Analysis of Adhesive and Surface Properties on Poly Vinyl Chloride (PVC) Treated By Dc Glow Discharge Plasma

Arjunan Suganya, Gurusamy Shanmugavelayutham*

Plasma Physics Laboratory, Department of Physics, Bharathiar University,
Coimbatore - 641 046, Tamilnadu India

Abstract: ***Polyvinyl chloride (PVC) film was treated by DC glow discharge Air and Argon Plasma. Plasma was generated by DC Power supply operating at a 300V, (Power=100W) and maintaining constant pressure 0.2 mbr. The samples were treated for different plasma exposure time from 3, 5, 7, 10,12,15,18 and 20mins. The surface properties of the PVC surface after plasma treatment were monitored by Fourier Transform Infra Red Spectroscopy (FTIR), Surface energy while the wettability effects were studied by WCA (water contact angle measurements). Surface crystallanity and Morphology was studied by X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Further the Etching rate and T-peel study were carried out for to measure the adhesive properties. We reported that the PVC film is etched, and oxygen-containing polar groups are introduced into the surface for after Argon plasma treatment than the air plasma treatment. These two processes can induce a remarkable decrease in water contact and a remarkable increase in adhesive nature of PVC films. It is shown that the improvement of hydrophilicity and adhesiveness depends on the different plasma forming gas and plasma treatment time.***

Keywords: DC glow discharge, Polyvinyl chloride, Contact angle, Etching**.**

1. Introduction

Poly (vinyl chloride) (PVC) is one of the most common thermoplastic materials employed today, with applications ranging from packaging to healthcare devices, toys, electrical wire insulation, clothes, furniture, packaging, interior decoration, building materials and the car industry [1]. PVC possesses the largest share of the medical market, constituting 40% of all dedicated polymeric materials [2]. The PVC is relatively low cost and first choice for medical applications of polymers with desirable properties such as durability, flexibility, high transparency and chemical inertness is facility of sterilization and strength responsible for their widespread application [3, 4]. Basically PVC is a rigid and hydrophobic polymer, so its affect the Wettability, adhesion, printability, biocompatibility, chemical reactivity and sensitivity to light and surface energy, in these situations, to implement the application, the modification of the surface properties [5].

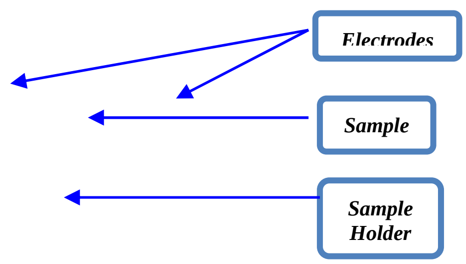
In order to overcome these problems, the surface modifications have been investigated over the last decades, trying to modify the surface property of polymeric materials. So far, approaches for improving surface wetting characteristics include chemical treatment, mechanical and flame methods, ion-assisted reaction, irradiation using a low-pressure mercury lamp (that mainly emits 254 nm light), electron beam irradiation and plasma treatment and laser irradiation. Among them, plasma treatment is considered to be an effective method and is commonly used to modify polymer surface into hydrophilic [6].

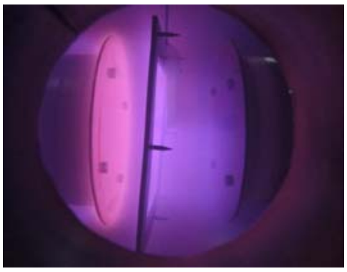
Glow discharge plasma surface treatment is a powerful method used to modify surface characteristics of thin film surfaces without affecting material bulk. Plasma is an ionized gas including both charged and neutral particles, such as electrons, ions, atoms, molecules and radicals. Depending on the gas composition and treatment conditions, ions, electrons, fast neutrals, radicals and UV radiation contribute to the polymer treatment, resulting in etching, activation and/or cross-linking [7–9]. The action of the plasma promotes the formation of free radicals that can act as interlock points for active species (polar groups) which increase surface hydrophilicity.

However, with respect to input power with other methods such as Radio frequency, microwave, ion implantation the lowest interaction energies can be achieved by DC glow discharge plasma. So comparing with other plasma treatment, to produce the DC glow discharge plasma with lower power is required. Several reports have shown the efficacy of different plasma method for the controlled modification of polymer properties.

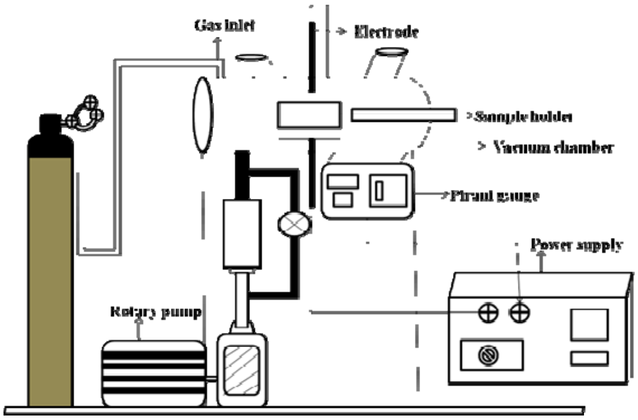
In this study, the surface properties of PVC modified by DC glow discharge plasma were investigated. An innovative idea of adopting the various gases such as Air, Ar to produce the active particles such as electrons, ions and free radicals to pre- treat the PVC surface and increase the activating energy of hydrophilic nature is proposed. In this paper it is investigated that the effect of the air and Argon plasma treatment on the PVC, gives the better hydrophilic and adhesive properties. The main objective of the present work was to investigate the extent of the different gases (Air, Ar,) and different plasma treatment time.

2. Experimental





(a)



(b)

Figure 1: (a) cross section view of the plasma inside the chamber (b) Schematic image of DC glow discharge plasma

2.1Materials and methodology

PVC $(C_2H_3Cl)_n$ powder was supplied by Sigma Aldrich, Pvt. Ltd India. The solvent tetra hydro furan (THF) was obtained from Pricison, Coimbatore, India. The purity of Ar gas, which was supplied by Sri Venkateswara gas agency, Coimbatore, India was more than 99%. The experiment done with deionized water.

2.2 Preparation of the PVC film and plasma treatment

Poly Vinyl chloride films were prepared by solvent evaporation method. PVC powder 10 wt% was dissolved in THF (Tetra Hydro Furan) solution using magnetic stirrer 2 hours for homogenous mixture and it was poured into glass Petri plates. Then, the Petri dishes were stored in reduced pressure for 48 hours. Subsequently, films were removed from the dishes and ultrasonically cleaned with ethanol for 45 min, prior to surface plasma treatment experiments. The prepared polyvinyl chloride film (0.3mm thickness) was cut into 5x5 cm for plasma treatment. The glow discharge plasma was generated in a plasma chamber with power 100 W, potential 300V and pressure 0.2mbr.The PVC film was inserted with its surface perpendicular to the discharge axis between the electrodes. The plasma treatment time was varied from 3 to 20 mins for the constant base pressure and power.

3. Results and Discussion

3.1XRD Analysis

XRD is used to investigate the crystalline nature and bulk properties of the plasma treated and untreated PVC film.

The results in Fig. 5 reveal that both the air, Argon plasma treated PVC and native PVC exhibit the presence of four large humps (amorphous halos) centered around 17°,19°,24° , and 39°, due to the diffuse scattering of amorphous PVC.

For Air and Argon plasma PVC, the amorphous humps are correspondingly stronger than the Untreated PVC and a peak at 2θ values of 17°,19°,24° , and 39°, is observed, corresponding to PVC (001), (101), (201), (202) crystal planes (JCPDS 15-0999).

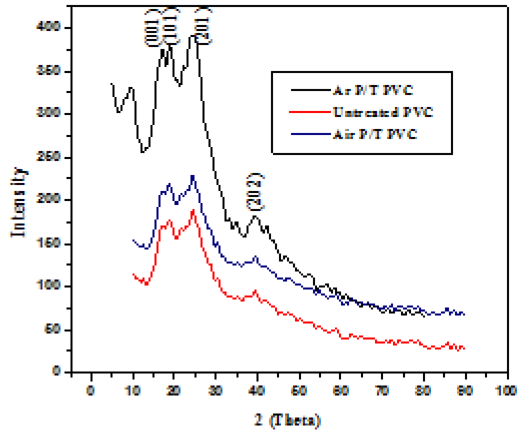


Figure 2: XRD spectra of the untreated and plasma treated PVC *film*

It is clearly seen that there is no significant change in shape and position of the diffraction peaks, except that the peak is more intense for the argon treated one. So the argon plasma treatment gives the better crystalline nature of PVC than the air plasma treated one. These results confirm that the plasma treatment improve the degree of crystallinity of the PVC film surface, and does not affect the bulk properties ***[5].***

3.2 Infrared Spectroscopy study

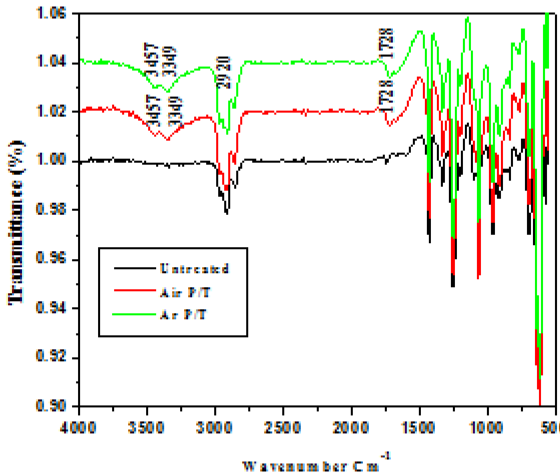


Figure 3: ATR-FTIR spectra of the untreated and plasma treated PVC film

FTIR spectroscopy in attenuated total reflection (ATR) mode is one of the methods used to bring out the finer surface information ***[10].*** We used this technique to characterize the untreated and plasma treated PVC film surface. The spectra of the air, Argon treated and the untreated samples are compared to observe the chemical changes. Data were acquired by averaging over 512 scans at 4 cm^{-1} resolution between 4000 cm^{-1} and 600 cm^{-1} (the over limit of sensitivity for ATR) with an angle of incidence of 45^0. The PVC untreated sample was used as reference background under the same conditions. The quite strong vibration band appeared at 1726 cm^{-1} and 1450 cm^{-1} which could be assigned to the symmetric and asymmetric stretching mode of carboxyl (COO–) sreching due the Air and Argon plasma treatment compared with untreated PVC. The strong vibration band at 3457 cm^{-1} and 3359 cm^{-1} could be attributed to hydroxyl (–OH) stretching which is also absent in the untreated PVC. When inert gas plasma treated polymer samples are exposed to the atmosphere after the treatment the plasma activated surface readily adsorbs the moisture that is present in the environment which is indicated by the broad band at 3400 and 1700 cm^{-1}. The exposure of the polymer to the inert gas plasma (in the present case argon) is sufficient to abstract hydrogen and to form free radicals at or near the surface which then interact to form the cross-links and unsaturated groups with the chain scission. The plasma also removes the low-molecular weight materials or converts them to a high-molecular- weight by cross-linking reactions. As a result, the weakly bound layers formed by the low-molecular weight materials are removed. ***[11,12].*** So the ATR-FTIR study confirms the plasma treatment produce the polar functional groups on the polymeric surface and makes the surface becomes hydrophilic.

3. 3Etching and Weight loss measurements

The weight of PVC films were obtained in an electronic analytical balance (Mettler AE240) before and after Air and Argon plasma treatment. The plasma etching effect described by weight loss was calculated using the following expression

$$W = \frac{(m_1 - m_2)\,x100}{m_1}$$

Where W is the weight loss rate (%), m_1 and m_2 are the masses of PVC films before and after air and Argon plasma treatment, respectively ***[13].*** Fig. 4 displays the photo induced weight loss of the plasma-treated PVC samples under atmosphere air and argon. The weight loss rates were higher for the Argon plasma-treated PVC–than for the air plasma treated PVC. The weight of the plasma treated PVC film steadily decreased with argon atmosphere, presenting 2.1%s of 20 mins treatment time while the PVC–air plasma treated film suffered only 1.8% of weight loss under identical experimental conditions. By increasing treatment time in both Air and Ar plasma treatments, weight loss of the PVC surface was increased. Bombardment by energetic particles such as electrons, ions, radicals, neutrals and excited atoms/molecules and UV–vis radiations with the surface of polymer films causes rapid removal of low molecular contaminants such as additives, processing aids, and adsorbed species resulting in etching of the surfaces. ***[14]***

Different gases cause different reaction on the polymeric surface and loss in the weight of the sample. In this present study, we found that treatment in argon plasma results in loss of weight and is depicted in Fig. 4, which increases with time of plasma exposure (20 mins) than the loss of weight after air plasma treated one (20mins). This was happens because of the Argon plasma produce more free radicals than the air plasma, so these free radicals react with the pvc surface and produce the weight loss.

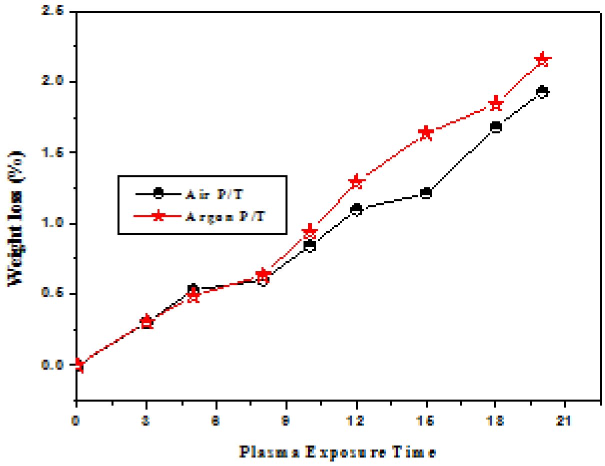


Figure 4: Weight loss (%) of plasma-treated PVC film as a function of different exposure time

3.4 Contact Angle measurements

Static contact angle (**KRUSS DSA E20 Germany**) was used to determine changes in the surface wettability after air and Argon treatment. As indicated above, all measurements were made 48 h post-treatment in order to allow for any surface relaxation to occur. Contact angles on the surfaces were measured with two liquids (distilled water and ethylene glycol). The readings are stabilized and taken 50 s after dropping. To lessen the effect of gravity, the volume of each drop is regulated to about 2 µL by a micro-syringe At least five readings were performed per sample type and the corresponding average values and standard deviations were recorded.

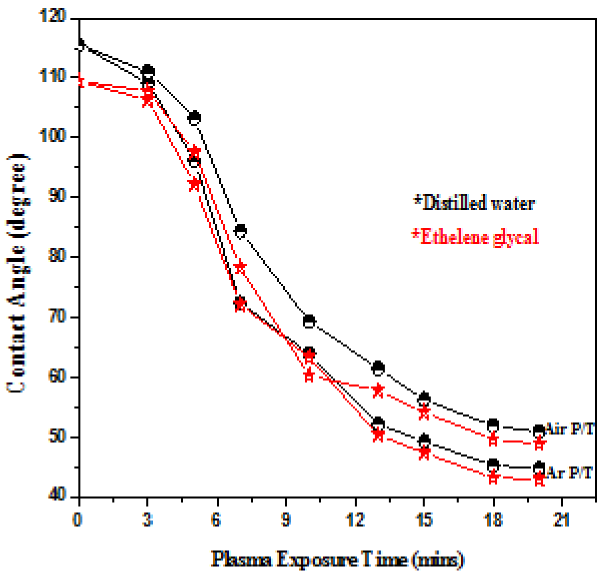


Figure 5: contact angle of plasma-treated PVC film as a function of different exposure time

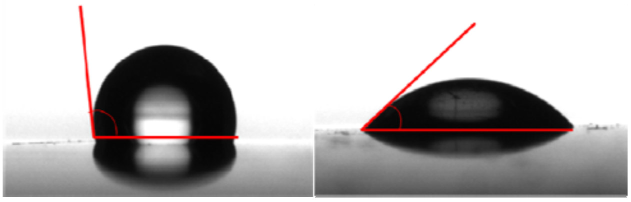


Figure 6: Before the plasma treatment (Hydrophobic) After the plasma treatment (Hydrophilic)

Fig. 5 shows the variation in the contact angle of the air and Argon PVC films for different treatment times. The initial contact angle values of the untreated PVC are 115.6 and 109.5 for water and ethylene glycol as test liquids, respectively. Beyond 3min, the decrease of contact angle of PVC in the argon plasma is more than that in the after air plasma treatment under the same conditions. For 18 mins treatment time, the reduction in the water contact angle for Argon plasma treated PVC films are 45.3(water) 43.2(ethylene glycol) and for air plasma treated PVC films are 51.9 (water), 49.6 (ethylene glycol) respectively, while the decrease of air plasma contact angle is smaller. However, the difference is rather small in the different exposure time. The decrease of contact angle suggests that the formation of hydrophilic groups on the plasma treated polymer film surfaces which may be explained as follows: the plasma creates radical species on the polymer surface, mainly through polymer chain scission or hydrogen abstraction by bombardment of plasma particles. This species can combine with oxygen in the air, thus also contributing to increase the amount of polar groups such as such as –OH, C O, COOH and COO– on the plasma treated polymer surfaces. The exposure of the polymer to the inert gas plasma (in the present case argon) is sufficient to abstract hydrogen and to form free radicals *[10]* than the air plasma or near the surface which then interact to form the cross-links and unsaturated groups with the chain scission. The argon plasma also removes the low-molecular weight materials or converts them to a high-molecular- weight by cross-linking reactions. As a result, the weakly bound layers formed by the low-molecular weight materials are removed. Hence these argon plasma treatment make the polymer surfaces become more hydrophilic compared to the air plasma treated and untreated polymer surface. *[15-17]*

3.5 T-peel analysis

The T-peel strength was measured as a function of different plasma exposure time and different gas (air, argon) to understand the effect of adhesive strength of PVC film surfaces. The values of peel strength are plotted against time of exposure in Fig. 12. It is seen that the peel strength increases linearly for different exposure time and exhibits better adhesive nature than the untreated PVC film surface. It is clearly seen that the adhesive transferred on unmodified film is 0.61Nm^{-1} and for longer exposure times (20 min) it is 1.53 Nm^{-1} (Air), 1.64 Nm^{-1} (Argon) Plasma treatment of polymeric surface is commonly believed to be effective because it creates wettable polar surfaces on which the adhesive may spread spontaneously and thus provide extensive interfacial contact. It is known that extensive interfacial contact is a necessity, but not a sufficient condition for forming strong joints. The primary function of surface oxidation techniques is to remove the weak boundary layer. In fact, if the surface oxidation alone occurred without the removal of a weak boundary layer, only weak adhesive joints would be obtained *[18]* Treatment of polymer film in a argon plasma environment incorporates more hydrophilic groups, which contribute to the increase in wettability and adhesive properties. As a result, the adhesive layer spreads on the surface more easily for argon treatment. Moreover, when these functionalities come in contact with adhesive material, it forms a weak bond due to van der Waals force. This force of attraction between the plasma treated polymer surface and adhesive material contributes to the observed increase in bonding strength. As seen from the AFM photographs, the surface becomes rough and hence the effective surface area increases after air and argon plasma treatment. Thus, the adhesion will be facilitated by all these factors.

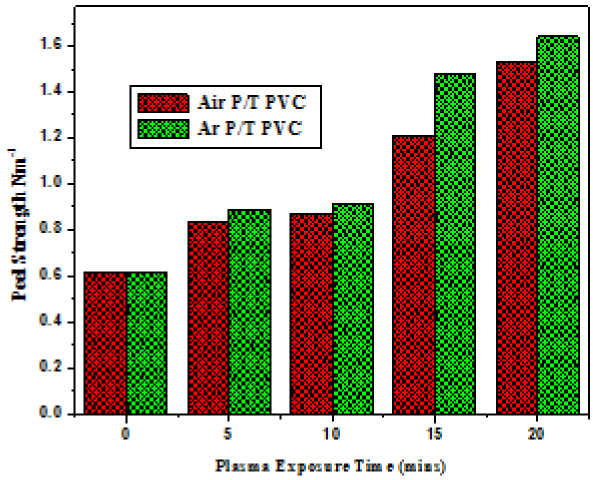
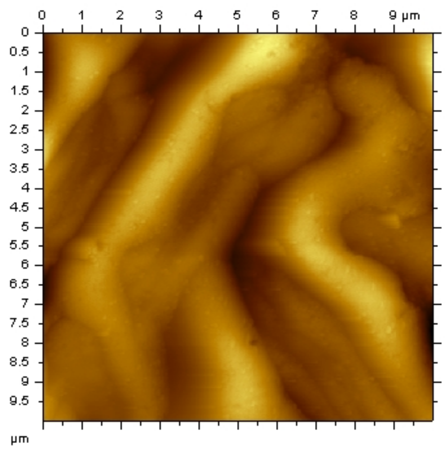


Figure 6: Adhesive properties of plasma-treated PVC film as a function of different exposure time

3.6 Atomic force microscopy

The surface morphologies of untreated and air, argon plasma treated PVC film were characterized by atomic force microscopy (AFM; Nanosurf_ easyScan2, Nanoscience Instruments Inc., AZ, USA) in the tapping mode in air. The average roughness (Ra) was calculated from the AFM images.



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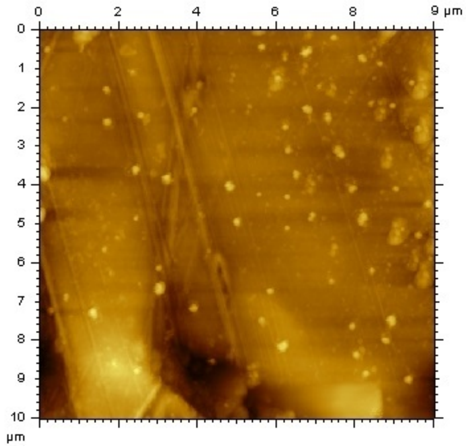

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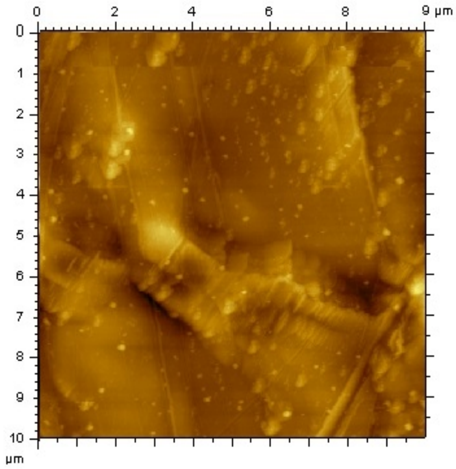

(c)

Figure 7: AFM image of untreated and plasma treated PVC polymeric film surface (a) untreated (b) air plasma treated (c) argon plasma treated PVC

The PVC surface is analyzed by AFM technique to detect the 2D surface topography and to calculate the changes in surface roughness, and the AFM images of PVC surface before and after 15 mins air and argon plasma treatment are shown in Fig. 7. As shown in Fig. 7(a), the untreated PVC surface is relatively smooth and without specific morphological aspects. A modified morphology after the homogeneous air and Argon plasma treatment is observed in Fig. 7(b), (c) which suggests that the obviously physical effect is induced by the plasma treatment. It can be seen from Fig. 5(c) that after the argon plasma treatments, the surface of PVC film shows rough morphology, and lots of hill-like protuberances than the air plasma treated PVC film surface.

So the results indicates the plasma treatment produce the surface roughness and bonding strength.

4. Conclusion

Air and Argon DC glow discharge plasma was employed to modify the surface of PVC. Both processes can significantly enhance the O to C ratio and oxygen containing functional groups on the surface. However, the optimal conditions for these two processes are different. It has also been observed that the extent of the modification is strongly dependent on the different plasma treatment time and different plasma forming gas used to excite the discharges. Depending on the process conditions, the PVC can become more hydrophilic by argon plasma treated than the air and untreated material.

Acknowledgement

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Reference

[1] Hakkarainen M. New PVC materials for medical applications the release profile of PVC/poly caprol actone-polycarbonate aged in aqueous environments. Polymer Degradation & Stability 2003;80:451–8.
[2] Anonymous. Medical Polymers Market to 2015—Polyvinyl Chloride (PVC) dominating the medical devices and packaging markets. GBI Research Global Business Intelligence; 2010.Market-to-2015-Polyvinyl-Chloride-PVC-Dominating-the- Medical-Devices-and-Packaging Markets &Report Type=Industry Report & core industry = ALL & Title=Chemicals. Accessed March 2013. 116 pp.
[3] E.C. Rangel et al. / Applied Surface Science 258 (2011) 1854– 1861 Treatment of PVC using an alternative low energy ion bombardment procedure.
[4] F. Chiellini et al. / Progress in Polymer Science 38 (2013) 1067– 1088 Perspectives on alternatives to phthalate plasticizedn poly(vinyl chloride) in medical devices applications
[5] K.N. Pandiyaraj et al. / Surface & Coatings Technology 202 (2008) 4218–4226. The effect of glow discharge plasma on the surface properties of Poly (ethyleneterephthalate) (PET) film
[6] Z.K. Wang et al. / Applied Surface Science 257 (2011) 10427– 10433 Investigation on femtosecond laser irradiation energy in inducing hydrophobic polymer surfaces
[7] E.M. Liston, L. Martinu, M.R. Wertheimer, J. Adhes. Sci. Technol. 7 (1993)1091–1127.
[8] A.C. Fozza, J.E. Klemberg-Sapieha, M.R. Wertheimer, Plasmas Polym. 4 (1999) 183–204.
[9] S.M. Mirabedini, H. Arabi, A. Salem, S. Asiaban, Progress Org. Coat. 60 (2007) 105–111.
[10] S. Guruvenket et al. / Applied Surface Science 236 (2004) 278–284.
[11] R.H. Hansen, H. Schonhorn, J. Polym. Sci. B 4 (1966) 203.
[12] H. Schonhorn, R.H. Hansen, J. Appl. Polym. Sci. 11 (1967) 1461
[13] K.N. Pandiyaraj et al. / Applied Surface Science 255 (2009) 3965–3971
[14] P.I. John, Plasma Science and the Creation of Wealth, Tata McGraw-HillPublishingCompany Limited, New Delhi, 2005, p. 109.
[15] K.N. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, C.Y. Gao, Adhesive properties of polypropylene (PP) and polyethylene terephthalate (PET) film surfaces treated by DC glow discharge plasma, Vacuum 5 (2008) 332–339.

[16] M.R. Sanchis, O. Calvo, O. Fenollar, et al., Characterization of the surface changes and the aging effects of low-pressure nitrogen plasma treatment in a polyurethane film, Polym. Test. 27 (2008) 75–83.
[17] Q. Wei, Q. Li, X. Wang, F. Huang, W. Gao, Dynamic water adsorption behaviour of plasma-treated polypropylene nonwovens, Polym. Test. 25 (5) (2006) 717–722.
[18] Clark DT, Feast WJ, editors. Polymer surface. New York: John Wiley and Sons; 1978.]