International Journal of Physical Sciences Vol. 7(15), pp. 2264 - 2273, 9 April, 2012
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS11.1781
ISSN 1992-1950 ©2012 Academic Journals

Full Length Research Paper

Studies on adhesive properties of polypropylene (PP) and polycarbonate (PC) film surfaces using DC glow discharge plasma

K. A. Vijayalakshmi[1], M. Mekala[2]*, C. P. Yoganand[3] and K. Navaneetha Pandiyaraj[4]

[1]Department of Physics, Sri Vasavi Arts College, Erode- 638316, India.
[2]Department of Physics, PKR Arts College for Women, Gobi- 638476, India.
[3]Department of Plasma Combustion, Korea Institute of Machinery and Materials, Daejeon, South Korea.
[4]Department of Physics, Sri Shakthi Institute of Engineering and Technology, Coimbatore- 641062, India.

Accepted 23 March, 2012

Direct current (DC) glow discharge plasma has been used to increase the adhesive properties of polypropylene (PP) and polycarbonate (PC) film surfaces and make them suitable for technical applications. The modified surfaces were characterized by contact angle, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) analysis. Also, improved adhesion properties were analyzed using T-Peel strength test. The results show that the surface wettability has been increased due to decrease in contact angle and increase in surface energy. After plasma treatment the root mean square (RMS), roughness of PP and PC films were gradually increased with different exposure time. XPS results detected polar functional groups on plasma treated PP and PC film surfaces. T-Peel strength test for adhesion strength measurement showed that the surface modified PP and PC films were increased with adhesive properties.

Key words: Glow discharge, polypropylene (PP), polycarbonate (PC), contact angle, surface energy.

INTRODUCTION

Polymer materials show excellent mechanical properties, good corrosion resistance, light weight, low cost and bio compatibility. Because of this, it has been widely used in engineering and medical fields to prepare plastic vessels, machine parts, compact disc, optical fiber, biosensor and bone internal fixation devices, etc., (Bag et al., 1999; Friedman and Gerard, 2002; Sanchis et al., 2006; Sakthikumar et al., 2007). The major properties of polycarbonate (PC) like clarity, high strength and impact resistance, good heat resistance, low water absorption and bio compatibility, etc., have led to its use in a wide range of critical devices, and also, polyolefin, like polypropylene (PP) have gained a lot of interest in both science and technology. Commonly, polymer materials are with low surface energy and consequently they have poor adhesion properties. In order to increase surface free energy and poor adhesion of additional coatings, it is necessary to improve some of the surface properties of the polymer without changing the bulk properties (Richard and Robert, 1997). Numerous techniques have been used to modify the polymer surfaces for increased adhesion, wettability, printability, etc., (Deepak et al., 2003). Non thermal direct current (DC) glow discharge plasma is generally used for surface improvement of polymers. Due to plasma treatment on the surface, the top most nano layers of the material are altered without affecting the bulk properties (Rajesh and Mark, 2003). The DC glow discharge plasma has more advantage than the corona and atmospheric pressure discharge type of plasma. In this method, the plasma treatment takes place at low or moderate temperature which is more suitable for polymer materials (Bhowmik et al., 2001). In addition, DC glow discharge plasma is environmentally friendly. The

*Corresponding author. E-mail: mekalanadarajan@yahoo.co.in. Tel: 91 9360513397.

Table 1. Operating parameters for plasma treatment.

Discharge potential	400 V
Pressure	0.2 mbar
Exposure time for PP	1 - 20 min
Exposure time for PC	1 - 20 min
Electrode separation	3 cm
Plasma gas	Air
Samples	Polypropylene and polycarbonate films

Table 2. Surface energy of liquids.

Liquid	γ_1 (mJ/m^2)	γ_1^d (mJ/m^2)	γ_1^P (mJ/m^2)
Distilled water	72.8	21.8	51.0
Glycerol	64.0	34.0	30.0

plasma is generated using DC current or low power radio frequency (RF) current. Air plasma treatment introduces free radicals on the surface of polymer films where the free radicals interact with some functional groups on the polymer surface. This will enhance the surface properties of polymer films (Gavrilov et al., 1998; Sellin et al., 2003). In this study, PP and PC films were exposed to DC glow discharge air plasma under different treatment times with an aim of increasing the surface properties of these films. Increase in hydrophilicity of plasma treated PP and PC films was characterized by measuring the contact angle as a function of time. The surface morphology of the modified PP and PC films was analyzed using atomic force microscopy (AFM). The chemical composition of the plasma treated PP and PC films was characterized by X-ray photoelectron spectroscopy (XPS). The adhesion of PP and PC films before and after treatment was analyzed using T-peel strength test.

EXPERIMENTAL SETUP

PP and PC films were cut into pieces of 5 × 5 cm size for plasma treatment. The PP and PC films were ultrasonically washed in acetone and with distilled water for 15 min and were dried. DC glow discharge plasma of low-pressure was generated in a glass chamber of 29 cm length and 10 cm internal diameter size. Vacuum of 10^{-3} mbar was maintained inside the chamber using a vacuum pump. Required vacuum was maintained using fine control gas needle valve. Pirani gauge was used for pressure measurement. Circular shaped electrodes made of aluminum with a diameter of 5 cm were fixed inside the chamber. The electrodes were separated by a distance of 3 cm. Air was used as the working gas. High tension DC power supply of 1.5 kV was used. The films were placed perpendicular to the discharge axis between the parallel electrodes using a holder. Plasma chemical conversion of the working gas produces chemically active particle that are able to modify polymer surfaces via chemical reactions after impinging on the surface. The radicals generated inside the plasma region must be given the opportunity to move the polymer surface. After plasma generation, the movement of charged particle produces current, which is displayed in ammeter. Operating parameters influence the surface modifications. The operating parameters are listed in Table 1.

The contact angle is defined as the angle between a solid surface and tangent of a liquid-vapour interface of a liquid drop. The hydrophilicity of a solid surface is usually expressed in terms of wettability that can be estimated by contact angle measurements. It is a simple and convenient method to determine the surface wettability. Contact angles are influenced by interfacial tension, roughness and molecular orientation in the polymer material.

The angle of contact was measured using sessile drop method and surface energy was estimated. The liquids water and glycerol with known γ^p (polar component) and γ^d (dispersive component) were used for calculating the surface energy of PP and PC films. The height (h) and radius (r) of the liquids were measured by using microscope, and the contact angle was calculated using the following equation (Bhat et al., 2003):

$$\text{Contact angle (D)} = \sin^{-1}(2rh) \,/\, (r^2 + h^2) \quad (1)$$

Three readings were taken at different places of the sample surface and an average was determined. The error in the measurement of contact angle was found to be ± 2°. Similarly, the contact angle measurements were carried out with respect to glycerol. The values of polar and dispersive components of testing liquids are given in Table 2 (Vijayalakshmi et al., 2011).

The polar and dispersive components of the surface energy of the polymer film surface were calculated using the Fowkes approximation (Subedi et al., 2008):

$$\gamma_1(1+\cos\theta) = 2(\gamma_1^d \gamma_s^d)^{1/2} + 2(\gamma_1^p \gamma_s^p)^{1/2} \quad (2)$$

Where θ is the contact angle of testing liquids, γ_1 is the liquid surface tension and γ_1^p and γ_1^d are the polar and dispersive components of the test liquids. Similarly, the solid surface tension (γ_s) is expressed in terms of its polar and dispersive components:

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (3)$$

The adhesion work $W_{adh,}$ a quantity related to the surface wettability, was estimated using the relation:

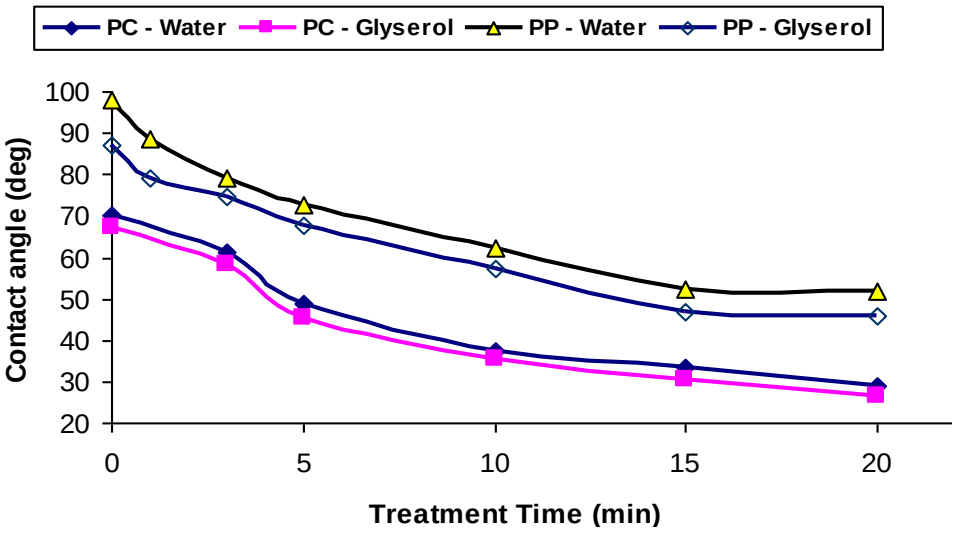

Figure 1. Contact angle variations in PP and PC films at different treatment time.

$$W_{adh} = \gamma_1 (1 + \cos\theta) \quad (4)$$

The surface polarity (P) of the plasma treated polymer films was estimated using the expression:

$$P = \gamma_s^p / (\gamma_s^p + \gamma_s^d) \quad (5)$$

Where γ_s (mJ/m^2) is the total surface energy of the polymer film and γ_s^p (mJ/m^2) and γ_s^d (mJ/m^2) are the polar and dispersion components of surface energy of the polymer film (Dumitrascu et al., 2005).

The surface morphology of PP and PC films were analyzed by AFM of model SPM Lab Version 1, Veeco di Caliber high value scanning probe microscope. The difference in root mean square (RMS) of the vertical Z-axis value, within the area of observation, was noted as the change in surface roughness of the plasma treated PP and PC films. The RMS can be calculated using the following equation (Selli et al., 2001):

$$RMS_{xy} = \left[\sum_{xy=1}^{N} ((Zxy - Z_{average})^2)/(N^2) \right]^{1/2} \quad (6)$$

where $Z_{average}$ is the average Z-axis value within the observed area, Z_{xy} is the local Z-axis value and N indicates the number of points observed. Every surface roughness value was calculated as the average of minimum 10 measurements, in the different areas of observation on PP and PC film surfaces.

XPS spectra for untreated and plasma treated PP and PC films were taken to estimate the variation in surface elemental composition (Seidel et al., 1999).

To study the effect of plasma treatment on adhesion, that is, to understand the effect of hydrophilic groups on bonding strength, a standard T-Peel strength test was carried out using constant rate of extension (CRE) tensile testing machine at a rate of 100 mm/min at room temperature. For the test, a transparent adhesive tape of 5 cm width was pasted over a length of 17 cm on the PP and PC films. T-Peel test was carried out after fixing one end of the sample in one jaw and the adhesive tape with a piece of paper adhered to it in another jaw. The bond strengths were reported as the force of peel per unit length of sample width (Clark and Feast, 1978; Ardeleana et al., 2005).

RESULTS AND DISCUSSION

Surface analysis: Contact angle and surface energy

The hydrophilic properties of plasma modified PP and PC films were analyzed by measuring contact angle. Figure 1 shows the change in contact angle of PP and PC films at different treatment times. The contact angle of untreated PP and PC films is 98 and 70.3°, respectively. After 20 min of treatment time, the contact angle decreases to 51.7 and 28.7° for PP and PC films. The decrease in contact angle of PC film is more as compared to PP film under same treatment condition. This decrease in contact angle shows that the polar functional groups on PC film increases and it becomes more hydrophilic. The contact angle value does not change significantly with longer exposure time and slightly smaller values are observed for treatment time of 20 min range.

The decrease in contact angle is related to the rate of chemical reaction taking place in the surface of the film. The adsorption characteristics of PP and PC film surfaces depend on adhesion work. It controls all the physical interfacial changes happening on the polymer surface. The work of adhesion and polarity for the plasma modified PP and PC film were calculated using Equations 5 and 6. The values are tabulated in Table 3.

From this we can note that when the treatment time increases, the W_{adh} and polarity of plasma modified PP and PC films were also increased. Figure 2 shows a plot of the surface energy γ_s from the measured contact angles on the PP and PC surfaces as a function of treatment time. From this study, we absorbed that the

Table 3. Work of adhesion and polarity.

Treatment time (min)	Polypropylene		Polycarbonate	
	W_{adh}	Polarity	W_{adh}	Polarity
0 (untreated)	62.67	0.1204	97.34	0.702
3	86.32	0.5838	107.87	0.752
5	94.33	0.5848	120.86	0.754
10	106.98	0.6536	130.79	0.800
15	117.42	0.6745	133.65	0.788
20	117.92	0.6648	136.66	0.802

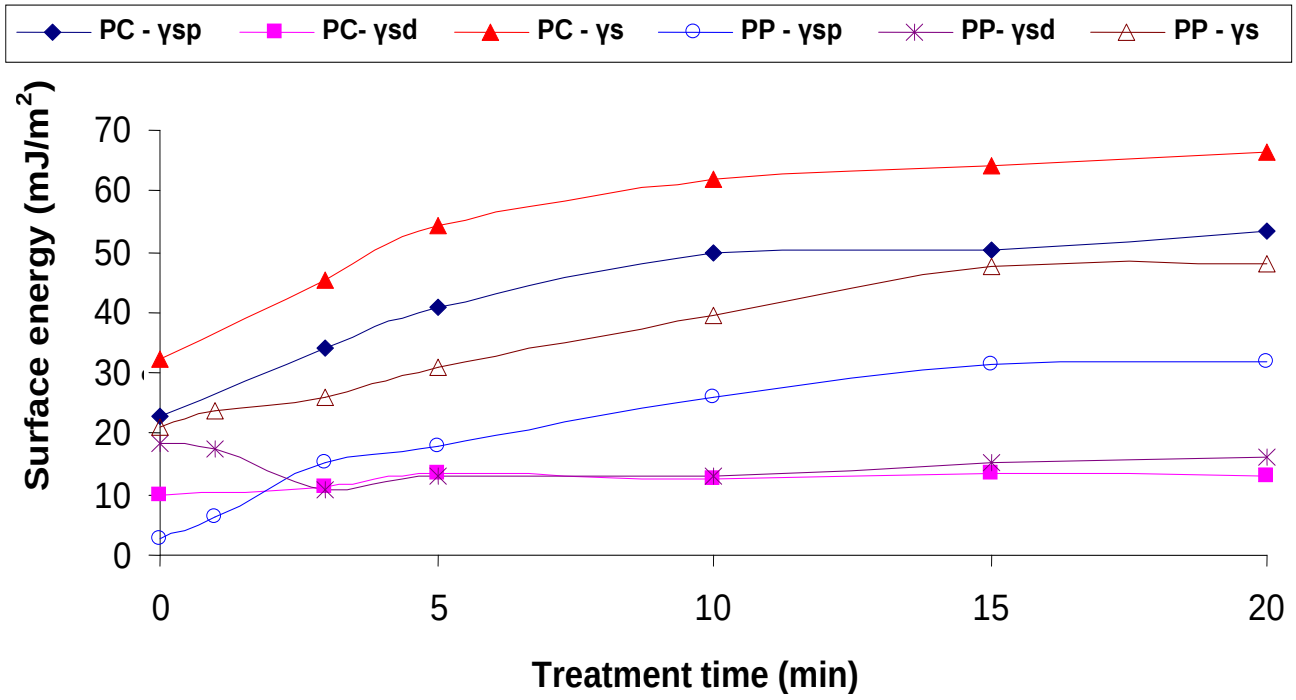

Figure 2. Surface energy variations in PP and PC films at different treatment time.

plasma generates radical species on the polymer surface. This species interact with oxygen from air and produce more polar groups on the polymer film surfaces. These polar groups make the polymer film surface become more hydrophilic. The atmospheric pressure plasma generates more surface roughness and improves the surface free energy of the polymer faster and higher than the low pressure plasma under similar treatment conditions (Shen and Hosuk, 2008).

The surface energy increased from 20.88 to 47.82 mJ/m^2 for PP film and 32.5 to 66.69 mJ/m^2 for PC film. Similarly, γ_s^p the polar components increased as the treatment time increases and it is mainly due to the formation of polar groups, such as, CO, COO, OH, etc., (Briggs et al., 1980; Westerdahi et al., 1974). The surface properties like wettability, adhesion, etc., strongly depend upon the surface energy.

Morphological analysis: AFM results

The change in surface morphology of PP and PC films was analyzed using AFM results. Figure 3a, b, c and d shows the AFM image of PP film as a function of different treatment time. Similarly, Figure 4a, b, c and d shows the AFM image of PC film as a function of different treatment time. Figures 3a and 4a show the surface of the untreated PP and PC films which is smooth as compared to plasma treated surfaces. Atmospheric air plasma treatment results in rough surfaces, but when argon gas is used, the surface will be the smoothest due to the result of relatively homogeneous etching process (Junekwon et al., 2006). The RMS of roughness of untreated and plasma treated PP and PC films for different time duration are as shown in the Figure 5. It is seen that the RMS value increases with increase in

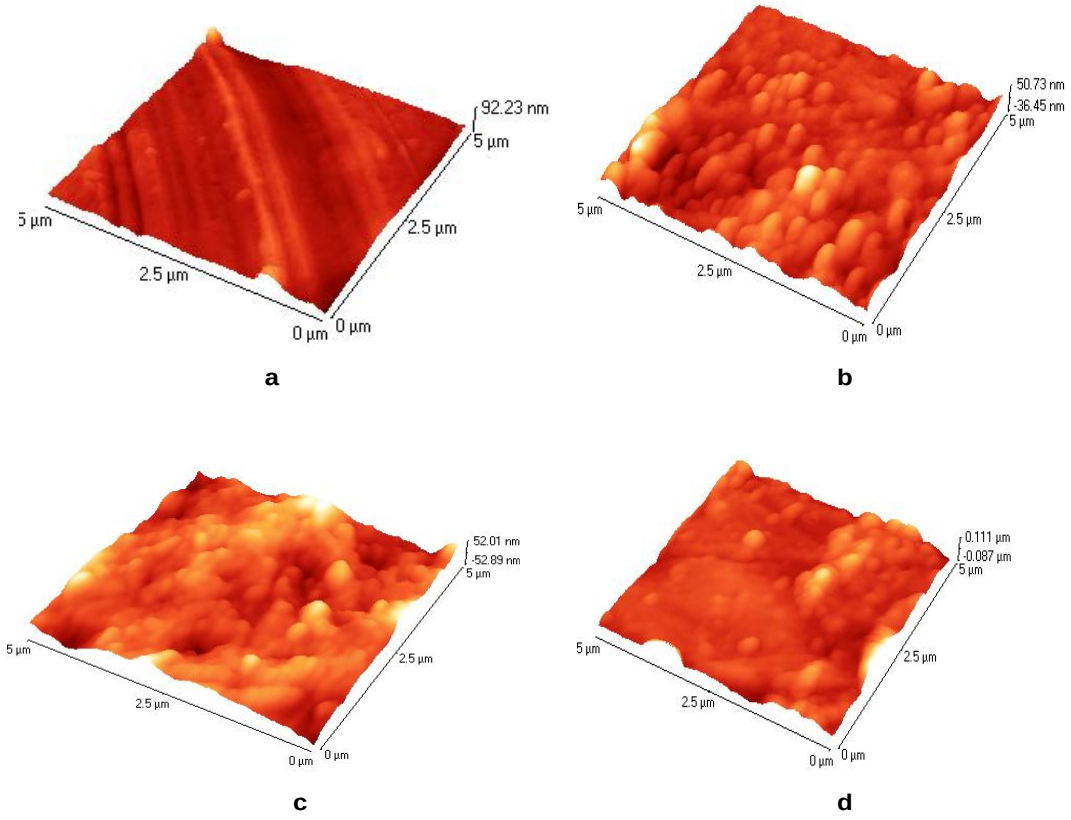

Figure 3. AFM image of (a) untreated, (b) 1 min treated, (c) 3 min treated and (d) 10 min treated PP films.

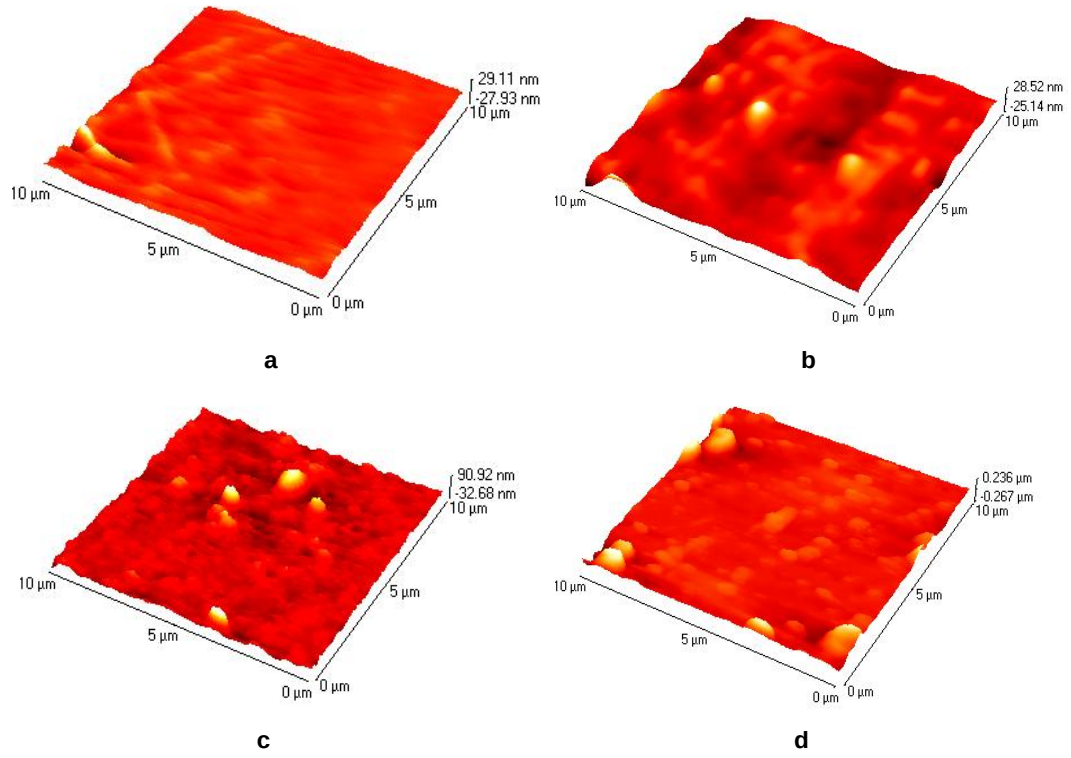

Figure 4. AFM image of (a) untreated, (b) 3 min treated, (c) 5 min treated and (d) 10 min treated PC films.

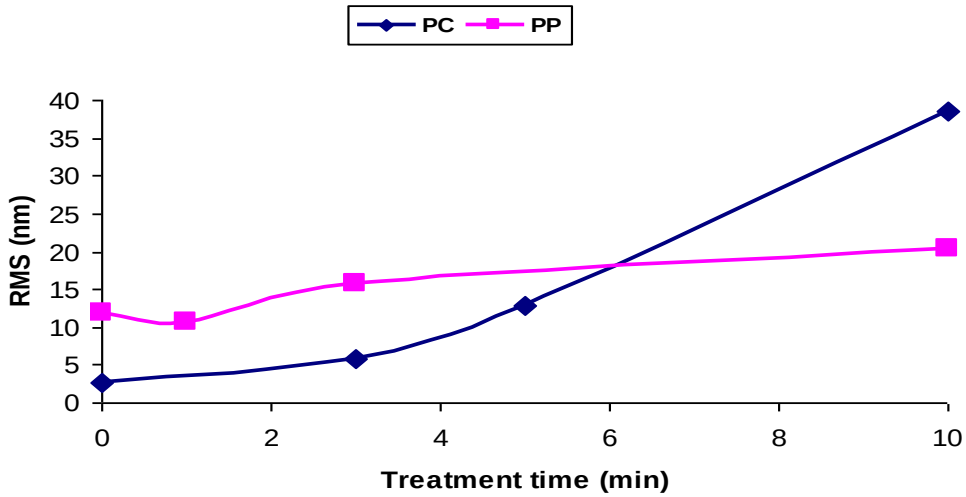

Figure 5. RMS variations for PP and PC films at different treatment time.

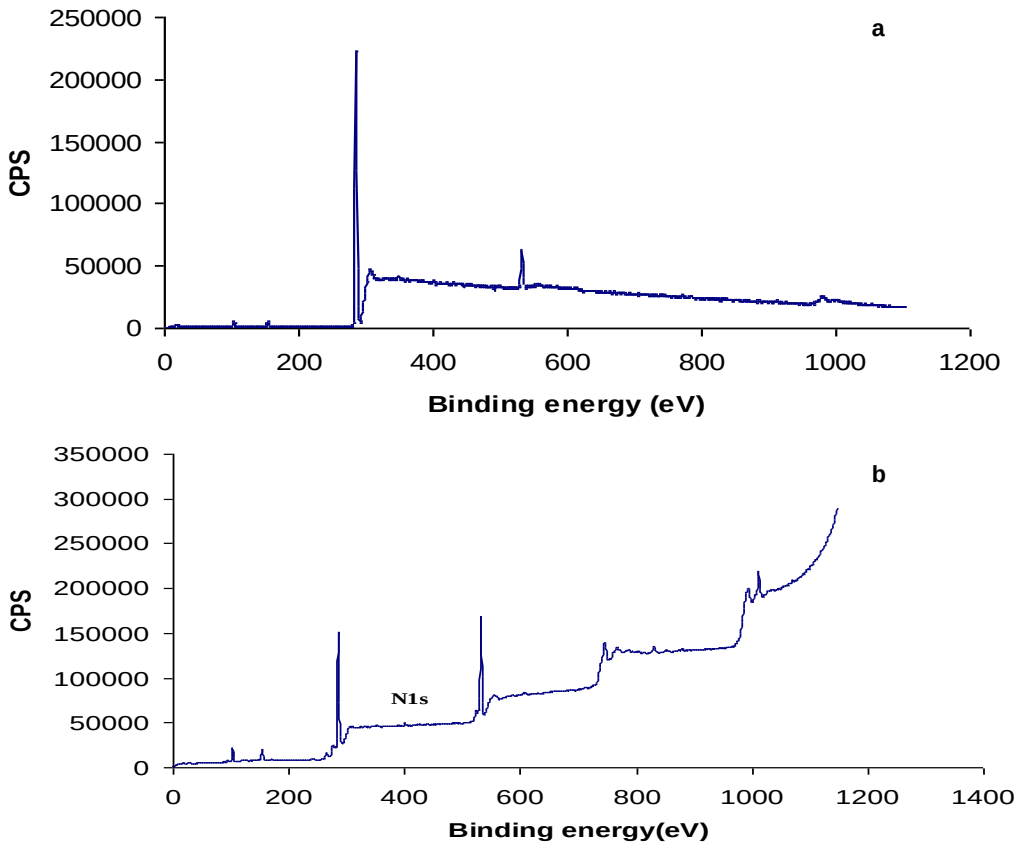

Figure 6. XPS spectrum of (a) untreated PP film and (b) plasma treated PP film.

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.

Chemical composition analysis: XPS results

The XPS spectrum of untreated and treated PP and PC films are shown in Figures 6a, b and 7. Plasma treatment

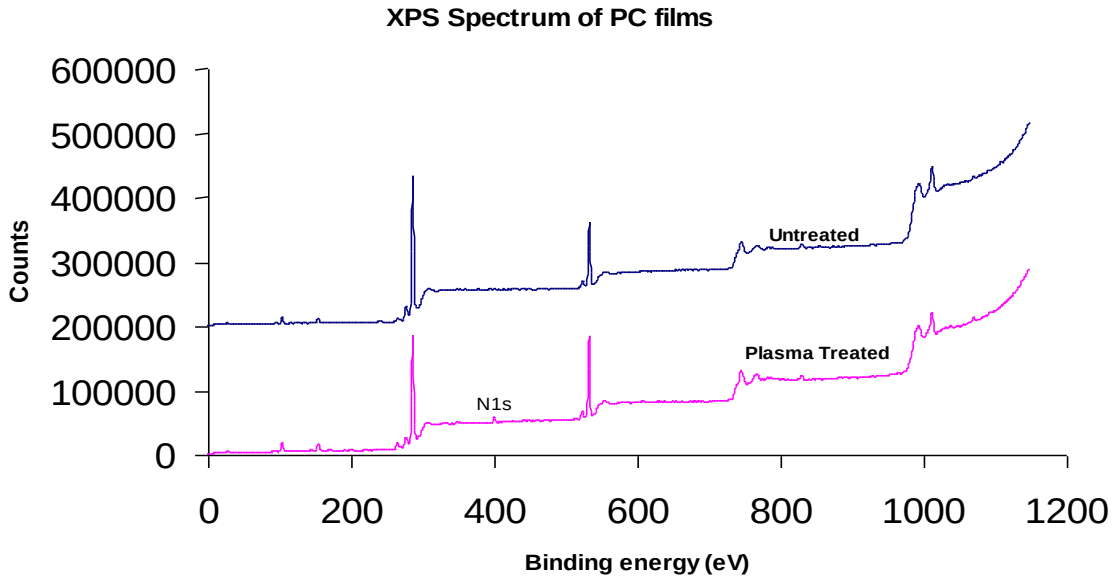

Figure 7. XPS spectrum of untreated and plasma treated PC film.

increases the intensity of O1s peaks in the surfaces of PP and PC films. Air plasma treatment introduces polar groups on polymer film surface, therefore O1s increases and C1s decreases. Introduction of polar groups is the main reason for the increase in hydrophilicity of polymer film surfaces. Air plasma treatment introduces N1s on the PP and PC film surfaces. It indicates the introduction of functional groups on the polymer film surfaces.

The result indicates that the sum of C-C/C-H bonds in the polymer surface may be broken due to plasma treatment and it is combined with oxygen atoms that are produced by the oxygen containing groups in the molecular chain of PP and PC surfaces (Besmson and Briggs, 1992). From this, we conclude that the oxygen containing polar groups plays an important role in decreasing the contact angle and increasing the surface energy, so that, the surface hydrophilicity increased on the polymer film surfaces.

Introduction of polar groups is the main reason for increasing hydrophilicity of polymer film surfaces. The spectra of C1s untreated PP film shows the presence of two peaks with binding energy of 284.80 and 286.40 eV for C-C/C-H and -C-O. The spectra of C1s of treated PP film shows the presence of additional peaks with binding energy of 287.5, 288.36 and 289.23 eV for C = O/O-C-O, O-C = O, O-CO– C.

The C1s are represented by three Gaussian functions which corresponds to the different bonding states of 284.5 eV aromatic C-H, 285.0 eV aliphatic C-H, C-C, 286.24 eV aromatic C-O correlated as shown in Figure 8.

The plasma treated PC films showed additional C1s peaks at 287.54 and 288.24 eV which may be due to C = O/O-C-O, O–C = O and O–CO–C groups, respectively (Wang and He, 2006; Inagaki et al., 2004). After plasma treatment, the C-C groups decrease, C-O and additional oxygen containing functional group increases with respect to treatment time as depicted in Figure 9a and b. These polar groups are responsible for the increase in surface hydrophilicity of the PC films.

Adhesion analysis

Both the plasma treated and untreated samples were tested to understand the effect of hydrophilic groups on bonding strength using T-peel test. For untreated PP and PC films, the peel strength was noted as 1 and 2 N/cm, respectively and for the 10 min plasma treated PP and PC films, the peel strength was 2 and 3 N/cm, respectively, which indicates the increase in bond strength due to plasma treatment. The plasma treatment of polymer surface is commonly believed to be effective because it creates wettable polar surfaces on which the adhesive may spread spontaneously and thus produce an extensive interfacial contact. The treatment of polymer film in a plasma environment incorporates hydrophilic groups, which contributes to the increase in wettability. As a result, the adhesion layer spreads on the surface more easily. Moreover, when these functionalities come in contact with adhesive material, it forms a weak bond due to Vander Waal's force. This force of attraction between the plasma treated polymer surface and adhesive material contributes to the observed increase in bonding strength. AFM images reveal the increase in surface roughness, and hence, there is increase in effective surface area due to plasma treatment. This observation shows the mechanical anchoring of adhesive on the surface of the PP and PC films (Navaneetha et

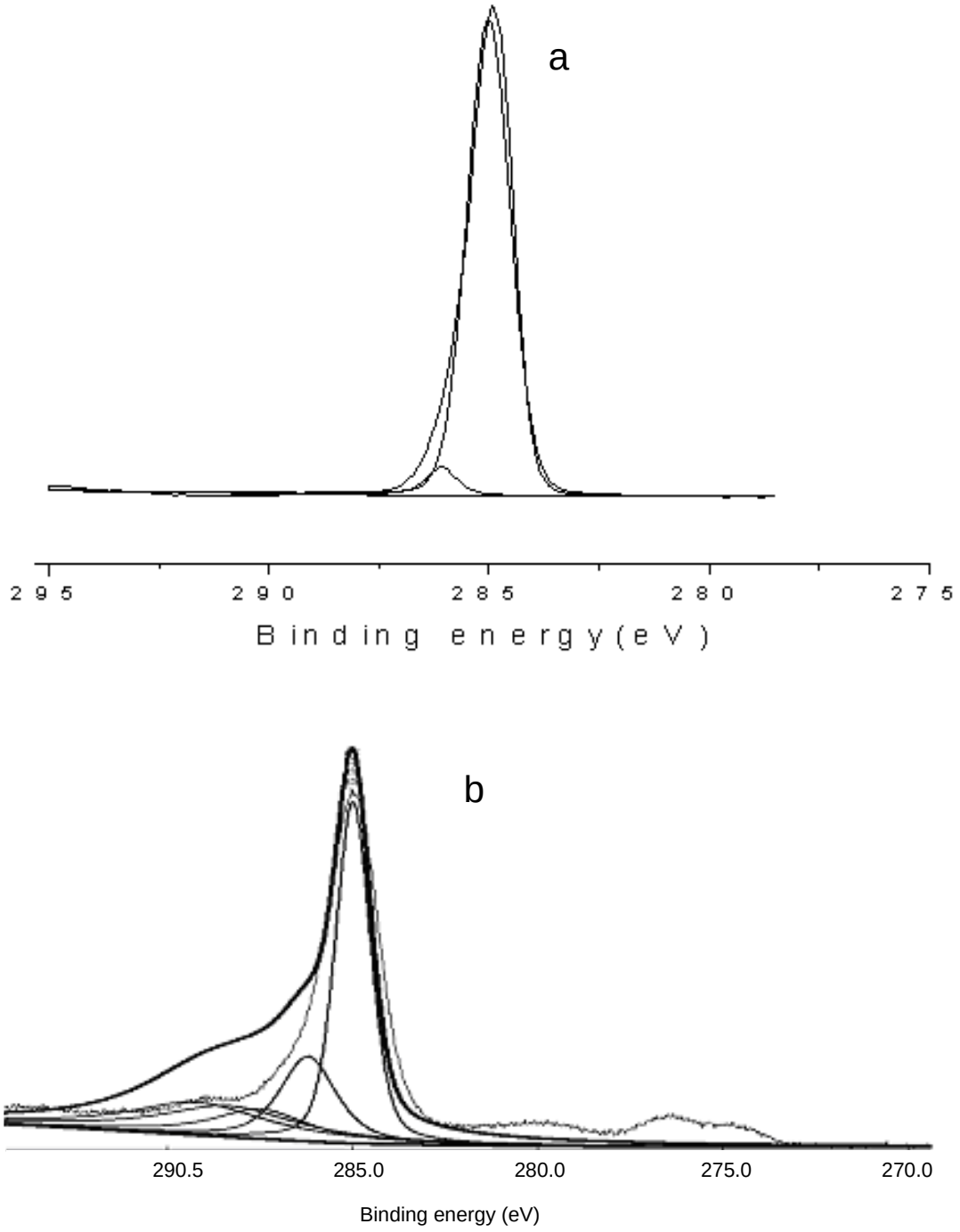

Figure 8. XPS spectra C1s peaks of (a) untreated PP film and (b) plasma treated PP film.

al., 2009).

Conclusion

A cold air plasma treatment has been used to modify the PP and PC film surfaces. It was found that the plasma treatment increased the adhesive properties of PP and PC film surfaces and made them suitable for technical application. The plasma treatment increases the polar functional groups on the surfaces of PP and PC film causing decrease in contact angle and increase in surface energy. AFM studies showed increase in roughness on PP and PC film surface. The XPS results detected polar functional groups onto the PP and PC films. The plasma treatment enhanced the bond strength

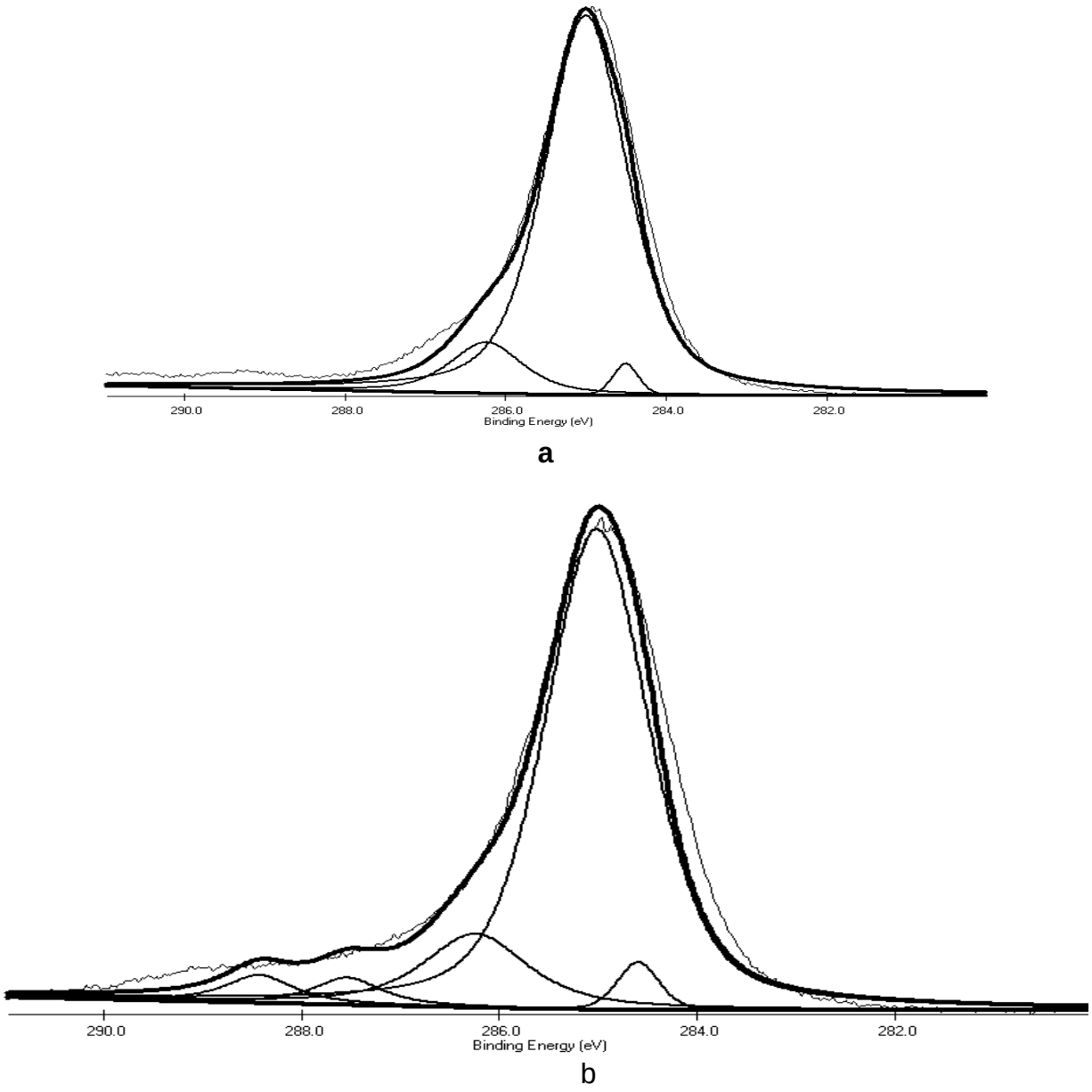

Figure 9. XPS Spectra of C1s peak of (a) untreated PC film and (b) plasma treated PC film.

of PP and PC film surfaces indicated by T-Peel strength test. This proves that adhesion can be improved by plasma treatment. All the changes in PP and PC film surface made them more hydrophilic.

ACKNOWLEDGEMENTS

The authors acknowledge with thanks Dr. P. Kulandaivel, Professor and Head, Department of Physics, Bharathiar University, Coimbatore for his kind support in carrying out this work. Sincere thanks are also to CECRI, Karaikudi for providing XPS analysis, DRDO-BU Coimbatore for AFM analysis and SGS India Private Ltd, Chennai for T peel strength test.

REFERENCES

Ardeleana H, Petib S, Lawrence, P, Marcusa P, Arefi- Khonsari F (2005). Effects of different laser and plasma treatments on the interface and adherence between evaporated aluminum and polyethylene terepthalate films: X ray photo emission and adhesion studies",Appl. Surface Sci., 243: 304-318.

Bag DS, Pradeep VK, Maiti S (1999). Chemical Modification of LDPE film. Chem. J. Appl. Polymer Sci., 71(7): 1041-1048.

Besmson G, Briggs D (1992). High resolution XPS of Organic Polymers", 'The Scienta ESCA 300 database,' John Wiley & Sons.

Bhat NV, Upadhyay O, Deshmukh RR, Gupta SK (2003). Investigation of plasma-induced photochemical reaction on a polypropylene surface", 'J. Phys. Chem. B., 107: 4550-4559.

Bhowmik S, Ghosh PK, Ray S (2001). Surface modification of HDPE and PP by mechanical polishing and DC glow discharge and their adhesive joining to steel, 'J. Appl. Polym. Sci., 80(8): 1140-1149.

Briggs D, Rance DG, Kendall CR, Blythe AR (1980). Surface modification of poly(ethylene terephthalate) by electrical discharge treatment', Polymer, 21: 895-900.

Clark DT, Feast WJ (Eds), (1978). Polymer Surfaces, John Wiley and sons, New York.

Deepak P Subedi, Lenka Zajickova, Vilma Bursikova, Jan Janca (2003). Surface modification of polycarbonate (bisphenol A) by low pressure RF plasma", 'Himalayan J. Sci., 1(2): 115-118.

Dumitrascu N, Topala I, Popa G (2005). Dielectric barrier discharge technique in improving wettability and adhesion properties of polymer surfaces", IEEE Trans, Plasma Sci, 33(5), 1710-1714.

Friedman M, Gerard W (2002). Review of new materials and trends", Polymer Eng. Sci., 42(8): 1756-1788.

Gavrilov NG, Yakusheva D, Kondyurin A (1998). Surface modification of plasma pretreated HDPE films by grate co-polymerization of adhesion improvement with evaporated copper", J. Appl. Polymer Sci., 69: 1071.

Inagaki N, Naushim K, Tuchida N, Miyazaki K (2004). Surface characteristics of plasma modified poly (ethylene terephthalate) film surfaces. J. Poly. Sci. Part: B, Polymer Phys., 42: 3727-3740.

Junekwon OH, Sung WM, Chang – Soo L, Choi SH (2006). Comparison of the surface characteristics of polypropylene films treated by Ar and mixed gas (Ar/O2) atmospheric pressure plasma", J. colloid Interface Sci., 295(2): 409-416.

Navaneetha PK, Selvarajan V, Deshmukh RR, Changyou G (2009). Modification of surface properties of polypropylene (PP) film using DC glow discharge plasma", J. Appl. Surf. Sci., 255: 3965-3971.

Rajesh D, Mark JK (2003). A model for plasma modification of polypropylene using atmospheric pressure discharges. J. Phys. D. Appl. Phys., 36: 666-685.

Richard MF, Robert DS (1997). Plasma treatment of polymers effects of energy transfer from an argon plasma on the surface chemistry of polystyrene, LDTE, PP and PET', J. Chem. Soc, Faraday Trans., 93(17): 3173-3178.

Sakthikumar D, Masayeri FujiOka, Kentaro Asano, Atsumu Shoji, Athipettah Jayakrishan, Yasuhike Yoshida, (2007). Surface modification of poly (ethylene terapthalate) by plasma polymerization of poly (ethylene glycol). J. Mater. Sci. Mater. Med., 18(9): 1831-1835.

Sanchis MR, Balanes V, Blanes M, Gracia D, Balart R (2006). Surface modification of low density polyethylene (LDPE) film by low pressure O_2 plasma treatment, 'Eur. Polymer J., 42(7): 1558-1568.

Seidel C, Kopf H, Gotsmann B, Vieth T, Fuchs H, Reihs K (1999). Argon plasma treated Al metalised polycarbonate: a XPS mass spectroscopy and SFM study, Appl. Surface Sci., 150:19-33.

Selli E, Mazzone G, Oliva C, Martin F, Riccardi C, Barini R, Marcandalli B, Massafra MR (2001). Characterization of poly (ethylene terephthalate) and cotton fibers after cold SF6 plasma treatment, J. Mater. Chem., 11: 1985-1991.

Sellin N, João Sinézio de, C. Campos (2003). Surface composition analysis of PP films treated by corona discharge, 'Mat. Res., 6: 163-166.

Shen T, Hosuk C (2008). Comparison of low and atmospheric pressure radio -frequency plasma treatment on the surface modification of poly (methyl metha crylate) paltes, J. Phys. Chem. C, 112(12): 4712-4718.

Subedi DP, Madhup DK, Adhikarai K, Joshi UM (2008). Physics of gases, plasmas and electrical discharges- low pressure plasma treatment for the enhancement of wettability of polycarbonate", Indian J. Pure Appl. Phys., 46: 540-544.

Vijayalakshmi KA, Mekala M, Yoganand CP, Pandiyaraj KN (2011). Studies on modification of surface properties in Polycarbonate (PC) film induced by DC glow discharge plasma. 'Int. J. Polymer Sci.,' Article ID 426057, p. 7 doi: 10.1155/2011/426057.

Wang C, He X (2006). Polypropylene surface modification model in atmospheric pressure dielectric barrier discharge. Suf. Coat. Tech., 201: 3377-3384.

Westerdahi CA, Hall JR, Schramn EC, Levi DW (1974). Gas plasma effects on polymer Surfaces. J. Colloid Interface Sci., 47: 610-620.