Evaluation of mechanism of non-thermal plasma effect on the surface of polypropylene films for enhancement of adhesive and hemo compatible properties

K. Navaneetha Pandiyaraj [a,*], R.R. Deshmukh [b], A. Arunkumar [a], M.C. Ramkumar [a], I. Ruzybayev [c], S. Ismat Shah [c], Pi-Guey Su [d], Mercy Halleluyah Periayah [e], A.S. Halim [e]

[a] Surface Engineering Laboratory, Department of Physics, Sri Shakthi Institute of Engineering and Technology, L&T by pass, Chinniyam Palayam (post), Coimbatore-641062, India
[b] Department of Physics, Institute of Chemical Technology, Matunga, Mumbai-400 019, India
[c] Department of Physics and Astronomy, Department of Materials Science and Engineering, University of Delaware, 208 Dupont Hall, Newark, United States
[d] Department of Chemistry, Chinese Culture University, Taipei 111, Taiwan
[e] School of Medical Sciences, Health Campus, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia

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ABSTRACT

The hydro-carbon based polymers have attracted attention of scientists for its use in bio-medical field as various implants due to inherent flexibility. However, they have poor surface properties; particularly they have low surface energy (SE). Hence, blood components (platelets, blood proteins, etc.)-polymer surface interaction is the major concern when it comes in contact with blood. Thus, surface modification is required to develop the perfect antithrombogenic property without affecting the materials bulk. The present study describes the improvement in adhesive and blood compatible properties of polypropylene (PP) by low temperature (non-thermal) plasma of various gases such as Ar, O_2, air and Ar + O_2 for biomedical applications. The changes in surface morphological, chemical and hydrophilic modification induced by the gaseous plasma treatment were analyzed by atomic force microscopy (AFM), X-ray photo electron spectroscopy (XPS), electron spin resonance (ESR) spectroscopy and contact angle measurements, respectively. Moreover, the stability of plasma effect was also studied for the different storage conditions. Variation in adhesive strength of the plasma treated PP film was studied by T-Peel and Lap-Shear strength tests. The blood compatibility of the surface modified PP films was investigated by *in vitro* analysis. It was found that gaseous plasma treatment improved the blood compatibility as well as adhesive strength of the PP films without affecting materials bulk which may be due to the significant morphological and chemical changes induced by the gaseous plasma treatment. Among the various gaseous plasma treatments, Ar + O_2 mixture has provided remarkable physico-chemical changes compared with other plasma treatments studied.

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1. Introduction

Polypropylene (PP) is one of the well-known versatile polymeric materials which have ample growth in miscellaneous industrial sectors like biomedical, automotive, food and textile industry, etc. due to its fabulous properties such as impact strength, chemical resistance, low cost, light weight, high thermal, chemical stability and so on [1–6]. Among the various fields of applications, the PP film play a vital role in biomedical industry which is extensively adopted in blood contacting devices such as hemodialysis components, blood vessels, heart valves, stents, blood bags, etc. [7,8]. The surface induced thrombus formation is a major problem of PP films when it comes in contact with blood, initiated by the adsorption of protein and activated platelets which may be due to the intrinsic properties of PP films (repeating unit of hydrocarbon) that probably leads to low surface energy and poor adhesion. Moreover, the interaction of PP surfaces with blood components such as plasma protein, platelets, etc. is considered to be establishing hemo-compatibility of PP films [9,10]. Hence the suitable surface properties of the material are the key factors in determining the hemo-compatibilty and also long term performance *in vivo* application. Owing to that designing of surface properties is intended. In the past few decades, various surface treatments such as wet chemical, UV irradiation, E-beam, and different types of plasma

* Corresponding author. Tel.: +91 9786452504 (mobile).
E-mail address: dr.knpr@gmail.com (K. Navaneetha Pandiyaraj).

treatment have been employed for surface modification of polymeric films with discriminating properties [11–16].

Among the various surface treatments, non-thermal plasma treatment is an attractive, effective and eco friendly approach to modify the surface properties of PP films without altering bulk properties because of involvement of active species such as ions, metastable radicals, photons and neutral atoms or molecules within plasma zone [17–21]. Various operating parameters which include power, duty cycle, pressure, flow rate, exposure time, reactor geometry, plasma gas, etc. have been used by the researchers to tailor the surface properties by plasma processing. Based on the plasma species; various concurrent processes occur on the material surfaces such as removal of surface contaminates or volatile products, etching of surface by the impact of plasma particles and change in surface energy by the creation of oxygen-containing entities such as carboxyl, carbonyl and hydroxyl groups through surface activation which may induce cross linking process [22–24]. On the other hand, the stability of the plasma surface treatment is one of the important issues. The changes obtained on the polymer surface are not permanent and can be lost with time, called as ageing effect. The instability (aging) is mainly caused by the reorientation of functional groups induced by the plasma treatment to their bulk which strongly depends upon the type of polymer, storage conditions, plasma gas, etc. [25,26]. Hence, major intention of this paper is to study the improvement of surface and biocompatible properties of the PP films through non-thermal gaseous plasmas and also investigate the influence of plasma forming gases on the surface properties of PP films for biomedical medical applications. In the present investigation, various plasma forming gases (O_2, air, Ar) and their mixture ($Ar + O_2$) have been used in establishing selective surface properties on the surface of PP films. The physicochemical changes obtained due to different gaseous plasma treatment on PP films were analyzed by various characterization techniques such as contact angle (CA), surface energy (SE), atomic force microscopy (AFM) and X-ray photo electron spectroscopy (XPS). Moreover, surface energy of the plasma treated PP films was estimated from contact angle data, which is very useful for the researchers dealing with surfaces and interfaces for various applications. Furthermore the durability of the plasma treated PP films was also investigated in different storage conditions. T-peel and Lap shear strength were used to investigate the adhesive strength of the PP films and also blood compatibility of the PP films were analyzed by *in vitro* tests.

2. Experimental

2.1. Materials

Low pressure plasma reactor was purchased from Hydro phenol Vac Technologies Bangalore, India. Polypropylene films having 80 μm thickness were kindly supplied by Reliance India Pvt Ltd., India. Other chemicals such as formamide, ethylene glycol, and acetone were obtained from MERCK, India. All blood proteins such as albumin and fibrinogen were purchased from Sigma, India.

2.2. Plasma treatment

The plasma surface treatment was carried out using direct current (DC) excited glow discharge plasma system. It consists of "D" type plasma chamber with a dimension of 30 cm W × 30 cm H. Plasma chamber made of stainless steel is breezed with copper tubing for water circulation to avoid the formation of excess amount of heat during the plasma treatment. Two circular (diameter = 10 cm) water cooled electrodes were fixed parallel to each other within the chamber as shown in Fig. 1a and the upper electrode is of

magnetron type, which is used to confine the plasma for homogeneous plasma surface treatment. The distance between the two electrodes was kept 5 cm. The plasma was generated between two horizontal electrodes using high tension dc power supply ($V_{max} = 3$ kV and $I_{max} = 1$ A). A circular sample holder and gas shower ring is placed in between the electrode (diameter 10 cm, 2 cm vertical distance to sample holder) (Fig. 1a). Hence the active plasma zone displays a cylindrical symmetry as shown in Fig. 1b. The gas inlet system enables gas mixing and flow control by electronic flow meter and mass flow controller (MFC). The pressure within the chamber was measured by pirani gauge. PP films having thickness 80 μm were cut in to 10 cm × 10 cm size and cleaned ultrasonically by acetone followed by distilled water to remove dust particles and organic contaminant adsorbed on the surface. Films were dried in air and kept in vacuum desiccators till further use. The chamber was initially evacuated to a low-pressure of $\sim 10^{-3}$ mbar using a rotary vacuum pump and purged three times by plasma processing gas ($Ar/O_2/air/Ar + O_2$). The working pressure inside the chamber was then adjusted and maintained at 0.2 mbar using MFC. A dc potential was applied between the two water cooled electrodes to generate a stable glow discharge plasma. Fig. 1b shows the glow regime of various plasmas during processing time. The samples were treated as a function of different gas atmosphere with a fixed potential, electrode separation, exposure time and pressure of 270 W, 5 cm, 10 min and 0.2 mbar, respectively. The typical operating parameters are listed in Table 1.

2.3. Characterization

2.3.1. Surface chemical compositional analysis

The changes in chemical states of PP films occurred due to the gaseous plasma treatment were analyzed using X-ray photoelectron spectroscopy (Omicron Surface Science Instruments with EAC2000-125 Energy Analyzer, Omicron Nano Technology GmbH, Limburger Strasse, Germany). Monochromatic AlKα X-rays (1486.7 eV) was employed. Typical operating conditions for the X-ray source were 400-μm nominal X-ray spot size (full width at half-maximum) at 15 kV, 8.9 mA and 124 W for both survey and high resolution spectra. The peak fitting and deconvolution of spectra was done using a combination of Gaussian and Lorentzian non-linear curve fittings with the help of XPSPEAK41 software.

2.3.2. Surface topographical analysis

The change in surface topography of PP films induced by the gaseous plasma was examined using atomic force microscopy by Seiko Instruments Scanning force microscopy (AFM, CSPM 4000, Ben-Yuan, China). The AFM was operated in tapping mode with horizontal and vertical resolution of 0.26 and 0.10 nm, respectively. The value of Ra and RMS is an average from five independent measurements on regions of 1 μm × 1 μm.

2.3.3. Radical analysis

The information about the free radicals on the surface of various gaseous plasma treated PP films was investigated by ESR Spectrometer (JES-FA200, JEOL, Japan) with X-band at room temperature. Plasma treated samples were stored in argon containing plastic pouches till ESR analysis.

2.3.4. Surface hydrophilic analysis

The surface hydrophilicity was analyzed by contact angle measurements using three different testing liquids such as distilled water (W), formamide (F) and ethylene glycol (EG) of known surface tension parameters (Table 2). The volume of the testing liquids was fixed at 2 μl and contact angle was measured using sessile drop
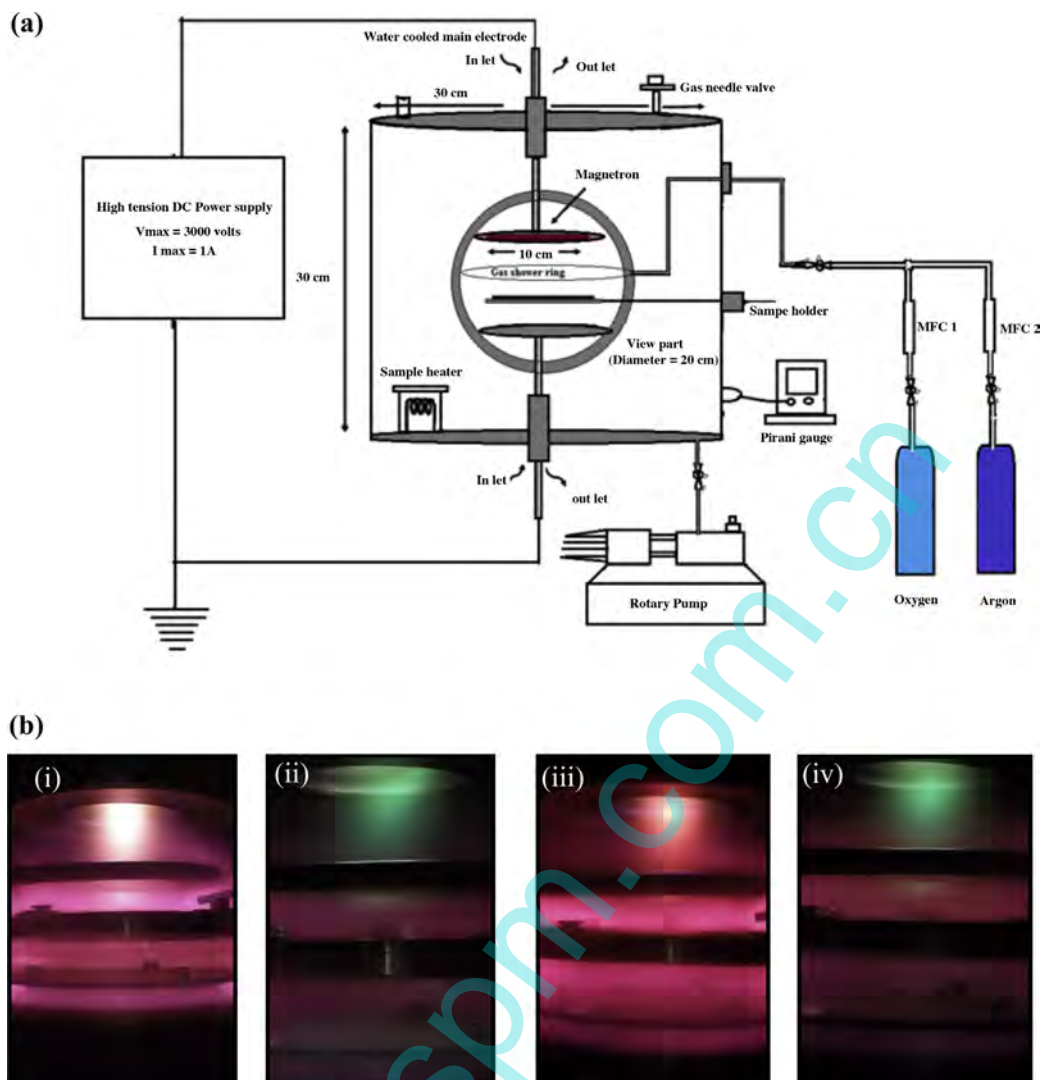
Fig. 1. (a) Schematic diagram of glow discharge plasma reactor and (b) glow discharge plasma during the surface treatment (i) Ar, (ii) O_2, (iii) air and (iv) Ar + O_2 plasma.

Table 1
Typical operating parameters for plasma processing.

Exposure time	10 min
Electrode separation	5 cm
Plasma gas	Ar, O_2, air, Ar + O_2
Pressure	0.2 mbar
Gas flow	Ar: 180 sccm, O_2: 30 sccm, air: 130 sccm and Ar + O_2: 130 + 20 sccm
Discharge potential	450 V
Discharge current	600 mA

method. The height (h) and the diameter ($2r$) of the spherical segment of the droplet was measured and contact angle was calculated using following equation [27].

$$\text{Contact angle} (\theta) = \sin^{-1} \left[\frac{2rh}{r^2 + h^2} \right] \qquad (1)$$

Table 2
Surface free energy components of the liquids.

Liquids	γ_l (mJ/m^2)	γ_l^p (mJ/m^2)	γ_l^d (mJ/m^2)
Water (W)	72.8	51.0	21.8
Formamide (F)	58.2	18.7	39.5
Ethylene glycol (EG)	48.0	19.0	29.0

where h and r are the height and radius of the spherical segment were measured. Ten readings were taken for each liquid to minimize the experimental error and was found to be ±2°. The relative humidity and temperature during the measurement was 55% and 27 °C, respectively. Furthermore, the samples were stored in air and distilled water up to thirty days to check the stability of plasma treatment by contact angle analysis.

2.3.5. Evaluation of surface energy

Evaluation of surface free energy of solid material is essential in the various fields of science and technology, especially in biomedical field. The existence of unbalanced inter molecular force among the molecules at the interface is the basis of surface free energy (also called as solid surface energy). However, the quantitative measurement of force at the interface is the most significant problem. The solid surface energy is one of the significant thermodynamical quantity; governing many processes in various technological applications. Moreover, the surface free energy of solid phase cannot be estimated directly due to lack of surface mobility at solid surface unlike liquids.

Fowke's proposed that the several independent components such as polar, dispersion, hydrogen bonding, acid–base, etc. components are needed to determine the quantity of γ_{sl} which is mainly based on the properties of testing liquids and solid surfaces.

According Fowke's, the solid surface energy can be considered as the sum of two major components such as polar and dispersion components, Hence,

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad (2)$$

where the superscript d and p represents the dispersion and polar contribution of the total surface energy. The polar component is the sum of various factors as,

$$\gamma_s^p = \gamma_s^h + \gamma_s^i + \gamma_s^{ab} + \gamma_s^o \qquad (3)$$

where γ_s^d, γ_s^p, γ_s^h, γ_s^i, γ_s^{ab} and γ_s^o are dispersion, polar, hydrogen bonding, induction, acid–base and other components of solid surface energy, respectively.

In order to determine the surface free energy of a solid by Fowke's method one need to measure contact angle values using minimum three testing liquids of known values of polar and dispersion components (Table 2). This approach is also called as multiple liquid method. More the number of test liquids used; better is the accuracy, hence this method is preferred.

Fowke's equation was extended by Owens and Wendt to evaluate the total surface energy (γ_s) and its components such as γ_s^p and γ_s^d of a solid surface (polymeric film in our case) as follows [28–31]

$$\left[\frac{1 + \cos\ \theta}{2} \right] \times \left[\frac{\gamma_l}{\sqrt{\gamma_l^d}} \right] = \sqrt{\gamma_s^p} \times \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \qquad (4)$$

The above equation is one of the accurate methods to evaluate the solid surface energy of materials which involve the use of more than two testing liquids.

The equation (4) is in the form of $Y\,(\text{LHS}) = mX\,(\text{RHS}) + C$ \qquad (5)

The plot of LHS vs RHS gave a straight line with intercept on Y-axis. Slope and intercept obtained from the plot were squared and added up to get the total surface energy. The results obtained by the above equations are highly reliable and it is based on the geometric mean approach. The added advantage of this method is that it gives polar and dispersion components of the total surface energy.

2.3.6. Adhesive strength analysis

A T-Peel and Lap shear strength (with a slight modification in ASTM D 1876 and ASTM D 1002, respectively) tests were carried out to evaluate the adhesive strength of PP films using LLOYED's Universal Testing Machine (UTM) (Model LR-10K Plus, Steyning Way, West Sussex, UK) at a rate of 100 mm/min at room temperature. Since there was a slight difference (from ASTM) in the dimensions of these joints, the details are given below for readers. For T-Peel test, a scotch tape (BOPP adhesive tape, Make: Amartara, purchased from local market) of width 2.5 cm was stuck over a length of 4.0 cm on the PP film. T-Peel test was carried out after fixing one end [Sample] in one jaw and the scotch tape end with a piece of paper adhered to it in another jaw. T-peel strengths are reported as force of peel per centimetre (N/m) of sample width (the width of the sample was 2.5 cm). Similarly lap shear joint was prepared using a double sided adhesive tape and the area of the joint was 10 cm². The strength of the lap shear joint is expressed in a unit of N/cm². While preparing these joints, a care was taken to see that there were no air gaps or wrinkles and was kept under pressure of 1.0 kg for 10 min. Three samples were prepared for T-peel strength and Lap shear measurement and the mean values are reported here.

2.3.7. Hemo-compatible analysis

Platelet-rich plasma (PRP) was prepared by collecting human blood in plastic syringes containing anticoagulation agents. The blood was centrifuged at 1300 rpm for 10 min at 4 °C and the supernatant was collected. Small coupons of the polymer films (15 mm
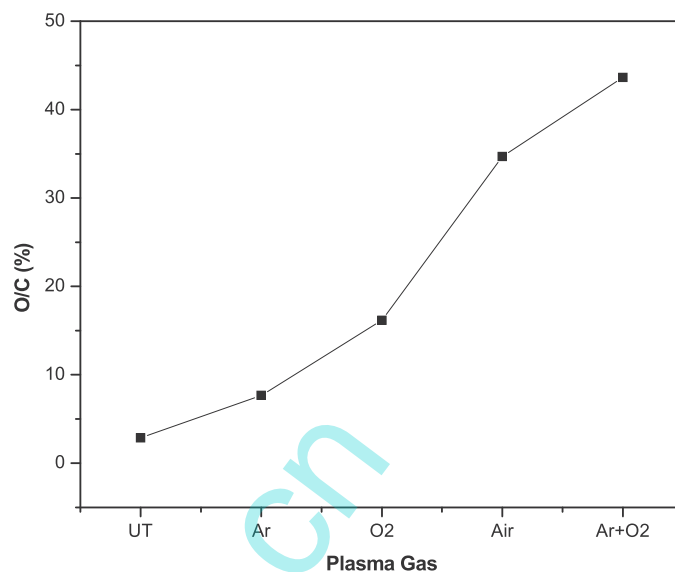

Fig. 2. O/C ratio of plasma treated PP film as a function of processing gases.

in diameter) were prepared with a punch and washed with phosphate buffered saline (PBS) for 24 h and placed at the bottom of the wells of a multiwall tissue culture plate; the PBS solution was removed from the multiwall tissue culture plate by pipetting. PRP (1 ml) was then seeded and incubated at 37 °C for 30 min [32,33].

After incubation, the coupons were recovered and rinsed three times with PBS to remove any weakly adsorbed platelets. After fixation in 2.5% glutaraldehyde PBS solution, the morphology of the adsorbed platelets was observed using a scanning electron microscope (FEI-QUANTA FEG 450, Netherlands). Human albumin and fibrinogen were used to study the adsorption behavior of proteins on the film surfaces. Polymer coupons were immersed in 1 mg/ml protein solutions in phosphate-buffered saline (PBS, pH 7.3–7.4) at 37 °C for 1 h. These coupons were then recovered, and changes in the protein concentrations of the solution were determined using a UV-spectrophotometer (at 280 nm) (Varioskan Flash, version: 4.00.53, U.S). In addition, the four different points were selected on the surface of PP films to calculate the quantity of adhered platelets which provided a good statistical average value of the adhered platelets on the surface of PP films as described by the procedure given by J. Wang et al. [34].

3. Results and discussion

3.1. Chemical composition analysis: XPS results

The information about the oxidation level on the surface of gaseous plasma treated PP films is elucidated by XPS analysis; which is one of the important key factors in determining the hydrophilicity of the materials. Fig. 2 depicts the ratio of O1s/C1s components of the untreated and plasma treated PP films; which reveals that the percentage of O/C ratio of the untreated PP film is just 2.88%. As such PP does not contain any oxygen atom; the trace amount of oxygen present on the surface is probably due to the oxygen adsorbed from the atmosphere. After argon plasma treatment, it increased slightly to 7.68%. Argon is an inert gas therefore argon plasma does not create any functional groups, it causes only bond breaking and chain scission, thus creating free radicals onto the polymer surface. However, when such a surface is exposed to the atmosphere after the plasma treatment, the oxygen present in the atmosphere interacts with these free radicals and oxygen moieties are formed. Obviously, when the PP films were treated in the oxygen containing plasma (O_2, Air and $O_2 + Ar$), the significant

increase in O/C ratio was observed. The increase in the percentage of O/C is in the order of Ar < O_2 < Air < Ar + O_2. Ar + O_2 plasma incorporate higher density of oxygen moieties on the surface of PP films and maximum value of O/C ratio (~43%) was obtained for 10 min Ar + O_2 plasma treated PP film. Moreover, very small amount (N/C ratio 1.78%) of nitrogen was detected on the surface of PP film when treated by air plasma; which suggest the occurrence of both

oxidation and nitrogenation on the air plasma treated surfaces. The incorporation of oxygen and nitrogen containing functional groups may be the main reason for the improvement of hydrophilicity as well as biocompatibility.

To have scrupulous information about the formation oxygen containing polar functional groups on the surface of gaseous plasma treated PP films, deconvolution of C1s core level spectra's were
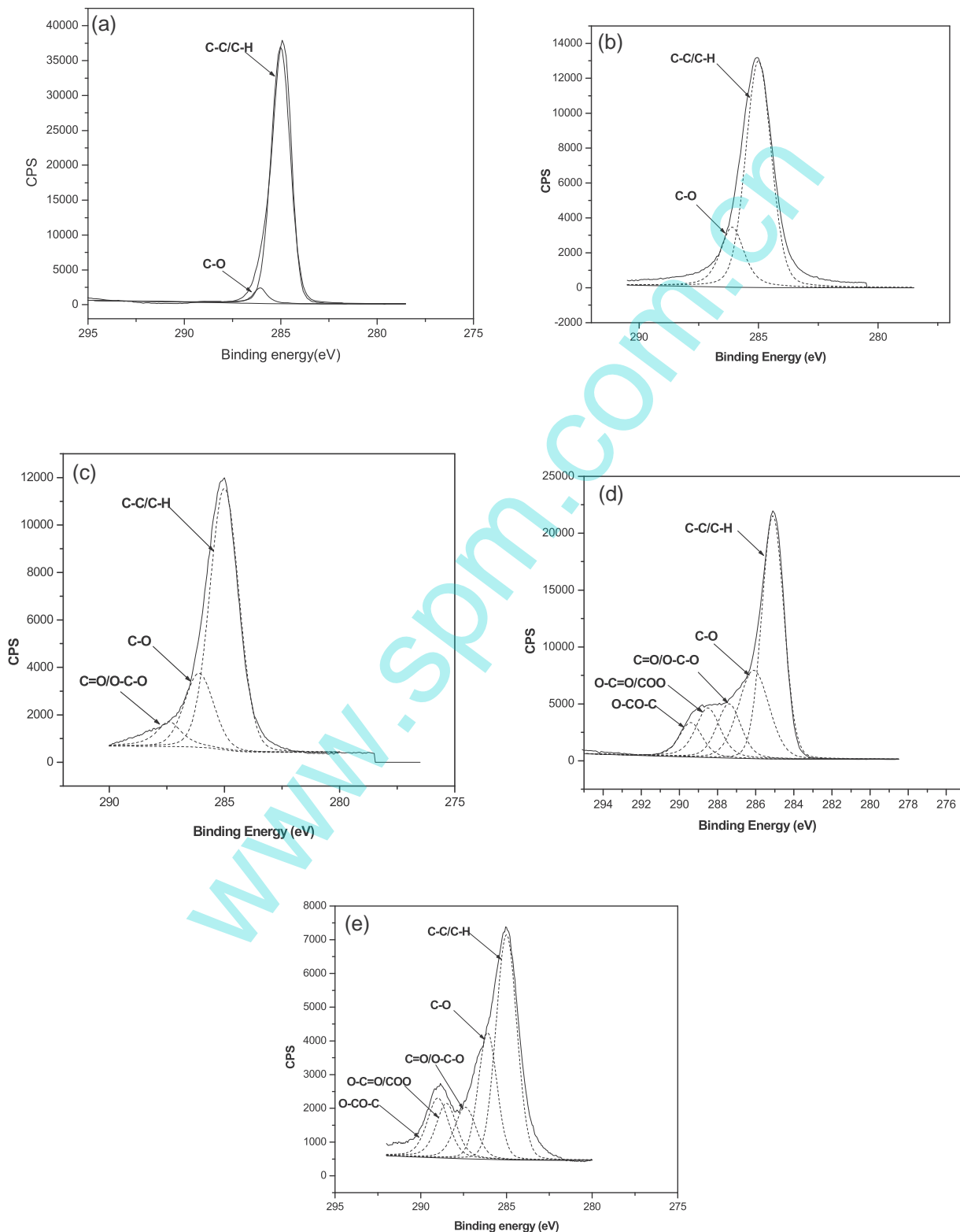
Fig. 3. C1s core level XPS spectra of (a) untreated, (b) Ar, (c) O_2, (d) Air and (e) Ar + O_2 plasma treated PP films.

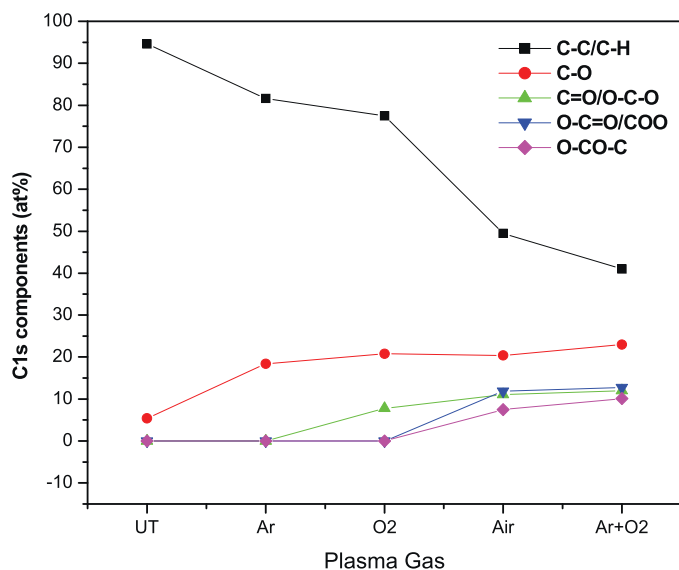**Fig. 4.** Quantitative investigation of C1s components of gaseous plasma treated PP films.

Fig. 5. ESR spectra of the plasma treated PP film as a function of processing gases.

fitted using Gaussian-Lorentzian non-linear curve fits. It was found that the surface of untreated PP films exhibited two peaks at 285 eV attributed to C–C/C–H bonds and a very small peak at 286.1 eV attributed to C–O due to adsorbed oxygen from the surrounding (Fig. 3**a**). After argon plasma treatment, intensity of C–O increased slightly whereas a slight decrease in C–C components on the surface was observed (Fig. 3**b**). Otherwise no significant functional change could be produced by the argon plasma as discussed earlier. Moreover, one more additional peaks was found at the 288 eV which can be attributed to C═O/O–C–O on the surface of oxygen plasma treated PP films. The intensity of the C–O was found to be increased with decrease in C–C components (Fig. 3**c**). Furthermore, for air as well as Ar + O₂ plasma treatment, two additional peaks at 288.5 eV and 289.4 eV were observed. These peaks can be attributed to O–C═O/COO and O–CO–C [35–37] (Fig. 3**d**–**e**). Fig. 4 shows the relative percentage contribution of C1s components of the gaseous plasma treated PP estimated from the C1s core level spectra.

It can be seen that the major contribution (>95%) of C1s component of untreated PP film surface exhibited C–C which decreased gradually with respect to gaseous plasma treatment in the order of UT < Ar < O₂ < Air < Ar + O₂, while the concentration polar function groups such as C–O, C═O/O–C–O, O–CO–C increased in the same order of gaseous plasma treatment as shown in Fig. 4. The above changes may be attributed to argon plasma treatment which produces enormous amount of free radicals on the surface of PP film through breaking of hydrogen bonds in the polymer network. However, feeble amount of C–O groups are formed on the surface of PP film by the interaction of free radicals with oxygen species in the environment when exposed in air. In contrast, the mechanism of oxygen containing plasma effect differ exclusively from argon plasma treatment because oxygen plasma produces polar functional groups onto the surface without creation of much cross linked network which mean *in situ* surface oxidation arises on the surface of PP films [37,38]. Furthermore, formation of polar functional groups on the surface of PP films by oxygen containing argon plasma (O₂ + Ar) has involved different simultaneous processes which include both the cross linking and the surface oxidation. In this processes plasma particles are initially able to interact with the polymer surface which break the hydrogen bond and creates carbon radials on the surface and it is immediately reacted with neighboring polymer chain. Due to the interaction between the two carbon radicals from the adjacent chains, cross linked
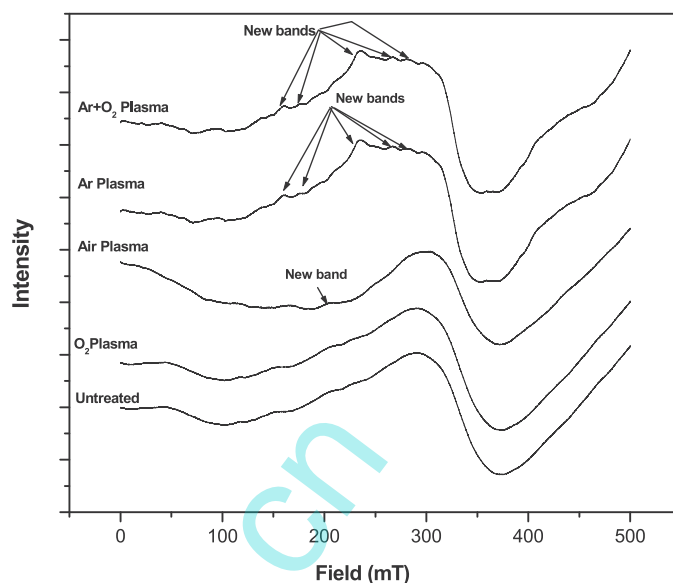
network is formed onto the PP film surface. At the same time, the free radicals also interact with oxygen atoms in the plasma leading to the formation of high dense of oxygen containing polar functional groups such as C–O, C═O/O–C–O, O–C═O/COO and O–CO–C on the polymer surface. Based on the above mechanism, Ar + O₂ plasma treatment yield high dense of polar functional groups on the PP film surfaces [39]. In addition, similar mechanism occurred on the air plasma treated PP film surfaces. However, different oxygen and nitrogen species (NO, NO₂, N₂O) and charged species (NO⁺, O₂⁺, O⁺) are involved to produce more amounts of polar functional groups on the surface of PP films during the air plasma treatment. Thus, our results clearly suggest the formation of polar functional groups such as C–O, C═O/O–C–O, O–C═O/COO, O–CO–C mainly depends upon the plasma forming gases. Air and Ar + O₂ plasma treatment creates high dense of functional groups on the PP film surface compared with other plasma treatments [37,40].

3.2. Radical analysis: ESR results

Electron spin resonance spectra (ESR) was employed to investigate the formation of free radicals on the surface of gaseous plasma treated PP films and is shown in Fig. 5. It clearly exhibits that there is no evidence for presence of paramagnetic species induced by the formation of radicals on the untreated, O₂ and air plasma treated PP films (Fig. 5). However presence of very weak signal was found when PP films were treated in air plasma. In contrast, Ar and Ar + O₂ plasma treated samples found that there are different new signals which are caused by the appearance of free radical on the surface of PP films. The above results clearly revealed that the occurrence of free radical are mainly due to abstraction (breaking) of C–C and C–H bonds by argon and oxygen plasma particles [41–44]. The radials produced by plasma particles are able to interact with oxygen species in the plasma regime or oxygen in air, results in the formation of oxygen containing polar functional groups. The above results are in good agreement with XPS results.

3.3. Morphological analysis: AFM results

Owing to the strong bombardment of plasma particles such as ions, electrons, and energetic species of neutral atoms and molecules on the surface causes the prompt removal of low molecular contaminant, processing aids and adsorbed species. This is called
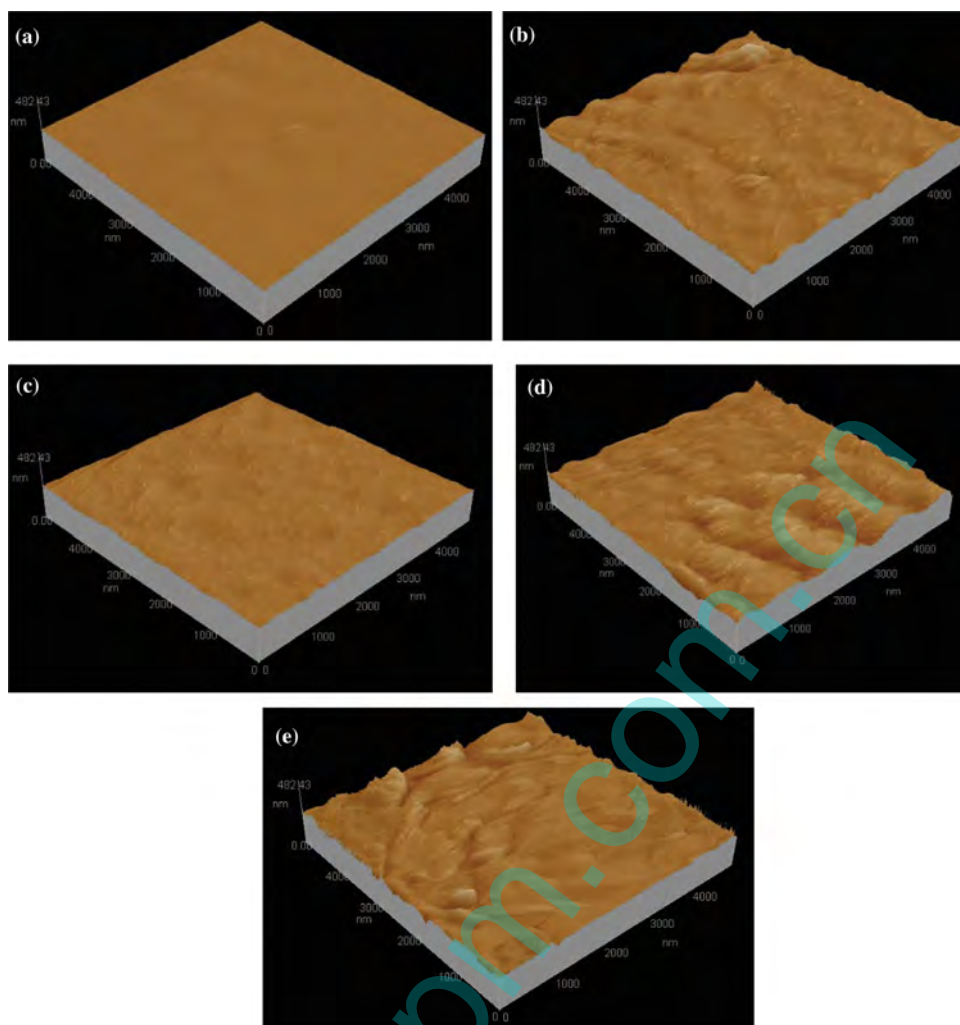
Fig. 6. AFM images of gaseous plasma treated PP film films (a) Untreated, (b) Ar, (c) O$_2$, (d) air and (e) Ar + O$_2$ plasma.

as plasma cleaning. After the plasma cleaning, breaking of bonds, chain scission, ablation and etching occurs. This results in the rougher morphology which in turn increases an effective area. The change in roughness induced by the plasma treatment might affect the surface properties by simple physical adsorption and/or by diffusion in various mechanical interlocking [45–48]. The etching process mainly depends upon the type of plasma forming gas. The extent of surface modification/roughness due to gaseous plasma treatment on PP films was examined by atomic force microscopy as shown in Fig. 6. PP films have smooth and uniform surface morphology as shown in Fig. 6**a**. Argon plasma treatment is known to cause surface roughness due to the collision of heavy ion bombardment resulting in surface etching as shown in Fig. 6**b**. However, the surface of the oxygen plasma treated PP films reveals the moderate surface morphology i.e. relatively smooth compared with argon plasma treatment which may be attributed to the reactiveness of O$_2$ plasma treatment which leads to the incorporation of oxygen containing polar functional groups onto the surface of the PP films (Fig. 6**c**). Furthermore, the combined effect of the mixture of gases (air and Ar + O$_2$) was observed. Thus the surface roughness caused by air and Ar + O$_2$ plasma treatment on PP film is more as compared to pure gases (Fig. 6**d**–**e**). It is evident from XPS study that plasma of gaseous mixture incorporates more functional groups than that of their pure counterpart gases. Thus it is advisable to use mixture of gases to get more pounced effect of the plasma treatment.

Fig. 7 shows that the values of Ra and RMS of the untreated PP film are 1.85 and 2.35 nm, respectively which increases in the following order UT < O$_2$ < Ar < Air < Ar + O$_2$ of plasma treatment. Hence the obtained results clearly revealed that Ar + O$_2$ plasma treatment is more efficient than other gaseous plasmas to promote an increase of the Ra and RMS surface roughness that may be attributed to the dependence of the process on the dimensions of the bombarding ions [45,46].

3.4. Hydrophilic analysis: contact angle results

The susceptibility to molecular interaction between polypropylene surface and liquid phase can be determined by contact angle analysis. It is one of the direct methods to investigate the hydrophilicity/hydrophobicity of materials which also provides the information about the high degree of sensitivity about the upper most layers of the solid–air interface. The influence of plasma forming gases on change in contact angle of different probe liquids with respect to PP films is depicted in Fig. 8. The higher values of contact angles such as 92.26° for distilled water, 87.34° for formamide and 83.45° for ethylene glycol indicate that the PP is hydrophobic in nature due low surface free energy. There is a slight decrease in the values of contact angles for argon plasma treated samples, which is due to the increase in effective area of contact and post plasma exposure of samples to the oxygen present in the
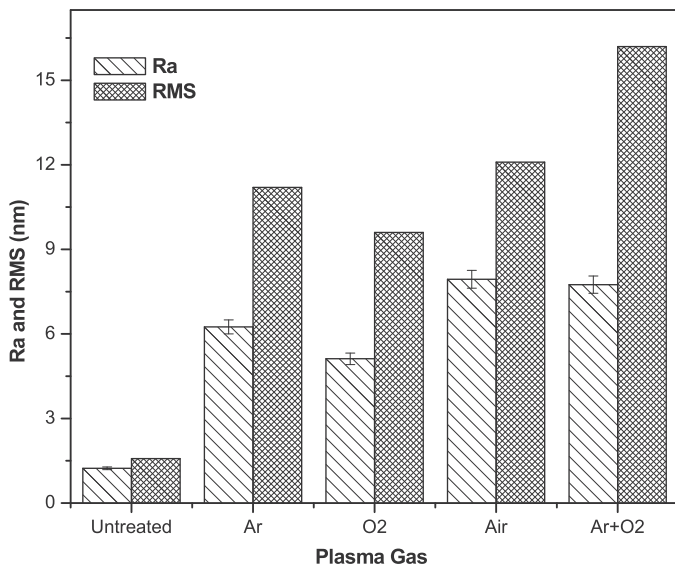
Fig. 7. Quantitative value of Ra and RMS of the PP films as a function of plasma forming gases.

Fig. 9. Estimation of surface free energy of the gaseous plasma treated PP film.

atmosphere. The substantial decrease in the contact angle values was observed for oxygen containing gaseous (O_2, air and $O_2 + Ar$) plasma treated samples as shown in Fig. 8. The changes in contact angle value of the PP film by plasma treatment clearly reveal the alteration of hydrophobic nature of the PP films to hydrophilic one as compared with untreated one. The modifications of surface chemistry of PP film play a significant role to improve hydrophilicity because the strong intermolecular interaction between the surface and liquid phase regulate the wetting properties of the materials rather than bulk. The introduction of polar functional groups on PP films surface by plasma treatment have greatly enhanced the intermolecular interaction, resulting in decrease in the contact angle values. The results exhibited that the change in hydrophilicity of the materials is not related to the material bulk, but depends on polar functional groups such as OH, COO, C=O, etc. on the surface of polymeric films; which increased to higher extent when material surfaces are exposed to the plasma [49–52].
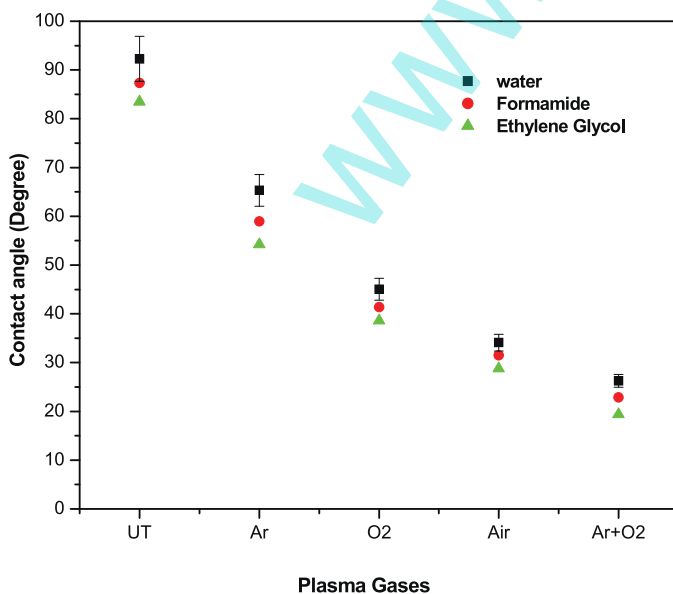

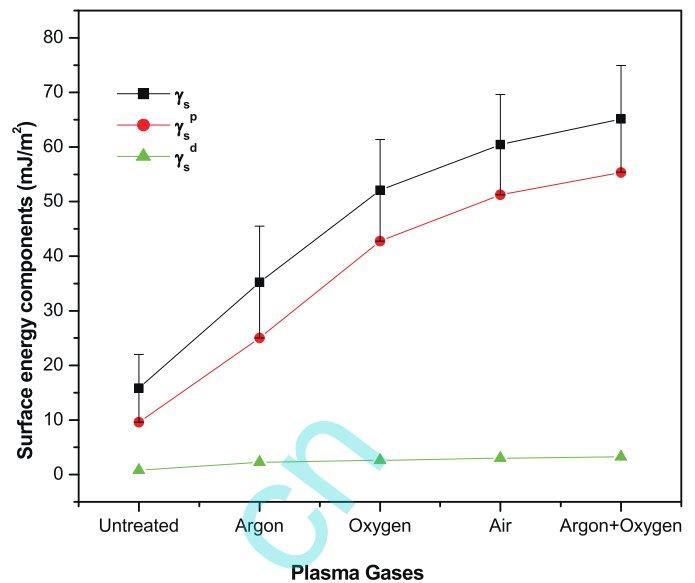**Fig. 8.** Contact angle of the gaseous plasma treated PP film.

Thus, contact angle values clearly indicate that the plasma surface treatment improves the hydrophilicity of the PP films.

3.5. Surface energy and its stability

The surface free energy is one the prominent factors to determine the hydrophilic properties of the plasma treated PP films which influence various surface related properties such as adsorption, wetting and adhesion. The change in surface free energy of the PP films by various gaseous plasma treatments is illustrated in Fig. 9. The surface free energy of PP films was calculated by Fowke's approximation method which provides total surface free energy components in terms of polar and dispersion (non-polar) forces. The polar contribution is mainly due to intermolecular forces (e.g., dipole–dipole interactions, hydrogen bonding, etc.) causes an increase in total surface free energy of the PP films. Hence, we believe that the Fowke's method is more useful as it gives us information that the increase in total surface energy is essentially due to the increase in polar components. Secondly, this method requires use of more than two liquids and the results are obtained from graph; thus minimizing error involved in the measurement of contact angle values. Fig. 10 clearly revealed that the surface energy of PP films was found to increase from 15.81 mJ/m^2 of untreated PP to various gaseous plasma treatments. The increase in surface energy of PP films was found in the following order UT < Ar < O_2 < Air < Ar + O_2. However, there is a marginal change in the values of the non-polar (dispersion) components with respect to plasma forming gases. The above surface energy results clearly describe least improvement in surface energy when PP film was subjected to Ar plasma treatment compared with other reactive plasma's such O_2, Air, O_2+, Ar. Oxygen containing plasma incorporates polar functional groups such as CO, COO etc as evident from XPS study. Inert/non-reactive gas (argon) plasma causes bond breaking and etching of the surfaces. The combined effect of reactive and non-reactive gaseous plasma may lead to the formation of cross-linked network through the free radicals. The cross-linked network resist the re-orientation of polar functional groups and thus ageing effect on such films is minimal. Finally, we conclude that the incorporation of high density of polar functional group and marked morphological change induced by the gaseous plasma treatment on the surface of PP films can facilitate to improve the
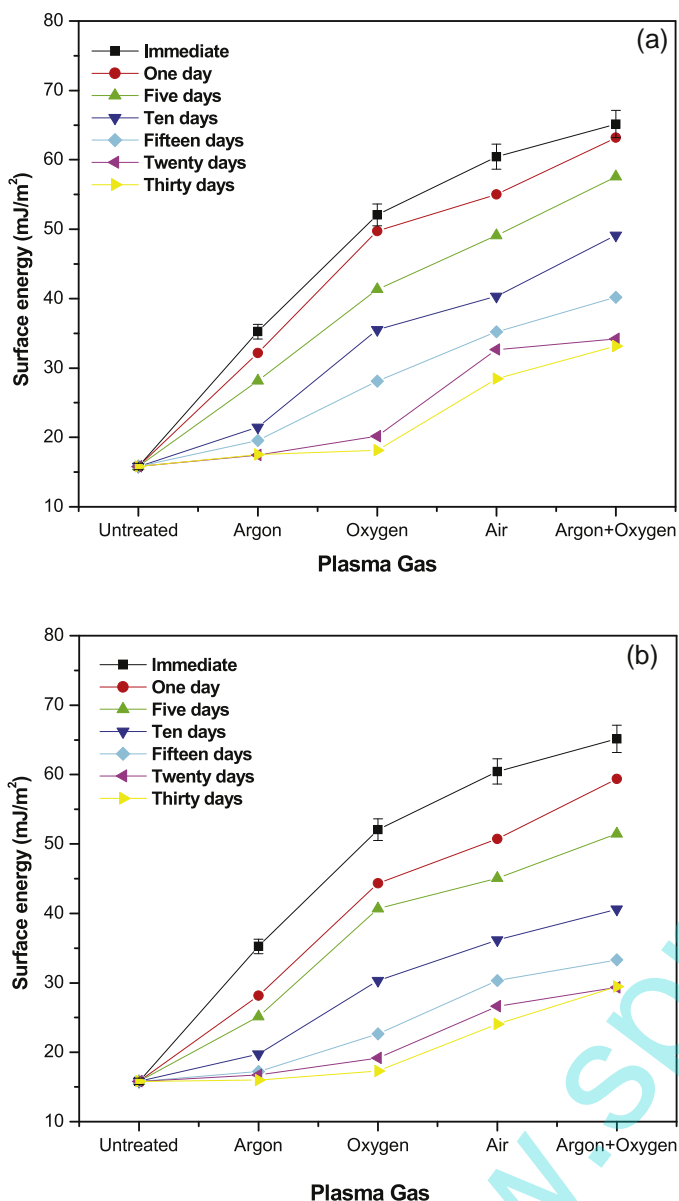
Fig. 10. Estimation of the hydrophobic recovery of gaseous plasma treated PP film surfaces. (a) Stored in air and (b) in water.

Fig. 11. (a) T-peel and (b) Lap shear strength of the PP film as a function of plasma processing gas.

surface free energy causes relocation of hydrophobic to hydrophilic one [29,53].

However, hydrophilic modification of the PP film which is acquired during the gaseous plasma treatment may recover partially to their original state or disappear when stored for longer time. The loss of stability of plasma treatments are caused by the re-orientation of polar functional groups into the bulk and the mobility of small polymer chain segment into the matrix leading to suppress the hydrophilicity [50–52]. Moreover, the instability of the plasma effect mainly depends upon various parameters such as the types of polymers, treatment time, storage condition etc. Thus, the stability of the plasma treatment needs to be investigated for the further industrial applications. In the present investigation, stability of the PP films was analyzed for thirty days of storage time in two different storage conditions such as air and distilled water by evaluation of surface free energy analysis (Fig. 10a and b). As it can be seen that the surface energy (γ_s) values of the gaseous plasma treated PP films decreased with respect to storage time when stored in air (Fig. 10a). However among the gaseous plasma treatment, stability
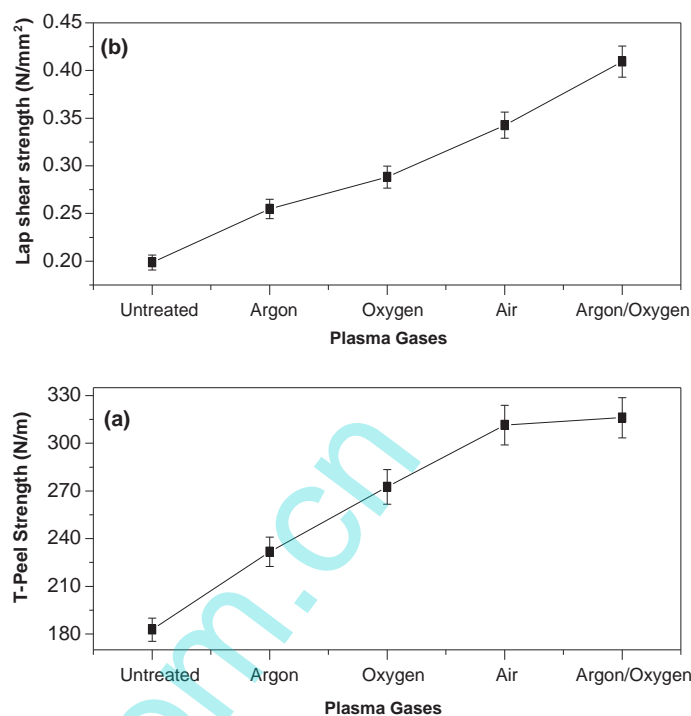
of the Ar + O$_2$ plasma treatment is better as compared with other gaseous plasma treatment due to production of cross linked oxidized structure on PP films surfaces which limit the reorientation of polar functional groups in their bulk [54,55]. Moreover, Ar + O$_2$ plasma treatment changed the surface morphology through surface roughness which reduced the instability of the plasma effect. In contrast, stability of plasma treatment is poor for the other plasma treatment due to less number of polar functional groups on the surface as well as lack of cross linking. Thus, the mobile polar functional groups easily reorient to their material bulk resulting in lack of stability. In addition, the PP films exhibited severe ageing when it was stored in water as compared to air which may be attributed to alter the hydrophilicity of the material through water quenching of surface of PP films [56–59]. The quenching effect passivating the polar functional groups and oxygen moieties on the PP film surfaces induced by gaseous plasma. Hence, PP films stored in water revealed severe instability compared with stored in air. Marginal change in hydrophobic recovery was observed from 15 to 30 days as compared to first 15 days ageing. However, the hydrophilcity of the aged PP films is still better as compared with untreated one. Therefore, such films could be useful for further industrial applications.

3.6. Adhesive strength analysis: T-peel and Lap shear test

To understand the effect of physico-chemical changes on the surface of PP films induced by the gaseous plasma treatments, a T-peel and Lap-shear strength test was evaluated as shown in Fig. 11. The T-peel strength of the untreated PP film is 182.73 N/m which increased slightly after argon plasma treatment. It is mainly due to improvement in surface roughness of PP films and also incorporation a few functional groups on the surface of PP films as evident from AFM and XPS, respectively. However the peeling strength values were further improved by O$_2$, air and Ar + O$_2$ plasma treatment as shown in Fig. 11a. The maximum peeling strength was obtained for the PP film treated by Ar + O$_2$ plasma. It was further observed
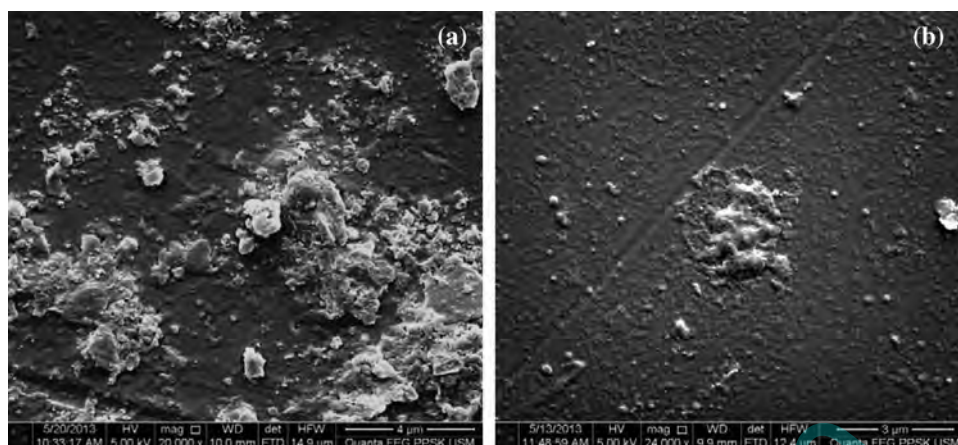
Fig. 12. SEM photograph of in vitro platelet adhesion tests: (a) untreated and (b) Ar + O₂ plasma treated PP films.

that the adhesive was partly transferred to the air and Ar + O$_2$ plasma treated PP films, thus cohesive break was observed in these samples. The changes are mainly caused by increase in high dense of polar functional groups such as C–O, C=O/O–C–O, O–C=O/COO and O–CO–C on the surface of PP films which clearly exhibited in the surface energy and XPS study. However, chemical modification alone is not only involved in the improvement in peeling strength, but the topographical modifications (increase in surface roughness and hence increase in effect surface area for contact) also contribute to the improvement in the adhesive joint strength. The interlocking of adhesive material takes place on the rougher surfaces leading to improved joint strength. The above physico-chemical modifications produced by the gaseous plasma treatment provide a path way to spread the adhesive layer on surface of PP films and weak bonds are formed with the adhesive material by Vander Waal's forces. Hence this attractive force between adhesive material and PP film surface contribute for increase in bonding strength [28,53]. Furthermore, similar results were obtained for Lap shear test of gaseous plasma treated PP films (Fig. 11**b**).

3.7. In vitro blood compatibility analysis:

Fig. 12 exhibits the *in vitro* platelet adhesion analysis of untreated and plasma treated PP films, which could be used to find blood compatibility of the material. It was found that the platelets are strongly adhering on the surface of untreated PP films. Also, the morphology of the platelets is also in deformed shapes with pseudoped. Hence the blood compatibility of the untreated PP film was found to be worst (Fig. 12**a**). In contrast, the adhesion and activation of the platelets are suppressed dramatically on the surface of Ar + O$_2$ plasma treated PP films due to its superior physico-chemical properties induced by the plasma treatment (Fig. 12**b**). In comparison to the other gaseous plasma treatment, Ar + O$_2$ plasma changes surface morphology and chemistry to a greater extend hence we have studied blood compatibility for these samples only. Fig. 13 clearly exhibited that ~52 platelets are adhered on the 1 μm^2 area of the untreated PP film surfaces and the same was decreased markedly on the surface of Ar + O$_2$ plasma treated PP film surfaces. In addition, investigation of the adsorption of human blood plasma such as albumin and fibrinogen on the surface of PP films are also important key factors to estimate the blood compatibility, because the adsorbed blood protein can induce the inherence of coagulation activity as well as increase the adhesion and activation of platelet causes formation of thrombus on the surface of the materials. The adsorption of albumin and fibrinogen on the surface of PP films was calculated through the measurement of optical density values at 280 nm (OD$_{280}$). The optical density (OD$_{280}$) value of
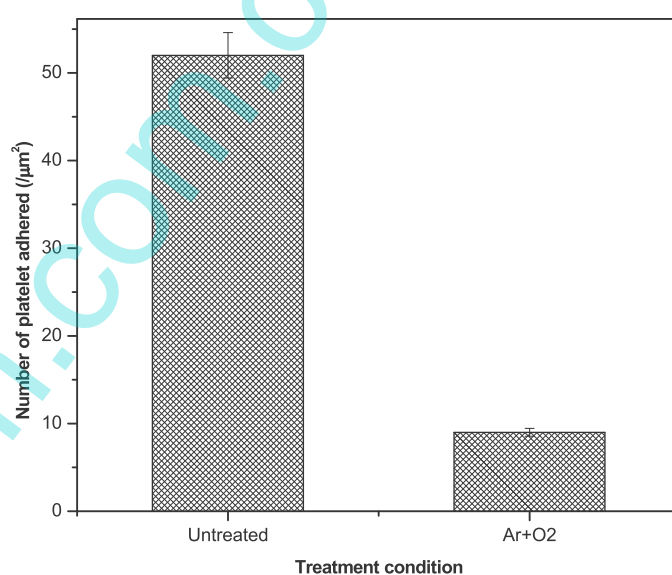

Fig. 13. Quantitative value of platelet adhered on the surface of untreated and Ar + O$_2$ plasma treated PP films.

albumin and fibrinogen of PP film are 3.51 nm and 3.38 nm, respectively and the same was decreased significantly by Ar + O$_2$ plasma treatment (2.50 nm for albumin and 2.43 nm for fibrinogen). The above results clearly revealed the plasma treated PP films surface strongly defend against adsorption of plasma protein which in turn suppress the coagulation activity on the PP film surface. Thus, the above results strongly suggest that the improvement in the physico-chemical (formation of polar functional groups and surface roughness) properties induced by the Ar + O$_2$ plasma treatment facilitates improvement in blood compatibility of the PP films [60–63].

4. Conclusion

Influence of various gaseous such as argon, air, oxygen and argon oxygen mixture plasma treatment on improvement of surface and hemo-compatible properties of PP films were investigated. Gaseous plasma treatment show incorporation of polar functional groups such as C–O, C=O/O–C–O, O–C=O/COO, O–CO–C onto the surface of PP films as evidenced by the XPS. AFM analysis revealed the topographical changes induced by the gaseous plasma treatment. The extent of chemical and morphological changes (roughness) was found to be maximum for Ar + O$_2$ plasma treated PP films in

comparison with the other gases used. The decrease in contact angle and increase in surface energy values indicates introduction of polar functional groups onto the plasma processed PP films, which is in good agreement with XPS study. The formation of free radicals on the surface of PP film is also confirmed by the ESR signals, which mainly caused by the cleavage of C–C/C–H bonds from the PP film surfaces. Finally, $Ar + O_2$ plasma treatment was found to be more effective to alter surface chemistry and morphology of PP films among other gaseous plasma treatments. On other hand, stability of the plasma effect was found to be suppressed with respect to different storage time and condition due to migration of polar functional groups into the PP film bulk. However, least ageing effect was found for $Ar + O_2$ plasma treated samples when stored in air or water. In addition, due to the fabulous effect of $Ar + O_2$ plasma treatment consequently improves the adhesive as well as hemo-compatible properties of PP films. Hence, the low temperature (non-thermal) plasma based surface modification technology have great potential for applications in bio-medical industry.

Acknowledgments

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