Influence of non-thermal plasma forming gases on improvement of surface properties of low density polyethylene (LDPE)

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ABSTRACT

Owing to the superior physico-chemical properties, the low density polyethylene (LDPE) has been widely used in the various industrial applications; especially in biomedical field for artificial organs, medical devices and disposable clinical apparatus. However, the poor anticoagulation property is one of the main drawbacks of the LDPE due to its poor surface properties. Therefore, in this paper we present the effect of plasma forming gases such as argon (Ar), oxygen (O_2), air and argon-oxygen (Ar + O_2) mixture on improvement of the surfaces properties of LDPE film using direct current (dc) excited glow discharge plasma. Contact angle with evaluation of surface energy, X-ray photo electron spectroscopy (XPS), atomic force microscopy (AFM) techniques were used to examine the change in surface properties such as hydrophilicity, chemical composition and surface topography, respectively. Furthermore, the hydrophobic recovery of the plasma treated LDPE was analyzed using ageing effect under different storage condition i.e. in air and water. The adhesive strength of the LDPE films was determined using T-peel test. In vitro tests were used to examine the blood compatibility of the surface modified LDPE films. It has been found that the hydrophilicity of the various plasma treated LDPE films was improved significantly due to the formation of oxygen containing polar groups such as OH, COO, C—O, C=O as confirmed by contact angle and XPS analysis. AFM revealed the changes in surface topography of plasma processed films. The gas mixture Ar + O_2 plasma influenced the remarkable improvement on the surface properties of a LDPE film compared with other gaseous plasmas. These physiochemical changes induced by the plasma on the surface facilitate to improve the adhesive strength and blood compatibility.

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1. Introduction

Polymeric materials are playing an ample role in diverse industrial applications such as biomedical, automotive, food packaging etc. due to their excellent mechanical properties, easy processing, and good resistance to corrosion, or ease of recycling and also it is relatively inexpensive to produce [1–3]. Especially, polymeric materials provide blood contacting surfaces such as those used in replacement of heart valves, artificial blood vessels, hemodialysis membranes, and stents etc. Among the various polymeric materials, low density polyethylene (LDPE) is an engineering polymer which is mainly used in various fields of automobile, appliances, engineering components and also widely used in biomedical applications [4]. However, the antithrombogenic properties of the material is still not good enough for the demanding blood contacting applications such as cardiovascular implants and devices, which may be due to its poor surface properties such as hydrophobicity, low surface energy, poor adhesion etc of LDPE. Hence, suitable surface treatment is required to improve the surface properties of the material which is a key factor to improve the process of blood-surface interaction. Thus, surface is first interacting with body environment and play significant role than bulk. Furthermore, the hydrophilic groups such as C=O, COO, OH etc can effectively improve the adhesion properties as well as reduce the

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thromobogenic response between the blood cell and hydrophilic surfaces. Owing to that the surface modification is considered as an effective approach to incorporate the hydrophilic (blood inert functionalities) groups on the surface of hydrophobic LDPE and also desirable approach to develop the materials while retaining the favorable bulk properties.

A number of procedures such as electron beam and gamma ray irradiation, corona and plasma treatment have been used to modify the surfaces of materials with desirable surface properties for biomedical applications. The non thermal plasma treatment seem to be highly dominant treatment technique among the other methods which could be applied to different materials and could change the surface properties to a large extent without affecting the materials bulk properties [4–6]. When the polymer surfaces come in contact with plasma, there are many reactions such as surface cleaning, etching, cross linking, and chemical modifications, occurring on the polymer surfaces which contribute to improved biocompatibility of polymers. The mechanism of non-thermal plasma highly depends on the processing gases which plays a leading role in improvement of surface properties of polymers. Moreover, another important challenge in the plasma surface treatment is the durability of the modification and effect of environment conditions which is to be the *Holy Grail* in biomaterial research. The durability of the plasma effect can be improved considerably by selecting the plasma processing gas and treatment conditions [7,8].

In this paper we describe the influence of plasma forming gases and gas mixtures (argon, O_2, air, $Ar+O_2$) on the surface properties of low density polyethylene (LDPE) using low pressure direct current excited glow discharge plasma. The change in surface hydrophilicity, chemical states and morphology of various plasma treated LDPE film was analyzed by contact angle, X-ray photo electron spectroscopy (XPS) and atomic force microscopy (AFM). Moreover, the durability of the plasma effect on LDPE was investigated in different environment (stored in air and water) using contact angle tests. T-peel test was used to examine the adhesive strength of the plasma treated LDPE. Furthermore, blood compatibility of the surface modified LDPE is analyzed by in vitro tests which include protein adsorption, thrombus formation, whole blood clotting time and platelet adhesion analysis.

2. Experimental setup and methodology

2.1. Materials

Smooth and homogeneous low density polyethylene (LDPE) films with the thickness of 40 μ were procured from Reliance Petro Chemicals Ltd., Mumbai, India. Before the plasma treatment, films were cleaned ultrasonically using acetone and de-ionized water to remove organic contaminants on the surface of the LDPE followed by drying in the oven at 50 °C for 1 h.

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. The chamber is fabricated by stainless steel and water cooling copper tube is breezed on the surface of the plasma chamber which is used to avoid the formation of excess amount of heat during the plasma treatment. Two circular (diameter = 10 cm) water cooled electrode were fixed parallel to each other within the chamber as shown in Fig. 1(a) 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 5 cm

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 = 500 V
Discharge current = 700 mA

Table 2
Surface energy of the testing 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

and the plasma excitation occurs between two vertical 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. 1(a)). Hence the active plasma zone displays a cylindrical symmetry as shown in Fig. 1(b). The gas inlet system enables gas mixing and flow control which is controlled by electronic flow meter and mass flow controller (MFC) and the pressure within the chamber was measured by pirani gauge. Initially, ultrasonically cleaned LDPE film was kept on the sample holder and the chamber was evacuated to a low-pressure of 10^{-3} mbar. After that the chamber was filled by plasma processing gas ($Ar/O_2/air/Ar+O_2$) which was controlled by MFC. The working pressure inside the chamber was maintained at 0.2 mbar. A dc potential was applied between the two water cooled electrodes and adjusted till a stable glow discharge plasma is generated. Finally, the samples were treated in the uniform plasma glow regime as a function of different gas atmosphere with a fixed power, electrode separation, exposure time and pressure of 350 W, 5 cm, 10 min and 0.2 mbar, respectively. The typical operating parameters are listed in Table 1. Furthermore, the plasma treated samples were stored in both air and distilled water up to 15 days before examining their hydrophobic recovery.

2.3. Surface analysis

The change in hydrophility induced by the gaseous plasma treatment on LDPE films was analyzed through contact angle measurements by sessile drop method [9]. Three testing liquids such as distilled water, formamide and ethylene glycol of known surface energy parameters (given in Table 2) were used to measure the contact angle with respect to LDPE films and the volume of the testing liquids was fixed at 2 μl. The very representative contact angle value was an average of 10 independent measurements and an average experimental error of the measurement was ± 2°. The contact angle measurements were made under controlled room temperature and humidity conditions (55%).

The polar $\left(\gamma_s^p\right)$ and dispersion $\left(\gamma_s^d\right)$ components of surface-free energy of the LDPE films were calculated using Fowke's equation extended by Owens–Wendt as follows [9,10]:

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

Eq. (1) is in the form:

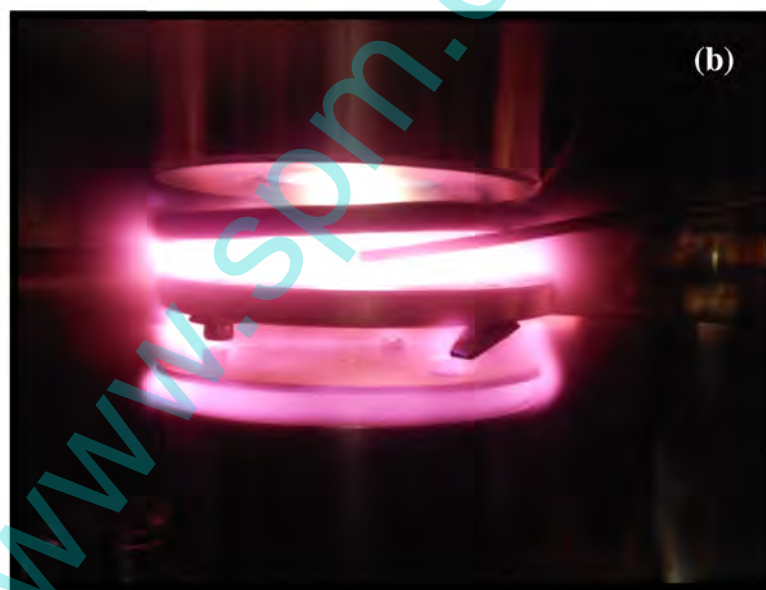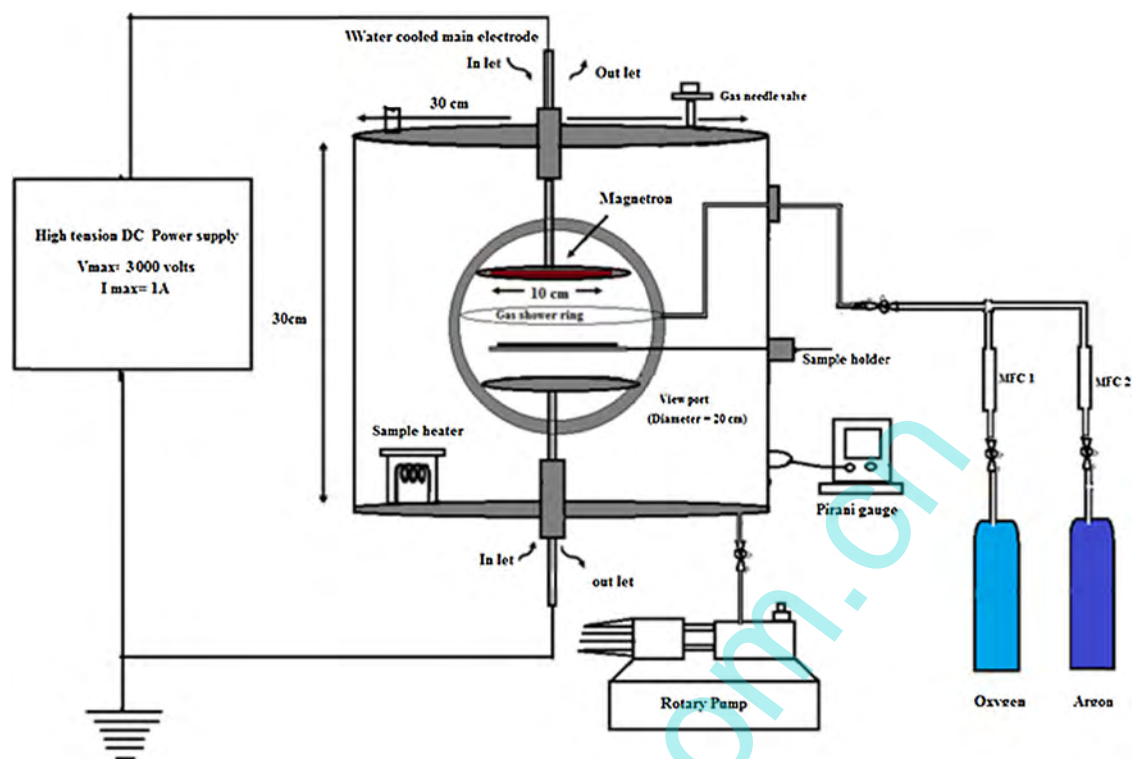$$Y(\text{LHS}) = mX(\text{RHS}) + C \tag{2}$$

Fig. 1. (a) Schematic diagram of glow discharge plasma reactor and (b) glow discharge plasma during the surface treatment.

where the value of LHS and RHS could be obtained by contact angle value (θ), surface energy of testing liquids (γ_l), polar $\left(\gamma_l^p\right)$ and dispersion $\left(\gamma_l^d\right)$ components of liquid used from Table 2.

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 give a total solid surface-free energy (γ_s) of the LDPE films as given in Eq. (3):

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad \left(mJ/m^2\right) \tag{3}$$

The surface topography of the untreated and plasma treated LDPE films was assessed using atomic force microscopy (AFM) by Seiko Instruments scanning force microscopy (AFM, Ben-Yuan, CSPM 4000). The AFM was operated in tapping mode with horizontal and vertical resolution of 0.26 and 0.10 nm. The value of Ra and RMS is an average from five independent measurements on regions of $1 \times 1\ \mu m$. The changes in chemical state of the LDPE films were examined using X-ray photo electron spectroscopy (Omicron Surface Science Instruments with EAC2000-125 Energy Analyzer). Monochromatic Al$K\alpha$ X-rays (1486.7 eV) was employed. Typical operating conditions for the X-ray source were a 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 C1s and

O1s envelopes were analyzed and peak-fitted using a combination of Gaussian and Lorentzian peak shapes obtained from XPSPEAK41 software package.

2.4. Adhesive strength analysis

A standard T-Peel test was used to evaluate the adhesive strength of LDPE film which was carried out using LLOYED's universal testing machine (UTM) (Model LR-10K Plus) at a rate of 100 mm/min at room temperature. For the above-mentioned study a scotch tape of width 2.5 cm was stuck over a length of 4.0 cm on the PE film. Care was taken to see that there were no air gaps or wrinkles and was kept under a pressure of 1.0 kg for 10 min. 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 meter of sample width. For every treatment, three samples were prepared for T-peel strength measurement and the mean values were taken.

2.5. Platelet adhesion and protein adsorption tests

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. Polymer disks were washed with phosphate buffered saline (PBS) for 24 h and placed in the bottom of the wells of a multiwell tissue culture plate; the PBS solution was removed from the multiwell tissue culture plate by pipetting. PRP (1 ml) was then seeded and incubated at 37 °C for 30 min. After incubation, the disks 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 microscopy (FEI-QUANTA FEG 450).

Human albumin and fibrinogen were used to study the adsorption behavior of proteins on the film surfaces. All blood proteins were purchased from Sigma. Small disks (15 mm in diameter) of the polymer films were prepared with a punch and immersed in 1 mg/ml protein solutions in phosphate-buffered saline (PBS, pH 7.3–7.4) at 37 °C for 1 h. The disks were then recovered, and changes in the protein concentrations of the solution were determined using a UV-spectrophotometer (at 280 nm).

2.6. Whole blood clotting time and thrombus formation analysis

Human whole blood (30 ml) from a healthy volunteer was collected and mixed with an aqueous solution containing 0.136 M D-glucose (anhydrous), 0.075 M sodium citrate dihydrate and 0.004 M citric acid monohydrate (ACD, 3 ml). The surface-modified LDPE film (4×4 cm^2) was attached to a watch glass and subjected to the thrombus formation test. The ACD-blood (200 μl) was placed on the sample, pre-swelled with distilled water, and incubated at 37 °C in a constant temperature bath. The clotting reaction was initiated by adding 0.1 M aqueous CaCl$_2$ solution (20 μl) to the blood. The sample was shaken gently by hand to mix the chemicals and the blood homogeneously. Distilled water (5 ml) was then added to stop the reaction after 30 min. The thrombus formed was extracted with a spatula, transferred into distilled water (5 ml) on a watch glass, left for 5 min at room temperature, and then placed in an aqueous 37% formaldehyde solution (5 ml) to fix the thrombus. The thrombus was dried under reduced pressure until the sample weight did not change. The weight of the thrombus formed was calculated relative to that formed on unmodified LDPE. The experiment was carried out six times, and the mean value was calculated.
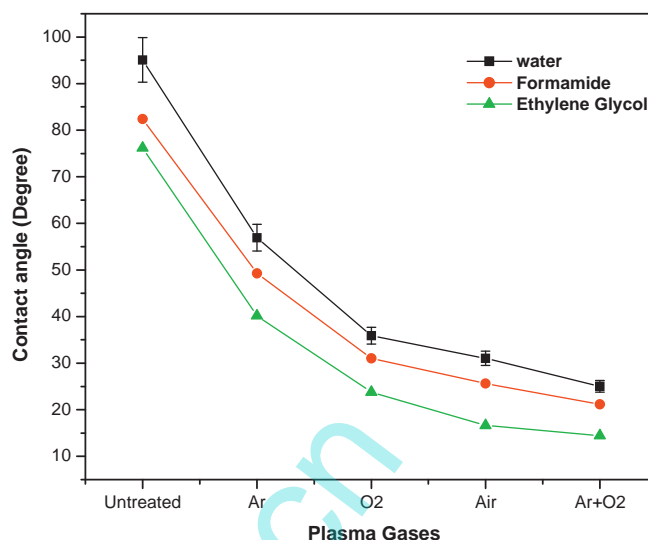

Fig. 2. Contact angle of the plasma treated LDPE film as a function of processing gases.

A volume of 0.1 ml blood was deposited onto each sample (untreated and treated polymer surfaces) and incubated at 37 °C in a constant temperature bath. The clotting time was recorded by manually deepening a stainless-steel needle into the drop to detect any fibrin formation. The time of detection of the first fibrin filament adhering to the needle was considered as the coagulation time [11].

3. Results and discussion

3.1. Hydrophilic analysis: Contact angle and surface energy tests

The rationale of hydrophilic behavior of the untreated and plasma treated LDPE films were estimated by measuring contact angle of LDPE film which also provided the information about the high degree of sensitivity regarding the very upper most layers of the LDPE/air interface. Fig. 2 describes the change in contact angle of LDPE films for different processing gases using different testing liquids. The contact angle of untreated film was found to be 95.02°, 82.41° and 76.17° for distilled water, formamide and ethylene glycol, respectively, due to the hydrophobic nature of the LDPE films. However, the value of contact angle decreased dramatically when the samples were treated by Ar, O$_2$, air and O$_2$ + Ar plasmas. Among the various plasma discharge treatment, O$_2$ + Ar showed significant effectiveness to reduce the contact angle of the LDPE films. The decrease in contact angle due to the plasma treatment clearly indicates the surface of the LDPE is transformed to hydrophilic one as compared with untreated one. The change in hydrophilicity is governed by molecular interactions in the outermost surface layer of a few angstroms. Thus, the forces dictating the wetting behavior of organic substances do not originate from the organic molecule as a whole, but rather from the outermost surface groups. Furthermore, for minimization of interfacial energy, the molecules tend to arrange themselves on the surface layer in such a way that only their low-energy or high-energy portions come into contact with the surrounding phase as the case may be. As a result, the wettability of an organic material is not related to its overall chemical structure, but depends on the chemical nature of energetically favored functional groups such as OH, COO, C=O etc and the extent to which these are exposed at the material surface.

The variations of surface energy characteristics of the LDPE films for various processing gases are shown in Fig. 3. The total surface energy components such as polar and non polar (dispersion)
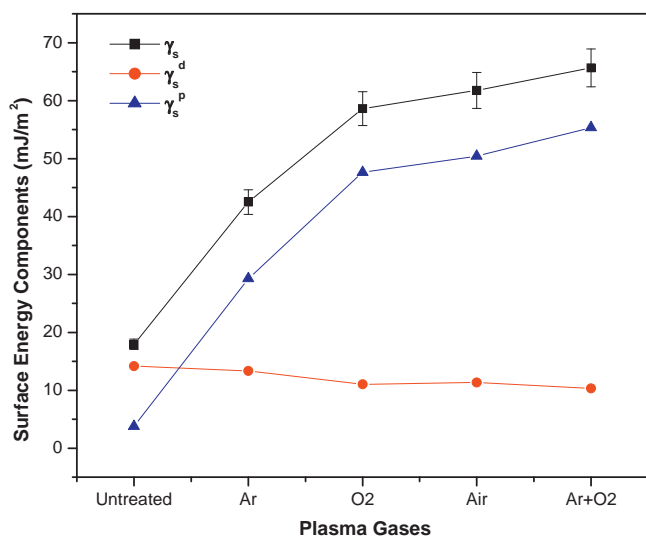
Fig. 3. Surface energy of the plasma treated LDPE film as a function of processing gases.

are estimated by Fowke's approximation using three testing liquids. The total surface energy of the untreated film was found to be 17.94 mJ/m^2 which is basically due to the hydrophobic nature of this hydrocarbon based polymer. When such polymer is subjected to Ar plasma (chemically non reactive) treatment, it causes chain scission, breaking of bonds due to bombardment of energetic plasma species and thus creating-free radicals on the surface. These free radicals react with the oxygen present in the atmosphere when the sample is exposed to the atmospheric conditions after the plasma treatment. Thus such non reactive gaseous plasma treatment can also incorporate oxygen containing functional polar groups onto the surface (evident from XPS study given in the next section) which intern decreases angle of contact and enhances surface energy (SE). Further Ar plasma treatment makes the surface rougher, which helps in spreading contact liquid. However, when such polymer is exposed to the reactive oxygen plasma, the effect is more profound. The degree of incorporation of polar groups in such cases is definitely enhanced and can be revealed from XPS study in the next section of this paper. The improvement in surface energy is more for air and (Ar + O$_2$) plasma treated films because the nitrogen present in air and Ar present in the mixture (Ar + O$_2$) gas leads to chain session and formation of free radicals as explained earlier. This helps in getting incorporated oxygen containing moieties present in the plasma chamber. Thus addition of non-reactive gas along with O$_2$ helps in further improvement of surface properties as compared to either pure reactive or non-reactive gases. The increase in surface energy in all the cases is essentially due to the incorporation of polar functional groups and therefore the trend of total SE (γ_s) and the polar components $\left(\gamma_s^p\right)$ is same as shown in Fig. 3 whereas dispersion components $\left(\gamma_s^d\right)$ more or less remain constant. Owing to formation of oxygen containing polar functional groups such as C=O, COO, OH on the surface of LDPE by the gaseous plasma treatment are responsible for the makeover of hydrophobic polymer to hydrophilic one [12,13].

3.2. Chemical composition analysis: XPS results

Figs. 4 and 5 show the wide scan and high resolution spectra of LDPE film which provides the information about the existing functionalities on the surface region and also incorporation of new functional groups on the surface induced by various gaseous plasma treatments. The wide scan spectra of the LDPE
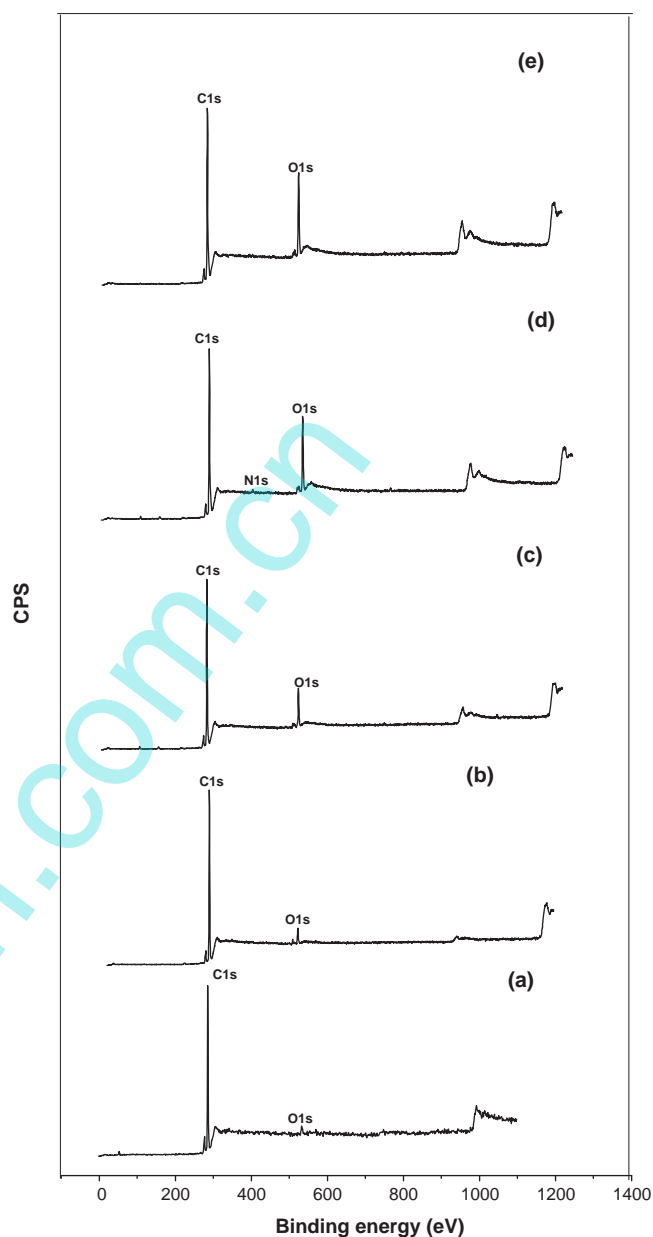

Fig. 4. XPS wide scan spectra of (a) untreated, (b) Ar, (c) O$_2$, (d) Air and (e) Ar + O$_2$ plasma treated LDPE films.

films as a function of various gas plasma treatments are shown in Fig. 4. It clearly shows C1s as the major component of the untreated LDPE with trace amounts of O1s component, which might be due to the adsorbed oxygen as well as surface oxidation. After argon plasma treatment, intensity of C1s components of LDPE films was found to be decreased with slight increase in O1s component. The reason behind this incorporation of oxygen moieties is the post exposure of samples to the oxygen present in the atmosphere. The intensity of the O1s component increased further significantly by O$_2$, air and Ar + O$_2$ plasma treatment. The analysis of the wide XPS spectra gave the evolution in surface elemental composition with respect to various gas plasma treatments.

The chemical composition of each component in the surface modified LDPE films is presented in Table 3. It clearly reveals that LDPE has only one major component i.e. C1s which decreases slightly after argon plasma treatment and further decreases after O$_2$ and air plasma treatment, while increase in O1s component
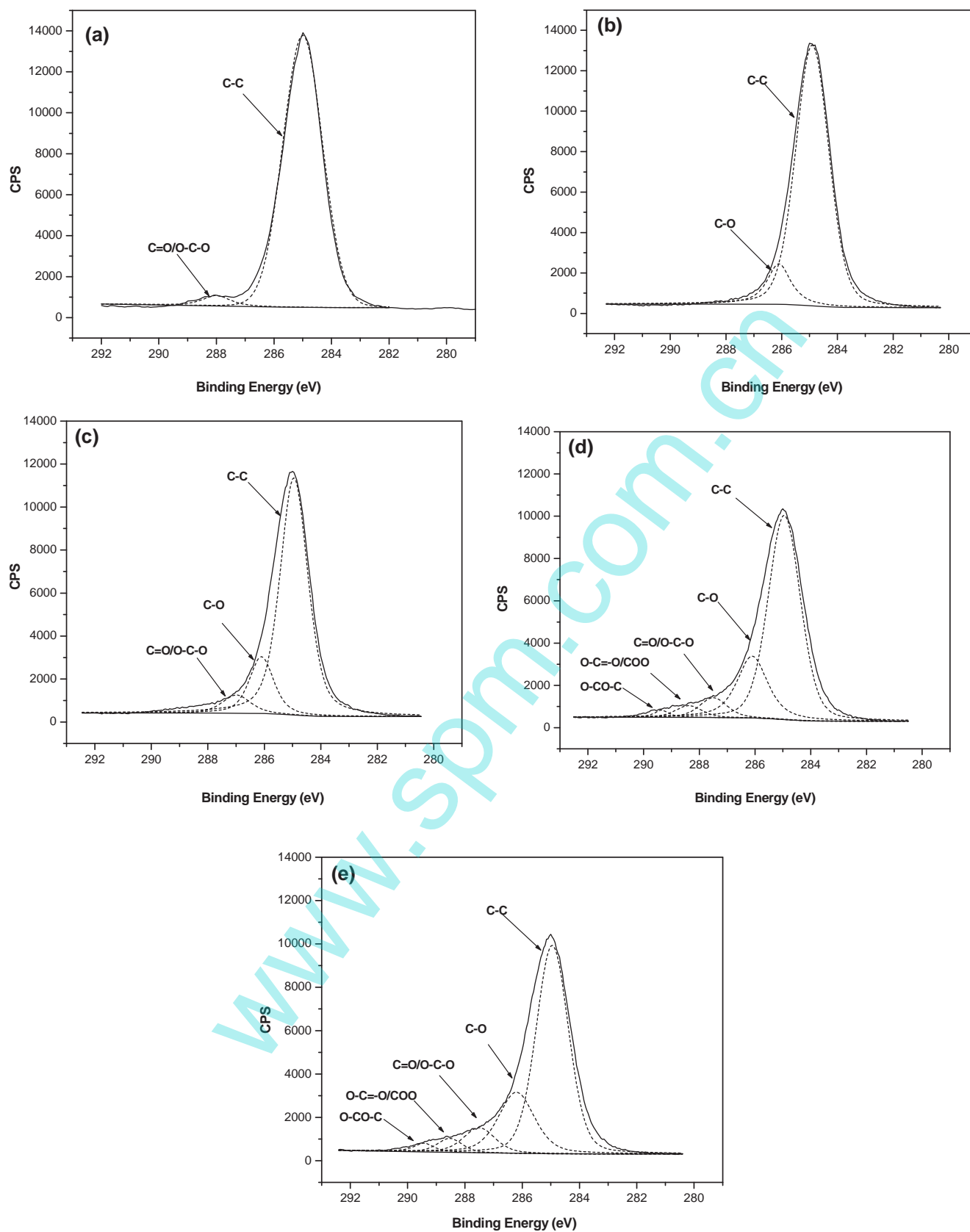
Fig. 5. XPS high resolution C1s spectra of (a) untreated, (b) Ar, (c) O_2, (d) Air and (e) Ar + O_2 plasma treated LDPE films.

Table 3
Elemental composition of the plasma treated LDPE film as a function of processing gases.

Processing gas	Elemental composition (at%)			Elemental ratio	
	C1s	O1s	N1s	O/C	N/C
Untreated	98.92	1.801		0.01	–
Ar	95.98	4.02	–	0.04	–
O_2	89.6	10.04	–	0.11	–
Air	82.58	15.18	2.24	0.18	0.02
$Ar + O_2$	81.97	18.03		0.21	–

Table 4
Representative XPS high-resolution C1s peak fit data for surface-modified LDPE films.

Plasma gas	C1s Components (at%)				
	C—C/C—H	C—O	C=O/O—C—O	O—C=O/COO	O—CO—C
UT	96.94	0.00	3.06	0.00	0.00
Ar	88.31	11.69	0.00	0.00	0.00
O_2	77.45	16.47	6.08	0.00	0.00
Air	67.57	20.48	7.94	2.91	1.10
$Ar + O_2$	63.45	23.02	8.02	3.45	2.07

on the surface of LDPE film. However, $Ar + O_2$ plasma treatment increases O1s component of LDPE film from 1.801 at% to 18.03 at%. Similarly, the ratio of O/C is in the order of $Ar < O_2 < Air < Ar + O_2$. These above results clearly exhibit that the oxygen content was incorporated on the surface of LDPE film after the various plasma treatments. The introduction of oxygen-containing polar groups onto the LDPE film surface may be the main reason for the improvement of hydrophilicity as well as biocompatibility. Furthermore, a small amount of nitrogen was detected on the surface of air plasma treated LDPE film which confirms the surface grafting of reactive species during the treatment.

The detail information about the introduction of polar functional groups on the LDPE films by different gaseous plasma treatment are analyzed using C1s high resolution XPS spectra as shown in Fig. 5. The C1s core level spectra of the untreated LDPE film shows two peaks at 285 and 288.00 eV due to aliphatic carbon (C—C/C—H) and intrinsic low level oxidized carbon center's on the LDPE surface (C=O), respectively. The low level oxidation of LDPE films may be attributed to incorporation of oxygen atom from the ambient condition during the cleaning process of LDPE films by acetone and de-ionized water. After argon plasma treatment, we found one addition peak at 286.1 eV that can be attributed to C—O groups and the peak at 288 eV is disappeared due to desorption of water molecules from the surface of LDPE films by ions, electrons, and neutral species and UV radiation in the plasma. The oxygen plasma treated LDPE films shows one more addition peaks at 287.4 eV which could be attributed to C=O/O—C—O groups. Furthermore, for air as well as $Ar + O_2$ 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 [14–16]. The relative percentage contribution of C1s components of the gaseous plasma treated LDPE estimated from the C1s core level spectra is given in Table 4. The untreated LDPE film contains 96.94 at% of C—C groups. Subsequently, the C—C group decreased, while the concentration the newly formed polar functional groups such as C—O, C=O/O—C—O, O—C=O/COO and O—CO—C increased significantly in the order of $Ar < O_2 < Air < Ar + O_2$ gaseous plasma treatment (Table 4). Argon is generally used for etching and cleaning of surfaces as it is inert. Argon plasma induces chain scission and bond breaking at LDPE surface, creating carbon radicals on the polymer surface through abstraction of C—H and C—C bonds. These radicals interact with adjacent polymer chains leading to cross-linked chains. However, few radicals are ready to interact with oxygen species when it is

exposed in the environment and hence very petite amount of oxygen containing group (C—O) incorporated on the surface of LDPE films [17]. The oxygen containing plasma forming gases play a vital role to incorporate the polar functional groups on the surface of LDPE films rather than inert plasmas. The glow discharge oxygen plasma treatment produced polar functional groups in-situ on the surface of LDPE by surface oxidation. It is well known that the reactive gaseous plasma such as oxygen containing plasma is responsible for surface functionalization whereas non-reactive gaseous plasma leads to CASING (cross-linking by activated species of inert gases) [18]. The glow discharge air plasma has different chemical compositions such as oxygen and nitrogen based species (NO, NO_2, N_2O) and charged species (NO^+, O_2^+, O^+) which are creating more reactive sites on the surface of LDPE film [19,20]. These reactive sites can facilitate to incorporate variety of polar functional groups on the surface of LDPE film. Moreover, the $Ar + O_2$ plasma treatment produces oxidized cross linked structure on the surface of LDPE film surface. The combined processes induced by the $Ar + O_2$ plasma can induce rapid hydrophilic transformation of hydrophobic LDPE film due to incorporation of high density of polar functional groups on the surface [21,22]. Hence $Ar + O_2$ and air plasma has more competence to create the polar functional groups on the surface of LDPE films compared with pure argon and O_2 Plasma. Chen et al. [23] studied formation of free radicals on the surface of various polymeric materials through different plasmas using ESR spectroscopy. He found that the relative intensity of the free radicals measured using ESR depends not only on the polymer substrate but also on the type of gas used to generate plasma. Furthermore, Rezníčková et al. [24], Kondyurin et al. [25], Tresp et al. [26] and Zanini et.al [27] have also reported the formation of free radicals on the surface of various polymeric materials. Thus, our study using XPS clearly indicates that the various gaseous plasmas induce polar functional groups such as C—O, C=O/O—C—O, O—C=O/COO, O—CO—C on the LDPE films surfaces to different levels.

3.3. Topographical analysis: AFM results

When the polymeric material come in contact with various concurrent processes such as surface activation, etching, grafting etc the alteration of surface properties takes place. Plasma etching is one of the important factors for facilitate to improve the surface properties of the LDPE film which is mainly due to consequence of the impact of the plasma particles such as ions, electrons, exited atoms, UV photons etc on the surface of polymer films which lead to generation of radicals and removal of molecular fragments from the surface results in increased surface roughness i.e. effective surface area. The change in roughness induced by the plasma treatment might affect the surface properties by simple physical adsorption or/and by diffusion in various mechanical interlocking [28]. The etching process mainly depends upon the type of plasma forming gas. Detailed information about the changes in surface morphology induced by the 10 min gaseous plasma treatment on LDPE films were investigated by AFM (Fig. 6(a)–(e)). It clearly shows that the surface of the untreated LDPE film is relatively smooth with moderate surface roughness (Fig. 6(a)). The surface roughness of the LDPE was improved slightly by oxygen plasma treatment as it is reactive in nature. Argon is non-reactive heavy atom and causes chain scission, making LDPE surface rougher. However, plasma created using the mixture of reactive and non reactive gases (air/$Ar + O_2$) yields maximum roughness, this may be due to synergetic effect of the individual gases present in the mixture. Moreover, the Ra and RMS are the quantified surface roughness values of the gaseous plasma treated LDPE film which is obtained from AFM images as shown in Fig. 7. It exhibits that the Ra and RMS of the untreated LDPE are 1.85 and 2.35 nm, respectively. The increase in Ra and RMS value of
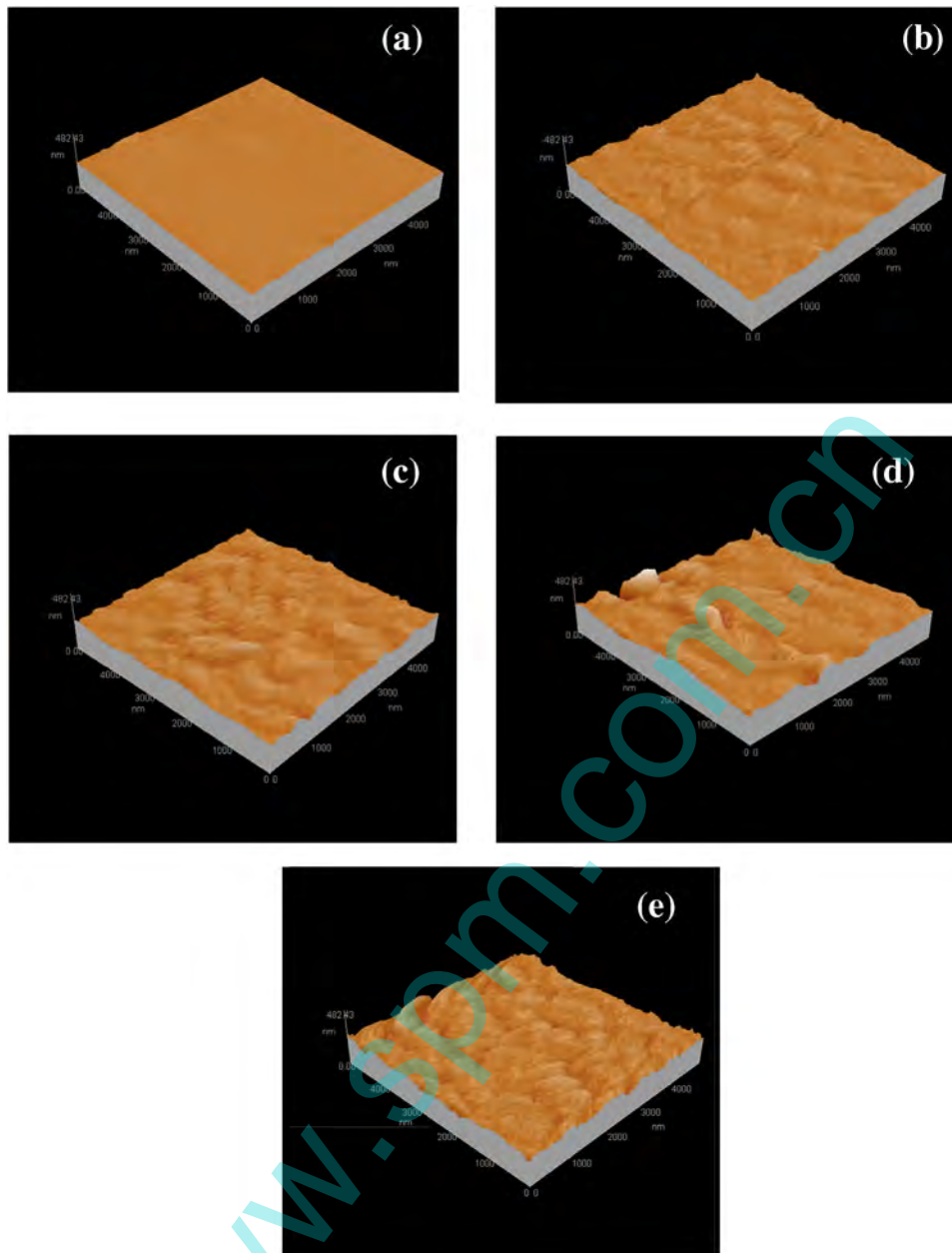
Fig. 6. AFM micrographs of (a) untreated, (b) Ar, (c) O_2, (d) Air and (e) Ar + O_2 plasma treated LDPE films.

the LDPE films are in the following order UT < O_2 < Ar< Air + O_2 which 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 which may be due to the dependence of the process on the dimensions of the bombarding ions [29].

3.4. Hydrophobic recovery: Ageing effect

Owing to the plasma surface treatment hydrophilicity of the hydrophobic polymers is improved significantly by incorporation of polar functional groups as well as remarkable surface roughness. However, determination of aging is one of the important factors to estimate the durability of the plasma surface treatment. The aging is mainly due to surface contamination, orientation of polar groups, blooming of additives, and absorption of ubiquitous contaminant which leads to an increase in hydrophobicity of the polymeric materials i.e. increase in the contact angle and decrease in the surface

energy value [30–34]. It is shown that the hydrophobic recovery depends on the polymer and on type of treatment. It is also important to note that not all the hydrophilic nature achieved by the plasma treatment is lost during the ageing process. The ageing itself can be considered as one of the steps of the treatment in a sense that it influences the outcome as determined by the properties imparted to the polymer surface. Fig. 8 shows percentage hydrophobic recovery of various gaseous plasma processed LDPE film examined from 1 to 15 days of ageing using contact angle measurement under different storage atmosphere like air and distilled water. The percentage of hydrophobic recovery of the LDPE films was calculated using following formula:

$$Hydrophobic\ recovery\,(\%) = \frac{\theta_a - \theta_i}{\theta_i} \times 100$$

where θ_i and θ_a are the values of contact angle of the LDPE films measured immediately (fresh sample) and after aged for
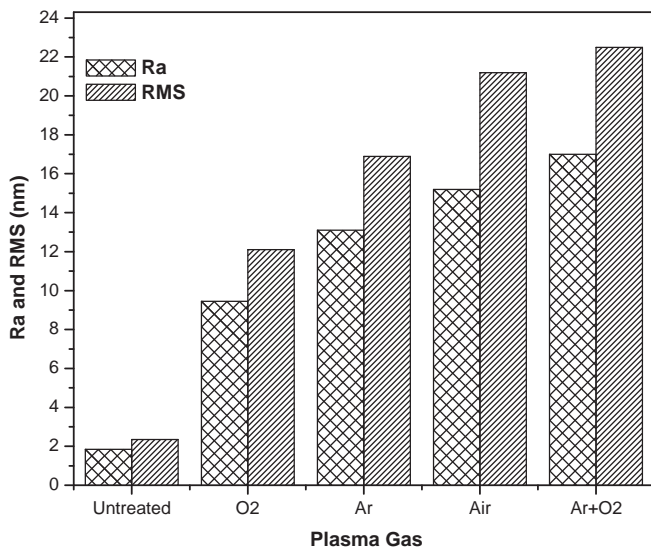
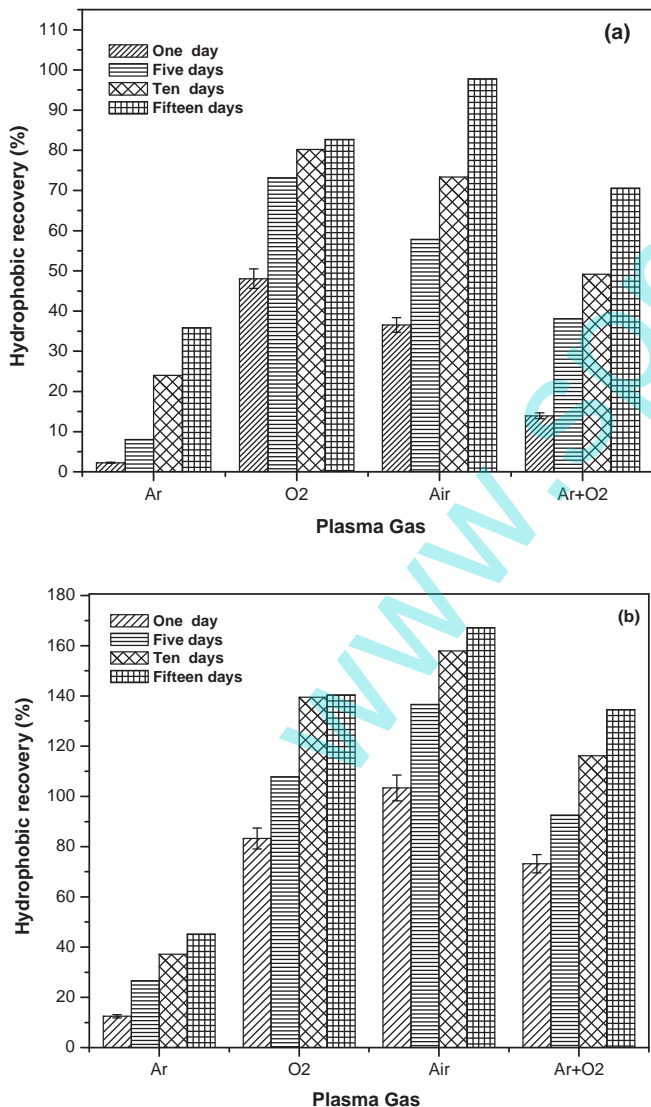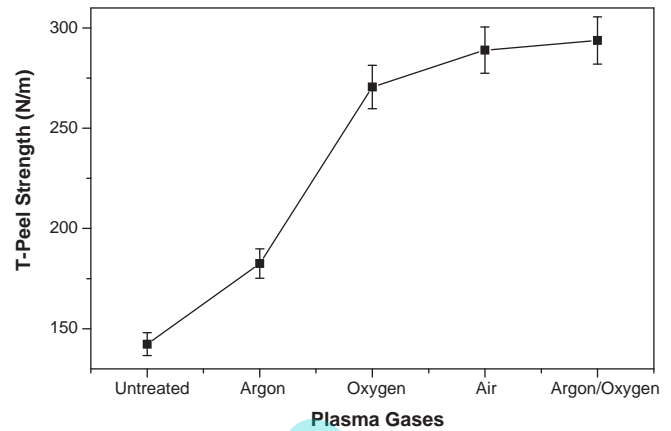**Fig. 7.** *Ra* and RMS values of the LDPE films as a function of processing gas.

Fig. 9. T-peel strength of the plasma treated LDPE film as a function of plasma processing gas.

specific duration, respectively. It was observed that the hydrophobic recovery of plasma processed LDPE film is considerable for shorter storage time and thereafter tend to saturate the ageing phenomenon for a long storage time. Moreover, as it can be seen from Fig. 8(a) that the percentage hydrophobic recovery for the samples treated in O_2 and air plasma is more as compared with Ar and Ar + O_2 plasma treated samples. The changes may be due to Ar and Ar + O_2 plasma produced high degree of cross linked network on the surface of LDPE film which restricted mobility of polar function groups on their polymer bulk. Hence reorientation of the polar functional groups formed on the LDPE film surface is reduced significantly. Similarly Ar and Ar + O_2 plasma makes surface rougher, which is a permanent change onto the surface; causing reduction in a contact angle value. In contrast, oxygen and air plasma treatment produced polar function groups on the surface without creating the cross linked network [35]. Therefore, the mobile polar functional groups get reoriented markedly to their original bulk resulting in higher hydrophobic recovery. Thus, degree of cross-linking induced by the plasma treatment plays a vital role to control the ageing effect. Furthermore, the gaseous plasma treated LDPE films stored in water (Fig. 8(b)) exhibited the severe ageing compared with stored in air as shown in Fig. 8(a). The rapid aging of LDPE stored in water is attributed to loss/transfer of free radicals, O_2 moieties, polar functional groups to water; which means that water acts as passivating agent for reactive oxygen species and surface functional groups. However, the contact angle of all the gaseous plasma treated LDPE film stored (aged) in air or water for different durations are still lower than the contact angle of the untreated one (95.09°). This illustrates the usefulness of plasma processing for LDPC. Hence such films can be suitable for further industrial applications [36,37,33].

3.5. Adhesive strength analysis: T-peel test

Non thermal plasma treated polymeric materials has superior physico-chemical properties which may be due to the incorporation of oxygen containing polar functional groups onto the surface as well as significant morphological changes i.e. enhanced surface roughness. These surface changes can facilitate to spread the adhesive layer on the material surface and thus provide better interfacial contact [9,10,38,39]. In this regard, gaseous plasma treated LDPE films were further subjected to T-peel strength test to determine the adhesive strength of the same. As indicated in Fig. 9, the peeling strength of the untreated LDPE film is around 142.31 N/m. After that the value of peeling strength increased great extent by oxygen plasma treatment compared with argon plasma. However, maximum peeling strength value was observed for the LDPE
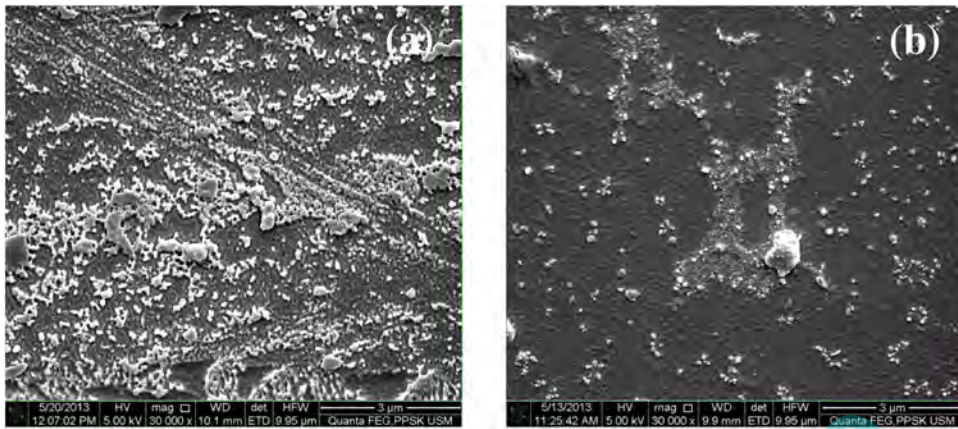

Fig. 8. Evolution of the percentage hydrophobic recovery of plasma treated LDPE film surface (a) stored in air and (b) in water.

Fig. 10. SEM photograph of in vitro platelet adhesion tests: (a) untreated and (b) Ar + O$_2$ plasma treated LDPE films.

films samples treated by Ar + O$_2$ plasma treatment which indicating that the Ar + O$_2$ plasma treated LDPE film possessed good adhesive strength compared with that of untreated one. It is clearly seen that the increase in adhesive strength of the LDPE is in the order of UT < Ar< O$_2$ < Air < Ar + O$_2$ plasma treatment which may be attributed to formation of high density of polar functional groups such as C=O, C—O, COO on the surface of LDPE films as well as improvement surface roughness induced by plasma treatment.

3.6. In vitro blood compatibility analysis

The interaction between foreign material and blood component is one of the major problems in the blood contacting devices manufactured for the use in biomedical field owing to adsorption of plasma protein followed by platelet adhesion and deformation which initiate the coagulation processes, resulting in formation of thrombosis. Hence platelet adhesion and protein adsorption are vital tests to determine the blood compatibility of the polymeric materials. Fig. 10(a) shows the SEM of the untreated LDPE films after contact with platelet rich plasma which clearly revealed the most of the platelets are accumulated and deformed shapes and they might be activated. After the plasma treatment the adhesion and activation of platelets are suppressed significantly (Fig. 10(b)).

Moreover platelet adherence on the plasma treated LDPE was isolated remarkably i.e. reduced the platelet activation. Fig. 11 shows the adsorption of albumin and fibrinogen onto LDPE surfaces which clearly show that the OD$_{280}$ (Absorbance) value of albumin and fibrinogen of LDPE film are 3.62a and 4.79, respectively. After plasma treatment the OD$_{280}$ value of albumin and fibrinogen are reduced significantly, since absorbance values (OD$_{280}$) is proportional to adsorption of protein on the surfaces of a LDPE film. Hence plasma treated LDPE film resist the adsorption blood plasma protein on the surface.

The whole blood clotting time (WBCT) on the different plasma treated LDPE film surfaces are shown in Fig. 12. It shows that the WBCT of the untreated LDPE film was 220s and same was elongated by various gaseous plasmas. However, WBCT was remarkably elongate by 52.78% on the Ar + O$_2$ plasma treated LDPE film. In addition, thrombus formed on the untreated LDPE film during 30 min contact with blood was considered 100%. After plasma treatment the formation of thrombus on the surface of LDPE film was reduced significantly and Ar + O$_2$ plasma reduced formation of thrombus up to 64%. Hence, the in vitro blood compatibility analysis clearly proves that the plasma treated LDPE film could inhibit the adhesion of platelet, adsorption of blood plasma proteins and also reduced the formation of thrombus on the surface of LDPE films which may be attributed to transformation of polymer surface from
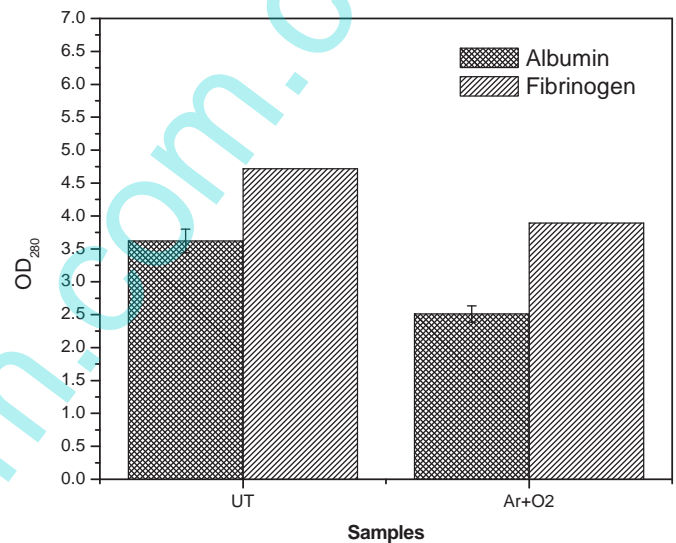

Fig. 11. Adsorption of plasma proteins on the surface of untreated and Ar + O$_2$ plasma treated LDPE film.
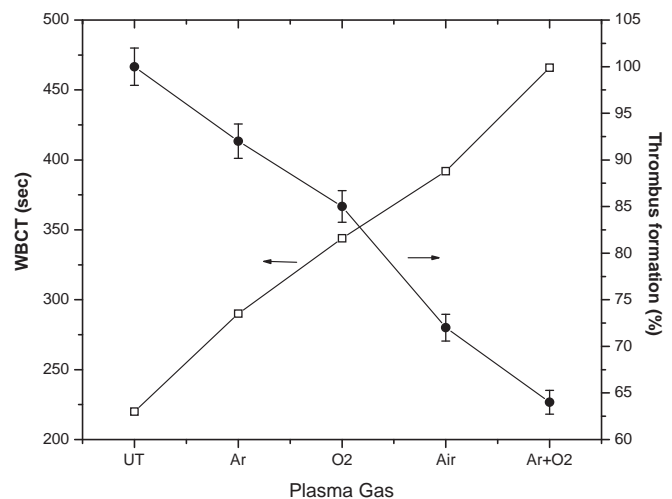

Fig. 12. Amount of thrombus formed and WBCT on LDPE film as a function plasma processing gas.

hydrophobic into hydrophilic nature by the formation of high density of polar functional groups such as C=O, C—O, OH, COO on the surface of LDPE films [11,40,41]. The hydrophilic behavior induced by the Ar + O$_2$ plasma treatment (as compared to other plasma treatments studied in the present investigation) on LDPE films play a vital role in their blood compatibility. Such a hydrophilic LDPE possessed higher surface energy which reduced the interfacial free energy between LDPE films causes the inhibition of platelet adhesion and protein adsorption. Hence the LDPE films which have higher hydrophilicity and surface energy prevents protein adsorption and platelet adhesion [42]. Hence, present surface engineering technology may offer potential application for biomaterial devices that are in direct contact with blood.

4. Conclusion

The paper investigate in detail about the influence of various gaseous plasma such as Ar, O$_2$, air and Ar + O$_2$ on improvement of surface properties LDPE film for biomedical applications using dc glow discharge plasma reactor. The hydrophilicity of LDPE films is improved markedly by the various gaseous plasmas which lead to the decrease in contact angle and increase in surface energy. The change in hydrophilicity may be due to incorporation polar function groups such as C—O, C=O/O—C—O, O—C=O/COO, O—CO—C etc which was confirmed by XPS analysis and also the gaseous plasma treatment improved the surface roughness of the LDPE films due to continues bombardment of plasma particles which was clearly examined by AFM. The increase in polar functional groups and surface roughness induced by the gaseous plasma was obtained maximum for the samples treated in Ar + O$_2$ plasma compared with other gaseous plasmas. On the other hand, the ageing process of the plasma treatment clearly showed that the effect was not permanent due to migration of polar groups into polymer bulk. However, the Ar + O$_2$ plasma-treated LDPE film is inhibited the hydrophobic recovery of LDPE film when it stored in air and water. The above significant physico-chemical changes induced by the gaseous plasma treatment contributed to enhanced/improved adhesive properties and blood compatibility of the LDPE films. This plasma based surface engineering technology has great potential for wide applications in biomedical industry.

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