Chapter 5

Summary and Conclusions

Abstract

This chapter summarizes the results derived from the present investigations using different techniques. It also derives the conclusions of the present study and future plan of work.

Summary and Conclusions

Plasma treatment proved itself to be a suitable technique to alter the chemical and physical properties of polymer surfaces. Commercially available polymer sheets were treated with the argon plasma at an energy of 600 eV for the time periods of 5 min,10 min and 50 min and consequently in the fluence range of 10^{12} to 10^{16} cm^{-2}. At low exposure energies, the plasma surface interactions only change the surface of the material to a region only several molecular layers deep. The resulting surface changes depend on the composition of the surface and gas used. The bond breaking occurs on the polymer surface and the molecule can do one of the three things; (i) it can form a bond with a near by free radical on a different chain (chain link) (ii) it can react with an adjoining free radicals on the same chain, forming a double or triple bond (called unsaturation) (iii) recombine with the by-products and revert back to its original state.

The surface modification of different polymers were studied using: contact angle measurement, X-ray photoelectron spectroscopy (XPS), Atomic force microscopy (AFM), ATR-FTIR spectroscopy and Vickers' Micro hardness measurement. The contact angle measurement was used to study the surface free energy, wettability and adhesion of low surface energy materials. The XPS method was used to observe chemical changes that occurred in the polymer surface during plasma treatment. Atomic force microscopy was used to determine the surface roughness of polymer films after plasma treatment. The micro hardness was used to study the mechanical property of the polymeric samples with treatment time. ATR-FTIR provides information about chemical

bonding and molecular structures. The following conclusions are drawn for each study.

(A) From XPS analysis, it is observed that O/C ratio (**Figure 5.1**) decreases in the order of PC > PET > PES > PTFE.

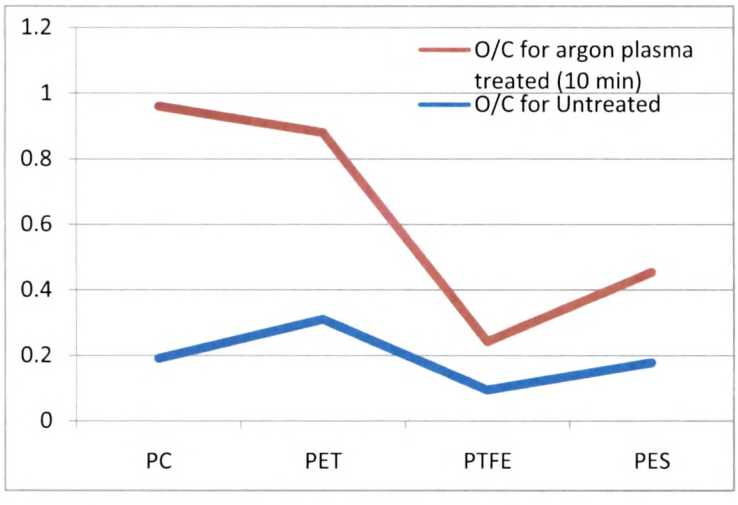

Figure 5.1: *O/C ratios for the studied polymers*

The reason for the remarkable increase of hydrophilicity of plasma treated samples is that the all polymeric films consist in the formation of oxygen containing groups on the surface.

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

1. XPS analysis results reveal an increase in O/C ratios due to plasma treatment for all the chosen polymers as shown in **Figure 5.1**.
2. No additional functionalities were observed as the plasma treatment was performed under high vacuum condition.

(B) ATR-FTIR measurements directly confirm the enhancement of carboxylic C=O bonds peaking in the region around 1730 - 1767 cm^{-1}. The decrease of carbon atoms involved in the carboxyl group was observed by XPS analysis as evidenced by the C1s peak at 284.8 eV binding energy. The quantity of oxygen

in O 1s (at 534.3± 0.1 eV binding energy) was increased from its original value. The increased oxygen content of the superficial layers, measured by XPS, do not alter the overall elemental composition of the polymer.

In order to summarize the results of ATR-FTIR, following conclusions can be drawn:

1. Only minor changes observed in the intensity of the peak of the treated/irradiated sample as compared to the pristine sample. This may be due to the breakage of few bonds in the structure.
2. Most of the peaks were unshifted and only the transmittance value of particular functional groups are changed.

(C) The static contact angle of thermoplastic polymer surfaces modified by argon plasma treatment measured and gives a direct indication of surface wettability. From these data, we were also able to determine both the polar and the dispersion components of the surface free energies of the modified surfaces. For the different substrates, we observed the percentage rise in surface free energy as shown in **Table 5.1**.

It is observed that the argon plasma treatment at low pressure can enhance the wettability of thermoplastic polymers significantly. Short treatment time was sufficient to cause substantial modification of the polymer surfaces. The argon plasma produced a better-modified surface that was more hydrophilic and had a lower water contact angle, hence the adhesion properties of thermoplastic polymers were strikingly increased.

Treatment	PC	PET	PTFE	PES
Untreated (mJ/m^2)	38.6	42.1	33.4	66.3
Argon plasma treated (5 min) (mJ/m^2)	71.8	66.2	52.5	79.9
Argon plasma treated (10 min) (mJ/m^2)	74.8	85.1	45.8	76.3
% rise (5 min)	86.0	57.2	57.2	20.5
% rise (10 min)	93.8	102.1	37.1	15.0

Table 5.1: Change *in SFE for untreated and argon plasma treated samples*

In order to summarize the results of surface free energies, following conclusions can be drawn:

1. Hydrophobicity of polymeric surfaces depends on the surface roughness for all the selected polymers.
2. The surface free energy at polymer surfaces increases with Ar plasma treatment due to increase in polar components.
3. This increase in surface free energy increases hydrophilic groups on the surface.

(D) The variation of Vicker's micro hardness number (*Hv*), as a function of applied load (*L*), is shown in **section 4.2** of **Chapter 4** for pristine and the argon plasma treated polymers. As the load is increased, the sample is subjected to greater strain hardening and *Hv value* is increased. Finally, when *Hv value* tends to saturate, the polymer specimen is fully strain hardened and became constant after 200 gf load for all polymers, so no appreciable change in the value of *Hv* is observed.

The RMS of roughness of untreated and argon plasma treated polymers for different time duration are shown in the **Table 5.2**. It is seen that the RMS value increases with increase in treatment time. This is due to the removal of top few mono layers of the polymer film surface during plasma treatment. The surface roughness increases the wettability and the bonding strength.

Polymers	RMS Roughness (nm)		
	0 min (Pristine)	10 min	% rise
PC	7.0	15.7	124.3
PET	5.8	16.5	184.5
PTFE	8.5	22.8	168.2
PES	6.9	23.7	243.5

Table 5.2: *RMS values for untreated and argon plasma treated samples*

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

1. Vicker's micro hardness of the films increases upon plasma treatment. This may be attributed to cross linking effect.
2. Beyond 200 gf, the interior of the bulk specimens is devoid of surface effects.

(E) The change in surface morphology of all the thermoplastic polymers considered was analyzed using AFM results. The influence of the plasma treatment on the surface roughness of the polymer film was measured for pristine and Ar-plasma treated samples.

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

1. 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 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.

Based on the results of the present work, the following conclusion can be drawn:

- Surface modification showed a large dependence on plasma treatment parameters and polymer surface chemistry. The surface modification of thermoplastic polymers selected has modified the surface tension, surface chemistry and surface morphology.
- The tendency of contact angle was found to be the same for all investigated polymers. The contact angle decreases for increase in plasma treatment time. Hence, the surface free energy increases.
- Chemical changes involved structural rearrangement, formation of new functional groups, cross linking, chain scissioning and double bond formation. Analysis of X-ray photoelectron spectroscopy showed that the very first changes under plasma treatment occurred in the outer most surface layer (1-2 nm).
- Plasma surface modification has been shown to increase the surface roughness.

Future plan of work

Surface Modification of polymers/polymer composites with low energy ion beams

Metallized polymers are widely used for different applications: packaging, decorative coatings, capacitors, magnetic tapes, etc. In such applications, a good adhesion between the polymer and the metal is required. It is well known that the interfacial interaction controls the quality and growth mechanisms of the metal layer. The study of the metal/polymer interface formation in the case where the metal reactivity towards the polymer functional groups is very low. This will be undertaken in order to investigate the influence of the surface modifications produced by an ion beam bombardment. The objective of the present work is to determine the sputter rates of different polymers as a function of the ion beam parameters; to modify the surfaces of organic films changing their chemistry, surface energy and roughness and finally to determine the influence of the ion beam parameters and polymer chemistry on the metal-polymer interaction[36, 133-134].

The objectives of the presented project are:

1) To change the physical and chemical properties of the polymer surface through the alteration of the polymer structure. Polymer chains undergo chain scissions under ion irradiation creating small mass molecules some of which can be desorbed, i.e. sputtered, and free radicals that participate in different chemical reactions creating cross-link networks, branching, and double bonds. If polymers are irradiated with oxygen or nitrogen ions, created free radicals react with reactive species inducing the formation of carbon-oxygen and/or carbon-nitrogen functional groups. To determine created functionalities, X-ray photoelectron spectroscopy (XPS) will be used together with angle resolved XPS analysis that allows us to determine the uniformity of the surface modification by variation of the take-off angle. The surface glass transition temperature measurements based on the noble metal embedding method [4] will be used to determine the change in polymer behavior under ion irradiation, i.e. cross-link formation and degradation;

2) To determine the influence of the ion beam parameters and polymer chemistry on the metal-polymer interaction using ATR-FTIR Spectroscopy.
3) Practical adhesion measurements will be done using contact angle tests which indicate a strong dependence of the adhesion on the polymer chemistry. In conjunction with these results, the adhesion mechanisms of metals on the ion modified polymer surfaces will be clarified. The influence of the ion beam on the surface roughness of the polymer films will be measured using atomic force microscopy (AFM).