation (oxygen absorption by the upper most atomic layers) of the polymer by active oxygen radicals resulting in a considerable increase in the number of functional polar groups on the polymeric surface. This results in an increased surface free energy rendering the surface hydrophilic (i.e attract water / improved wetting) and is beneficial as a pre-treatment prior to coating or printing.

The effect of bipolar argon plasma treatment on physical properties of following polymers was studied by measuring contact angle (surface free energy), Vickers' microhardnes indentation technique (mechanical property) and atomic force microscopy (surface morphology).

(i) PC [110-111],

(ii) PET [112],

(iii) PTFE [113] and

(iv) PES [114]

The polymers used in this study are discussed in **section 2.1** of **Chapter 2**. The plasma treatment was given at Facilitation Centre for Industrial Plasma Technologies (FCIPT), Institute for Plasma Research (IPR), Gandhinagar. The characterization techniques used are discussed in the section 2.3.

4.1 Surface free energy analysis

4.1.0 Introduction

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 has been used in the study of surface free energy, wettability and adhesion of low surface energy materials. [55, 128] 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 the studies of adsorption and wettability processes for many industrial applications of the materials. Measurement of contact angle of liquid with the solid surface permits a rapid and qualitative evaluation of surface free energy of polymer.

Analysis of the surface free energy of polymeric surfaces has been made on the basis of dispersive and non-dispersive components. Surface free energy (γ_s) and its polar (γ_s^p) and dispersion (γ_s^d) components of the sample were determined from two sets of contact angles (water and glycerin) using Eq. 2.11 as mentioned in **Section 2.3.1** of **Chapter 2**.

The values of the surface free energies of the test liquids obtained from the literature are given in **Table 4.1** [129].

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

Table 4.1: *Surface free energy and its polar and dispersion components of water and glycerin used to determine the surface free energy*

4.1.1 Surface free energy analysis of polycarbonate (PC)

The contact angles were measured by using equipment as mentioned in section 2.3.1 of chapter 2. The measured average contact angles for water and glycerin are listed in **Table 4.2**.

Sample	Water Contact Angle	Glycerin Contact Angle
PC Pristine	63	58
5 min	24	31
10 min	12	19
50 min	17	12

Table 4.2: *Contact angles for untreated and argon plasma treated PC samples*

Surface free energy (γ_s) and its polar (γ_s^p) and dispersion (γ_s^d) components of the sample were determined from two sets of contact angles (water and glycerin) using Eq. 2.11 (**Chapter 2**).The values of surface free energy and its components before and after the treatment in argon plasma are compared and shown in **Figure 4.1**.

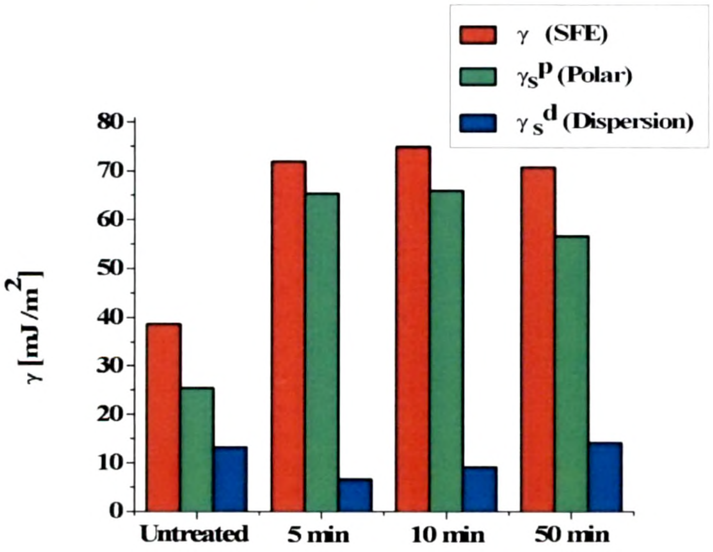

Figure 4.1: *Comparison of Surface free energy and its components before and after the treatment in Ar discharge*

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 electrodes. Another important factor for the modification mechanism is the UV (VUV) radiation emitted by the plasma. The exposure of the sample by 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 on the PC surface as well as the sputtering of the material from the surface.

Treatment Time	Polar (γ_p^s) mJ/m^2	Dispersion (γ_d^s) mJ/m^2	SFE (γ) mJ/m^2	Standard Deviation
Untreated	25.4	13.2	38.6	1.9
5 minutes	65.3	6.5	71.8	3.1
10 minutes	65.8	9.1	74.8	1.1
50 minutes	56.6	14	70.6	3.8

Table 4.3: *Comparison of surface free energy and its components before and after Ar plasma treatment*

For untreated PC, the values of polar and dispersion components of surface free energies are lower, but there is a substantial increase in the polar component after all subsequent treatments, whereas no remarkable change in the dispersion component is observed. The values of surface free energy and its components before and after the treatment with argon plasma are listed in **Table 4.3** with standard deviations. 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).

The total surface free energy (SFE) calculated for PC untreated and treated for different treatment times are compared in percentage. The percentage rise for various treatment time of plasma treatment is tabulated in **Table 4.4**. PC treated with 10 minutes treatment time shows the highest rise in SFE.

Treatment Time	**SFE (γ) mJ/m^2**	**% rise**
Untreated	38.6	----
5 minutes	71.8	86.0
10 minutes	74.8	93.8
50 minutes	70.6	82.9

Table 4.4: *SFE values for argon plasma treated PC samples with respect to untreated PC sample*

4.1.2 Surface free energy analysis of PET

The contact angles were measured by using equipment as discussed in **section 2.3.1** of **Chapter 2**. The measured contact angles for water and glycerin are listed in **Table 4.5**.

Sample	Water Contact Angle	Glycerin Contact Angle
Pristine	60	57
5 min	25	15
10 min	15	35
50 min	22	26

Table 4.5: *Contact angles for untreated and argon plasma treated PET samples*

Surface free energy (γ_s) and its polar (γ_s^p) and dispersion (γ_s^d) components of the sample were determined from two sets of contact angles (water and glycerin) by using Eq. 2.11. The values of surface free energy and its components before and after the treatment with argon plasma are compared and shown in **Figure 4.2**.

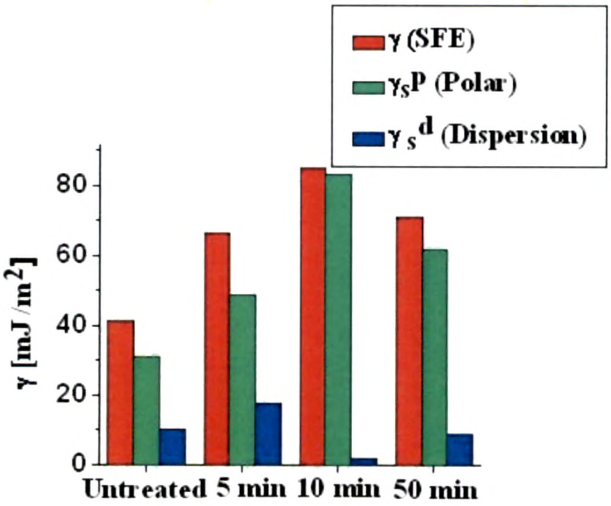

Figure 4.2: *Comparison of Surface free energy and its components before and after the treatment in Ar discharge*

The surface free energy is shown corresponding to the contact angles measured for untreated and treated samples for 5 min, 10 min and 50 min respectively. The values of surface free energy and its components before and after the treatment with argon plasma are listed in **Table 4.6** with standard deviations. It shows that the surface free energy and its polar component increased significantly for 5 min and 10 min treatment time, but decreases for the longest treatment time (50 min). This may be due to the thermal heating at the surface and leading to high damage to polymer chain. The exposure of the sample to the argon discharge is sufficient to break chemical bonds (C-C, C-H), leaving 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 of the PET surface as well as the sputtering of the material from the surface[130].

Treatment Time	Polar (γ_p^s) mJ/m^2	Dispersion (γ_d^s) mJ/m^2	SFE (γ) mJ/m^2	Standard Deviation
Untreated	30.8	11.3	42.1	3.9
5 minutes	48.6	17.6	66.2	1.3
10 minutes	83.2	1.9	85.1	1.2
50 minutes	61.8	9,2	71	4.0

Table 4.6: *Comparison of surface free energy and its components before and after Ar plasma treatment*

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 (C-O etc). The formation of covalent polar bonds plays an important role in adhesion at the interface.

The total surface free energy (SFE) calculated for PET untreated and treated with different treatment times are compared in percentage. The percentage rise for various treatment time of plasma treatment is tabulated in **Table 4.7.** PET with 10 minutes treatment time shows the highest rise in SFE.

Treatment Time	**SFE (γ) mJ/m^2**	**% rise**
Untreated	42.1	----
5 minutes	66.2	57.2
10 minutes	85.1	102.1
50 minutes	71	68.6

Table 4.7: *SFE values for argon plasma treated PET samples with respect to untreated PET sample*

4.1.3 Surface free energy analysis of PTFE

The contact angles were measured by using equipment as discussed in **section 2.3.1** of **Chapter 2**. The measured contact angles for water and glycerin are shown in **Table 4.8**. The water contact angle of untreated sample was found to be about 76°. With an increasing treatment time, it was decreased to about 60°. This shows the improvement in wettability of PTFE surfaces. Similarly, the contact angle for glycerin was measured on PTFE surfaces and it changes from 81° to 60° with increasing treatment time. Surface free energy (γ_s) and its polar (γ_s^p) and dispersion (γ_s^d) components of the samples were determined from two sets of contact angles (water and glycerin) using Eq. 2.11. The values of surface free energy and its components before and after the treatment are compared in **Figure 4.3**. Since PTFE is a chemically inert polymer, plasma treatment has little effect on surface activation i.e increase in surface energy. The increase in surface free energy is attributed to the functionalization of the polymer surface with hydrophilic groups on the surface.

Sample	**Water Contact Angle**	**Glycerin Contact Angle**
Pristine	76	81
5 min	49	51
10 min	55	54
50 min	60	60

Table 4.8: *Contact angles for untreated and argon plasma treated PTFE samples*

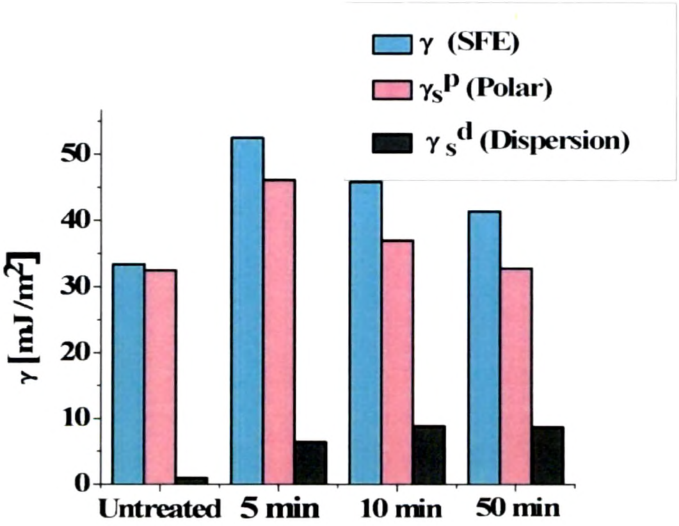

Figure 4.3: *Comparison of Surface free energy and its components before and after the treatment in Ar discharge*

The values of surface free energy and its components before and after the treatment with argon plasma are listed in **Table 4.9** with standard deviations.

Treatment Time	Polar (γ_p^s) mJ/m^2	Dispersion (γ_d^s) mJ/m^2	SFE (γ) mJ/m^2	Standard Deviation
Untreated	32.5	0.9	33.4	2.7
5 minutes	46.1	6.4	52.5	2.1
10 minutes	36.9	8.8	45.8	1.4
50 minutes	35.1	6.9	42.0	2.3

Table 4.9: *Comparison of surface free energy and its components before and after Ar plasma treatment*

For untreated PTFE, the value of polar component is comparable to SFE and dispersion component is not appreciable. There is a little increase in the polar component after all subsequent treatments; whereas remarkable change occurred in the dispersion component. This slight change in polar component is due to the chemically inert nature of PTFE. An important information obtained from the surface energy measurement is that the increase in polar component indicates the formation of covalent bonds.

The total surface free energy (SFE) calculated for PTFE untreated and treated with different treatment times are compared in percentage. The percentage rise for various treatment time is tabulated in **Table 4.10**. PTFE with 5 minutes treatment time shows the highest rise in SFE.

Treatment Time	**SFE (γ) mJ/m^2**	**% rise**
Untreated	33.4	----
5 minutes	52.5	57.2
10 minutes	45.8	37.1
50 minutes	42.0	25.7

Table 4.10: *SFE values for argon plasma treated PTFE samples with respect to untreated PTFE sample*

4.1.4 Surface free energy analysis of PES

The contact angles were measured by using equipment as mentioned in **section 2.3.1** of **Chapter 2**. The measured contact angles are listed in **Table 4.11.**

Sample	**Water Contact Angle**	**Glycerin Contact Angle**
Pristine	49	61
5 min	21	36
10 min	10	20
50 min	29	31

Table 4.11: *Contact angles for untreated and argon plasma treated PES samples*

The water contact angle of untreated sample was found to be about 49°. With an increasing treatment time, it was decreased to about 10°. This shows the improvement in wettability of PES surfaces. Similarly, the contact angle for glycerin was measured on PES surface and it changes from 61° to 20° with increasing treatment time. Five measurements were made for each sample to determine the average contact angle. Lower contact angles confirm that the plasma modified surfaces were changed to more hydrophilic surfaces.

The values of the surface free energy of the test liquids obtained from the literature are given in **Table 4.1.** Surface free energy (γ_s) and its polar (γ_s^P) and dispersion (γ_s^d) components of the sample were determined from the two sets of contact angles (water and glycerin) using Eq. 2.11. The values of surface free energy and its components before and after the treatment are compared in **Figure 4.4.** The increase in surface free energy is attributed to the functionalization of the polymer surface with hydrophilic groups on the surface. The values of surface free energy and its components before and after the treatment with argon plasma are listed in **Table 4.12** with standard deviations. Initially for untreated PES, the values of polar and dispersion components of surface free energies are lower and comparable, but there is a little increase in the polar component after all subsequent treatments, whereas remarkable change in the dispersion component was observed. An important information obtained from the surface energy measurement is that the increase in polar component indicates the formation of covalent bonds on the surface.

Treatment Time	Polar (γ_p^s) mJ/m^2	Dispersion (γ_d^s) mJ/m^2	SFE (γ) mJ/m^2	Standard Deviation
Untreated	66.1	0.2	66.3	1.2
5 minutes	77.3	2.6	79.9	1.4
10 minutes	68.2	8.1	76.3	0.7
50 minutes	57.2	9.3	66.5	2.3

Table 4.12: *Comparison of surface free energy and its components before and after Ar plasma treatment*

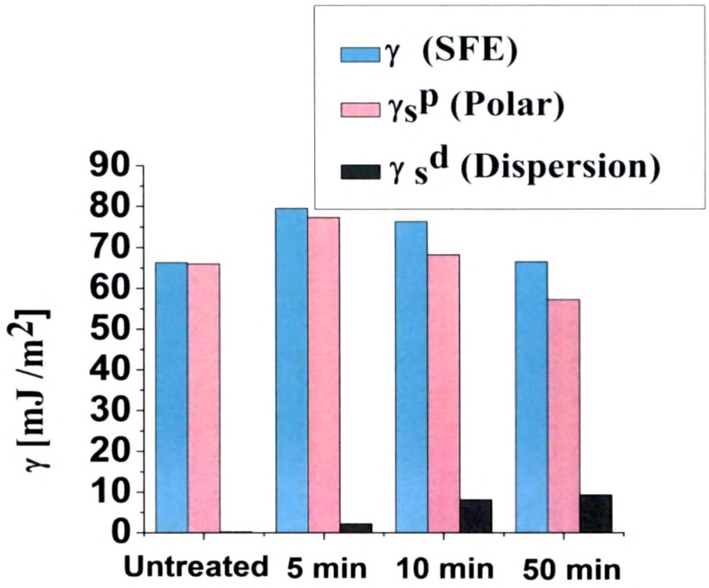

Figure 4.4: *Comparison of Surface free energy and its components before and after the treatment in Ar discharge*

The total surface free energy (SFE) calculated for PES untreated and treated with different treatment times are compared in percentage. The percentage rise for various treatment time of plasma treatment is tabulated in **Table 4.13**. PES with 5 minutes treatment time shows the highest rise in SFE.

Treatment Time	**SFE (γ) mJ/m^2**	**% rise**
Untreated	66.3	----
5 minutes	79.9	20.5
10 minutes	76.3	15.1
50 minutes	66.5	0.3

Table 4.13: *SFE values for argon plasma treated PES samples with respect to untreated PES sample*

4.1.5 Conclusion

Water contact angle measurements were done in order to measure the surface free energy. Contact angle measurements show that the polymer surface changes from hydrophobic to hydrophilic after argon plasma treatment. Contact angles were measured in air. It means that the treated polymers were removed from vacuum and reacted with atmospheric O_2. During these reactions oxygen containing functional groups were formed that influenced the experimental measurements. A decrease in the water angle on treated polymer surface indicates an increase in polymer surface energy, which may be important in case of adhesion.

In order to summarize the results of section 4.1 following conclusions can be drawn:

- The degree of hydrophobicity of polymeric surfaces depends on type of polymers. It is also affected if polluted layers are present on surface of the sample which will affect the hydrophilicity.
- It is observed that the surface free energy increases with argon plasma treatment due to increase in polar component as shown in **Table 4.14.** This may lead to improve the adhesion of polymer surface.

Treatment Time	PC	PET	PTFE	PES
Untreated	25.4	31.2	32.5	66.1
5 minutes	65.3	48.6	46.1	77.3
10 minutes	65.8	83.3	37.1	68.2
50 minutes	56.6	62.1	32.8	57.2

Table 4.14: *Polar components of surface energy*

- The increase in surface free energy by argon plasma treatment increases the hydrophilic groups on the surface.
- The molecular formulae of PC, PET, PES and PTFE is written as $[C_{16}H_{14}O_3]_n$, $[C_{10}H_8O_4]_n$, $[C_{27}H_{22}O_4S]_n$ and $[C_2F_4]_n$ respectively. The first three polymers show oxygen contains and last one shows fluorine contain. As observed from XPS analysis that the hydrophilic group (ie. attract water) attached at the surface. Generally C-C,C-H,C-S, C-F bonds degraded and carbonyl group (- C=O) enhanced. The surface energy increased for 10 min treatment time for PC and PET while for PES and PTFE, the surface energy increased for 5 min treatment. In the later case, the emission of sulpher and fluorine ie. de sulphonation and de fluorination took place. This may be the reason for these two polymers to have more surface energy for lower treatment time.

4.2 Vickers' Microhardness

4.2.0 Introduction

All the pristine and plasma treated samples (films) subjected to indentation test were studied at ambient temperature. The specimen to be indented is mounted on a horizontal platform inserted in the collect. Loads ranging from 10 - 500 gf were used for making indentations, keeping the time constant as 20 s in all cases. The indentation tests were operated in load-displacement controlled testing mode to accurately obtain precise displacements. The Vicker's micro hardness number (Hv) is determined by the indentation technique using Eq. 2.17 (section 2.3.2 of Chapter 2).

The specimen at a preselected force is held constant for duration of 20 sec. The diamond indenter makes the print on the sample surface. By reversing the motion, the indenter is removed and the indented region examined with the reading objective through the filler eye piece or CCD camera. The diagonal of the indentation mark is measured for different loads and Hv value was calculated.

For example, the indentation mark on the polymer surface is shown in **Figure 4.5**. It shows the change of size of indentation mark with loads.

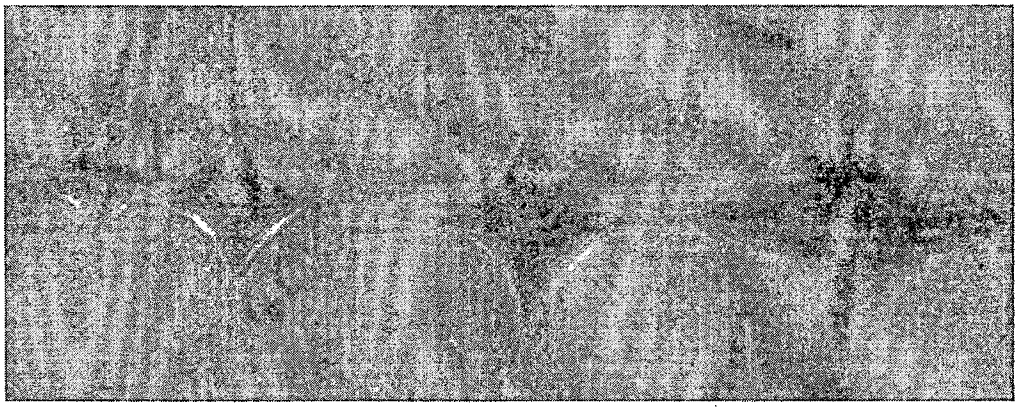

Figure 4.5: *Indentation marks on polymer surface*

4.2.1 Microhardness of PC films

The measured Vickers' microhardness value (Hv) with loads ranging from 10 to 500 gf for both untreated and argon plasma treated PCs is listed in **Table 4.15**. **Figure 4.6** gives the plots of the Vickers' microhardness (Hv) versus applied load (P) for different treatment times.

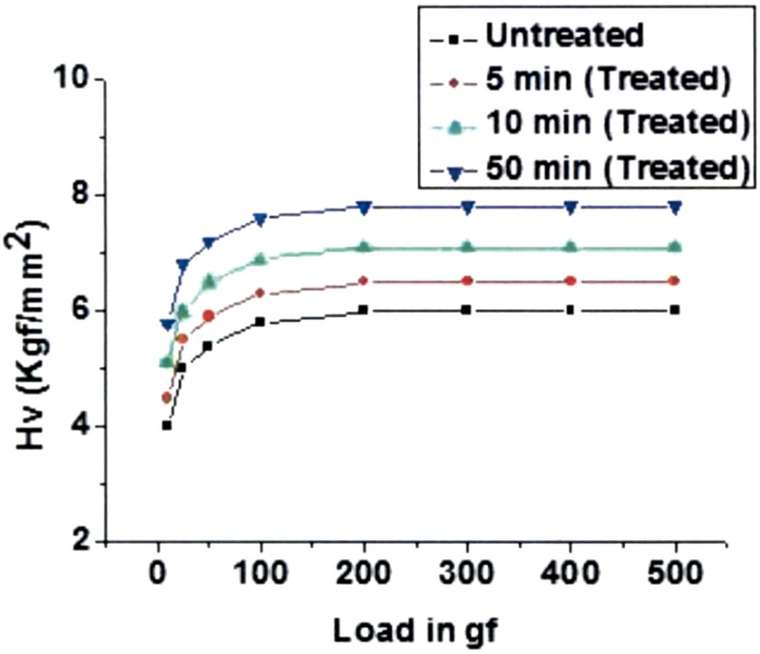

Figure 4.6: *Plot of hardness vs applied loads*

It is evident that the microhardness value increases with the load up to 200 gf and then saturate beyond this load of 200 gf. The increase of Hv with load can be explained on the basis of the strain hardening phenomenon. On applying the load, the polymer is subjected to some strain hardening. Beyond certain load the polymer exhausts its strain hardening capacity and the hardness tends to become constant. The rate of strain hardening is greater at low loads and decreases at higher loads [131, 132]. It can be seen that the hardness becomes independent of load for a load more than 200 gf. The value obtained from this saturation region represent the true hardness of the bulk materials. Since at high loads the indenter penetration depth is also high and surface effects became insignificant. It is also observed that the hardness increases as treatment time increases. This is attributed to the crosslinking effect [56]. This is also corroborated with XPS and FTIR analysis as explained in **Chapter 3**.

	Hv			
Load	**Untreated**	**5 min**	**10 min**	**50 min**
10	4	4.5	5.1	5.8
25	5	5.5	6	6.8
50	5.4	5.9	6.5	7.2
100	5.8	6.3	6.9	7.6
200	6	6.5	7.1	7.8
300	6	6.5	7.1	7.8
400	6	6.5	7.1	7.8
500	6	6.5	7.1	7.8

Table 4.15: *Hv values of pristine and argon plasma treated PC polymer with change in load*

4.2.2 Microhardness of PET films

The Vickers' microhardness (Hv) values for different loads are listed in **Table 4.16. Figure 4.7** shows the plots of Vickers' microhardnee (Hv) versus applied load (P) ranging from 10 to 500 gf for pristine and treated samples.

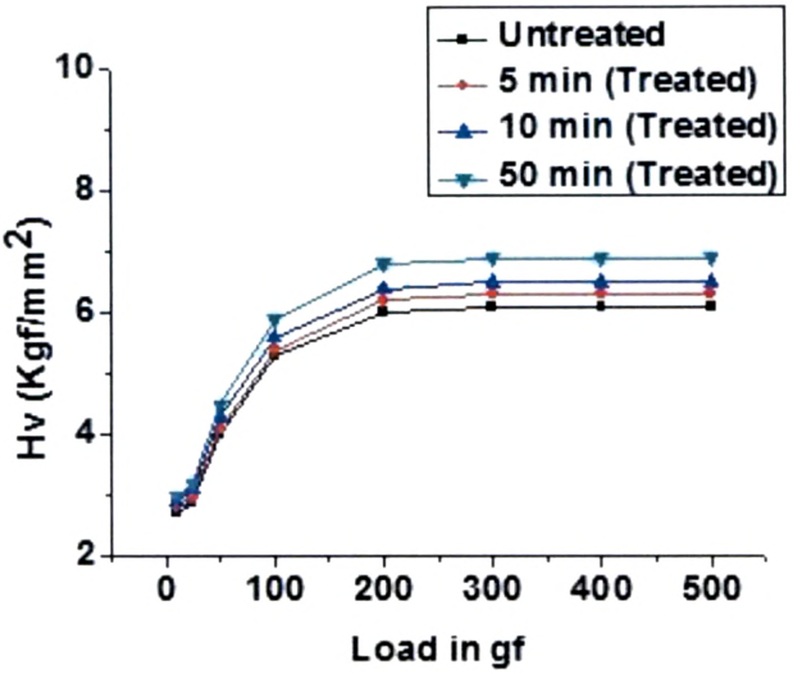

Figure 4.7: *Plot of hardness vs applied loads*

Load	Hv			
	Untreated	5 min	10 min	50 min
10	2.7	2.8	2.9	3.0
25	2.9	3.0	3.1	3.2
50	4.0	4.1	4.3	4.5
100	5.3	5.4	5.6	5.9
200	6.0	6.2	6.4	6.8
300	6.1	6.3	6.5	6.9
400	6.1	6.3	6.5	6.9
500	6.1	6.3	6.5	6.9

Table 4.16: *Hv values of untreated and argon plasma treated PET polymer with change in load*

It is observed that the microhardness increases with increasing load for all the samples up to 200 gf. However, beyond a load of 200 gf, the rate of increase of hardness slow down and then became constant. At higher loads ie beyond 200 gf, the interior of the bulk specimen is devoid of surface effects. The hardness value in saturation region represents the true value of the bulk and it is consequently independent of the load. The hardness is found to increase with treatment time. This may be attributed to cross-linking phenomenon as shown in **Figure 3.8**. It is also corroborated with XPS and ATR-FTIR analysis (**Chapter 3**) [49, 62, 110].

4.2.3 Microhardness of PTFE films

The Vickers' microhardness was determined and tabulated in **Table 4.17**. **Figure 4.8** illustrates the plots of Vickers' microhardness (HV) versus applied load (P) for pristine and plasma treated samples.

The Vicker's micro hardness increases as load increases up to a load of 200 gf for all samples. However, on increasing the load further, the rate of increase of hardness slow down and then became constant. The increase in hardness with load can be explained on the basis of strain hardening phenomenon. The rate of strain hardnening is greater at low loads and decreases at higher loads. The value obtained from saturation region represent the true hardness of the bulk materials. The hardness is found to increase as treatment time increases. This may be attributed to cross-linking phenomenon on the polymer surface [131, 132, 65] as shown in **Figure 3.9**. It is also corroborated with XPS and ATR-FTIR analysis (**Chapter 3**).

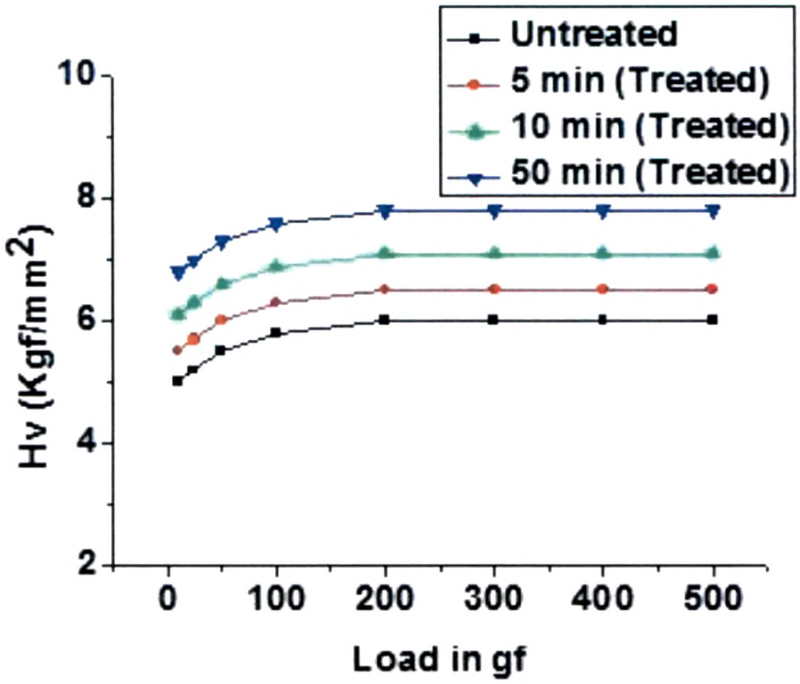

Figure 4.8: *Plot of hardness vs applied loads*

	Hv			
Load	**Untreated**	**5 min**	**10 min**	**50 min**
10	5	5.5	6.1	6.8
25	5.2	5.7	6.3	7
50	5.5	6	6.6	7.3
100	5.8	6.3	6.9	7.6
200	6	6.5	7.1	7.8
300	6	6.5	7.1	7.8
400	6	6.5	7.1	7.8
500	6	6.5	7.1	7.8

Table 4.17: *Hv values of argon plasma treated PTFE polymer with change in load*

4.2.4 Microhardness of PES films

We have studied the Vickers' microhardness (ie. mechanical property) by means of indentation method. The Vickers' micro hardness (Hv) value was calculated using the Eq. 2.17 as discussed in **Chapter 2**. The Vickers' hardness values are listed in **Table 4.18**. The variation of Hv with load ranging from 10 to 500 gf for both untreated and argon plasma treated PES is illustrated in **Figure 4.9**.

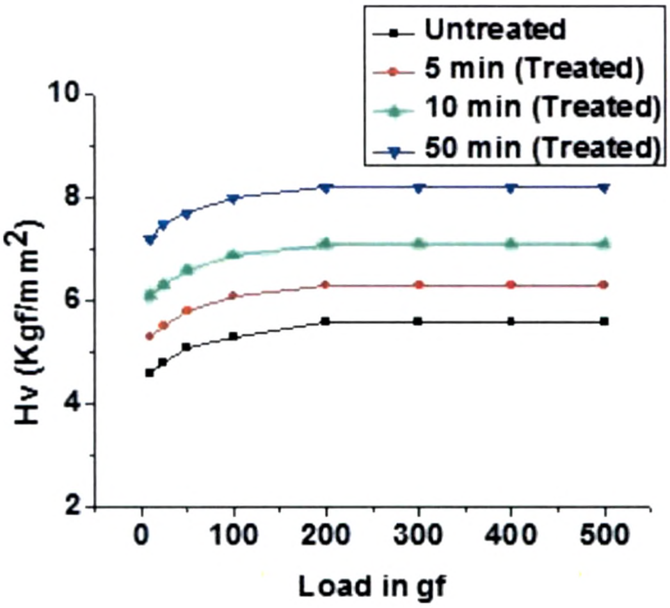

Figure 4.9: *Plot of hardness vs applied loads*

The Vickers' microhardness increases with load up to 200 gf and became constant beyond a loads of 200 gf for all samples. As can be seen that the hardness became independent of loads beyond a loads of 200 gf. The value obtained from saturation region therefore represents the true hardness of the bulk materials. At high loads the indenter penetration depth is also high and surface effects became insignificant. It is also observed that the hardness increases as treatment time increases. This may be attributed to cross-linking phenomenon at the polymer surface [131, 132] as shown in **Figure 3.10**. It is also corroborated with XPS and ATR-FTIR analysis (**Chapter 3**).

Load	**Hv**			
	Untreated	**5 min**	**10 min**	**50 min**
10	4.6	5.3	6.1	7.2
25	4.8	5.5	6.3	7.5
50	5.1	5.8	6.6	7.7
100	5.3	6.1	6.9	8
200	5.6	6.3	7.1	8.2
300	5.6	6.3	7.1	8.2
400	5.6	6.3	7.1	8.2
500	5.6	6.3	7.1	8.2

Table 4.18: *Hv values of argon plasma treated PES polymer with change in load*

4.2.5 Conclusion

In order to summarize the results of section 4.2 following conclusions can be drawn:

- Vicker's microhardness of the film increases upon plasma treatment. This may be attributed to cross linking effect. The increase in surface free energy (SFE) (Section 4.1) after plasma treatment is attributed to the functionalization of the polymer surface (cross-linking) with hydrophilic groups as supported from the above observations.
- 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 material and is consequently independent of the load.

4.3 Atomic Force Microscopy analysis

4.3.0 Introduction

The changes in the surface roughness of the plasma treated polymers surfaces were investigated by AFM. In contact-mode AFM, the tip either scans at a constant small height above the surface or under the conditions of a constant force. In the constant height mode the height of the tip is fixed, whereas in the constant-force mode the deflection of the cantilever is fixed and the motion of the scanner in z-direction is recorded using Eq. 2.22 of **Chapter 2**. For contact mode AFM imaging, it is necessary to have a cantilever which is soft enough to be deflected by very small forces and has a high enough resonant frequency to not be susceptible to vibrational instabilities. By using contact-mode AFM, even "atomic resolution" images are obtained.

4.3.1 AFM analysis of PC films

The AFM images of untreated and argon plasma treated samples on an area of 5 x 5 μm^2 were recorded and are shown in **Figure 4.10**. The changes in the surface morphology of PC surfaces and its dependence on the treatment time of argon plasma can be seen from the series of AFM images as shown in **Figure 4.10 (a-d)**.

It is to be noted that the treated samples do not appear to be flat (smooth) but seems to have the appearance of a "hill- like" contour ie. the surface topography shows heterogeneities (high and phase images) after plasma treatment. As treatment time increases the size of hill-like contour decreases ie. the number of hill like contour increases (ie heterogeneities became more pronounced) on the treated samples and surface became more rough.

The root mean square (RMS) roughness was found to be 7.0 nm, 8.1 nm, 15.7 nm, and 37.8 nm for untreated and argon plasma treated for 5 min, 10 min and 50 min 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 [48].

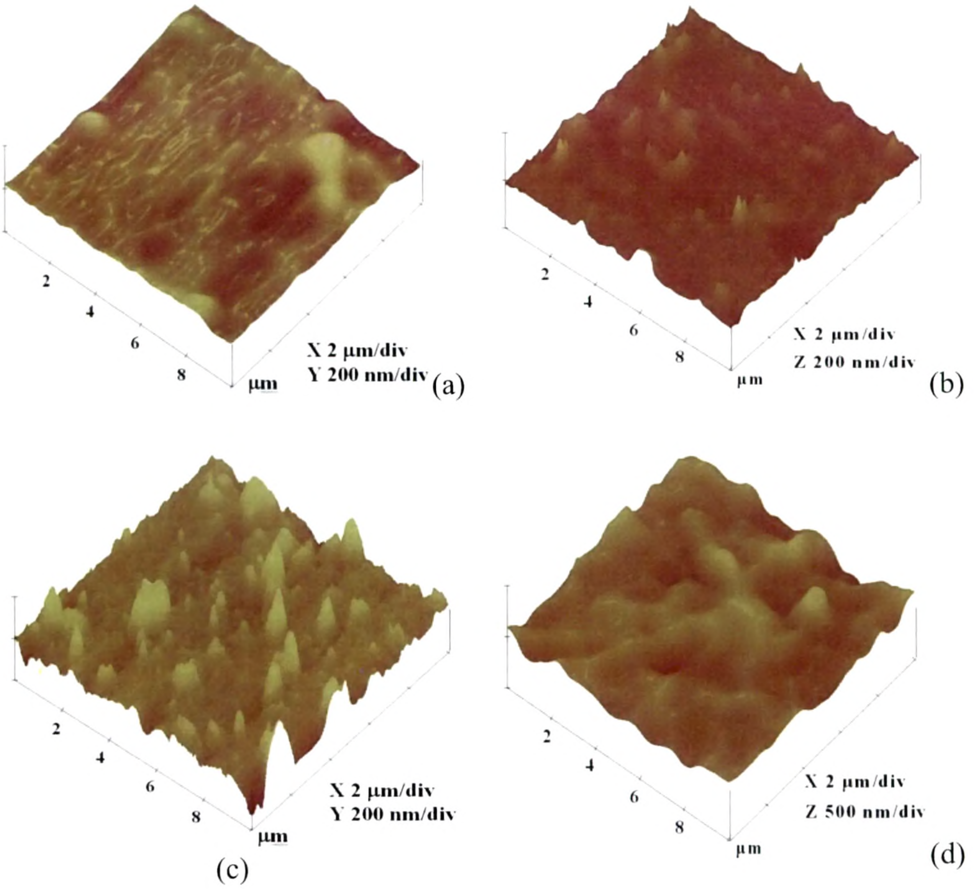

Figure 4.10: *AFM photomicrographs of (a) untreated PC film, (b) Ar plasma treated PC for 5 min, (c) Ar plasma treated PC for 10 min, (d) Ar plasma treated PC for 50 min*

4.3.2 AFM analysis of PET films

The surface morphology of argon treated PET films was measured by using atomic force microscope (AFM) on an area of 5 x 5 μm^2 and are shown in **Figure 4.11 (a-d)**. They are also showing ‘hill-like’ contours on the surface.

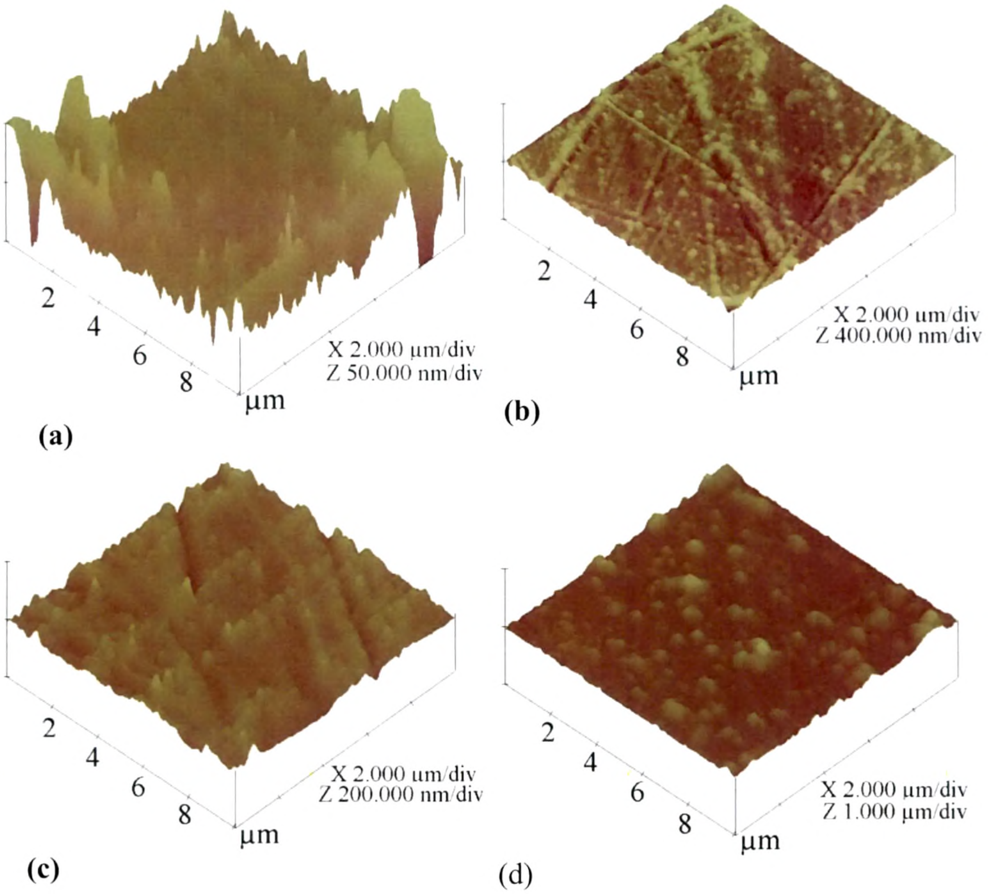

Figure 4.11: *AFM photomicrographs of (a) untreated PET film, (b) Ar plasma treated PET for 5 min, (c) Ar plasma treated PET for 10 min, (d) Ar plasma treated PET for 50 min*

The high and phase images of the unmodified polymer surface shows no significant differences in the high and phase profiles (local heterogeneities) of pristine film, except for local melting marks on the surface.

Each AFM image was analyzed in terms of average surface roughness (rms). The surface roughness increases with treatment time. The average surface roughness are 5.8 nm for untreated film and 6.2 nm, 16.5 nm and 42.7 nm for plasma treated films for the time 5, 10 and 50 min respectively.

4.3.3 AFM analysis of PTFE films

The surface morphology of argon plasma treated PTFE samples were measured by AFM in contact mode on an area of 5 x 5 μm^2 and are shown in **Figure 4.12 (a-d)**. It is noted that the treated samples do not appear to be a flat (smooth) but seems to have the appearance of 'hill-like' contours on the surface ie. more pronounce high and phase images (heterogeneities). As the treatment time increases, number of contours also increases (ie. high and phase images became more and more pronounced) and surface became more and more rough. Each AFM image was analyzed in terms of average surface roughness (rms), and increases with treatment time. The average surface roughness (r m s) for untreated film and argon plasma treated film for 5 min, 10 min and 50 min are 8.5 nm, 13.3 nm, 22.8 nm and 52.4 nm respectively. The roughness of the PTFE surfaces increases with treatment time; hence it can support the adhesion improvement [111]. This result is corroborated with surface free energy results.

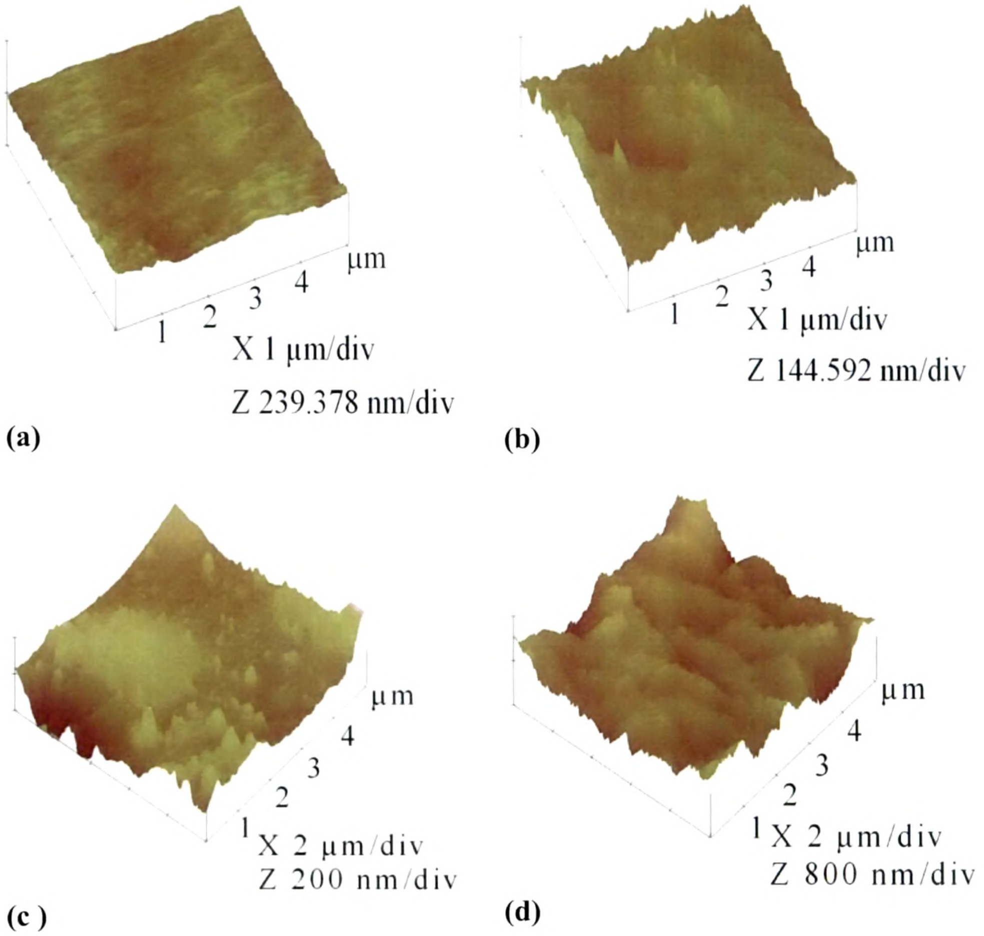

Figure 4.12: *AFM photomicrographs of (a) untreated PTFE film, (b) Ar plasma treated PTFE for 5 min, (c) Ar plasma treated PTFE for 10 min, (d) Ar plasma treated PTFE for 50 min*

4.3.4 AFM analysis of PES films

The surface morphology of argon treated PES samples were measured by AFM in contact mode on an area of 5 x 5 µm^2 and are shown in **Figure 4.13 (a-d)**. It also shows that the high and phase images became more pronounce on increasing the treatment time.

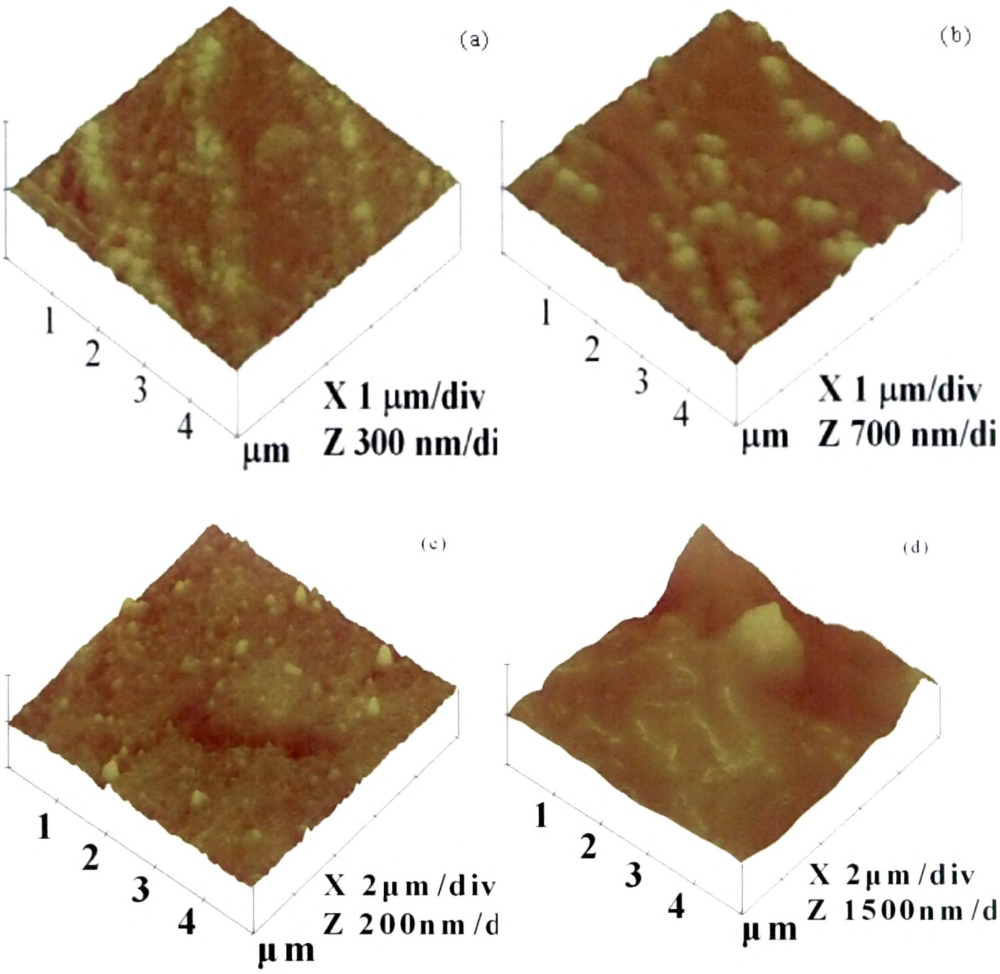

Figure 4.13: *AFM photomicrographs of (a) untreated PES film, (b) Ar plasma treated PES for 5 min, (c) Ar plasma treated PES for 10 min, (d) Ar plasma treated PES for 50 min*

Each AFM image was analyzed in terms of average surface roughness (r m s) and roughness increases with treatment time. The average surface roughness (r m s) for untreated film and argon plasma treated films for 5 min, 10 min and 50 min are 6.9 nm, 12.7 nm, 23.7 nm and 57.5 nm respectively. The roughness of the PES surfaces increases with treatment time, hence it can support the adhesion improvement. This result is corroborated with surface free energy results.

4.3.5 Summary and Conclusion

The atomic force microscope (AFM) is one of the foremost tools for polymer characterization with regard to both surface topography and surface mechanical properties. The influence of the plasma treatment on the surface roughness of the polymer film was measured. The technique is used to find the root mean square surface roughness of pristine and Ar-plasma treated samples. The root mean square surface roughness of argon plasma treated polymers is listed in **Table 4.19**.

Polymers	RMS Roughness (nm)			
	0 min (Pristine)	5 min	10 min	50 min
PC	7.0	8.1	15.7	37.8
PET	5.8	6.2	16.5	42.7
PTFE	8.5	13.3	22.8	52.4
PES	6.9	12.7	23.7	57.5

Table 4.19: *The root mean square (RMS) surface roughness of argon plasma treated polymers*

In order to summarize the results, the following conclusions can be drawn:

1. The polymer surface treated by plasma was exposed to excited and unstable particles, which could transfer their energy to the polymeric surfaces. The modification of polymers by Ar plasma led to a breakdown of the C-H and /or C-C bonds and creating free radicals on the polymeric surface (as observed from XPS analysis, Chapter 3). When subsequently exposed to air, these radicals react with oxygen into the air to form peroxides and hydroperoxides ie. formation of hydrophilic groups took place on the surface.

2. The plasma induced process is etching of polymeric surface, evidenced by AFM analysis. The removal of the polymeric material towards gas phase reasonably occurs through the formation of low molecular weight compounds, formed as by products during oxidation of the polymer. The etched surface leads to a rougher surface.

3. The AFM results of the surface topography and local heterogeneities (high and phase images) after plasma treatment are shown in Figures 4.9 to 4.12. The surface properties of each (sample) foil were measured at three different places, but no extensive differences were observed between these places. The high and phase images of the pristine polymer show no significant differences in the high and phase profiles (local heterogeneities), except for local melting marks on the surface. The high and phase images of pristine polymers are rather rough, but without observable in homogeneities. The rms values of pristine PC, PET, PTFE and PES polymers are 7.0 nm, 5.8 nm, 8.5 nm and 6.9 nm respectively. The plasma treated resulted in an appearance of very fine heterogeneities regions, and the polymer surface became more irregular. The local heterogeneities after treatment are more pronounced. The roughness of plasma treated surfaces increases two/three times higher compared to pristine polymer for 10 min treated samples.