

Surface Characterization of Polyethylene Films Modified by Gaseous Plasma

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ABSTRACT: Of the several techniques available for surface modification, plasma processing has proved to be very appropriate. The low temperature plasma is a soft radiation source and it affects the material only over a few hundred angstroms deep, the bulk properties remaining unaffected. Plasma surface treatment also offers the advantage of greater chemical flexibility. The improvement in adhesion was studied by measuring T-peel strength. In addition, printability of plasma-treated PE films was studied by cross test method. It was found that printability increases consid-

erably for plasma treatment of short duration. It was therefore thought of as interesting to study the surface composition and morphology by contact angle measurement, ESCA, and AFM. Surface energy and surface roughness can be directly correlated to the improvement in above-mentioned surface-related properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 449–457, 2007

Key words: PE; plasma; T-peel strength; printability; surface energy; ESCA; AFM; ATR-FTIR

INTRODUCTION

Polymers with well-defined functional surface properties are of interest for development of newer technology.¹ Many attempts, involving physical and chemical interaction, have been made to improve the surface chemical and mechanical properties of polymer.² In the polymer world polyethylene (PE) has diverse applications because of abundant supply, good chemical resistance, and low cost. It is widely used in packaging applications directly or in the form of laminates with aluminum foil, paper, etc. However, good adhesion between the two substrates is vital for high strength laminates. Generally the presence of polar groups and surface topography play a very important role for obtaining good adhesion and hence good mechanical properties of laminates. PE has limitations to its adhesion properties because of their nonpolar nature³ and is also difficult to print or paint.⁴ Various attempts have been made to improve the adhesion property of PE, e.g., flame treatment,^{5,6} corona discharge,^{7,8} plasma treatment,^{9–11} and chemical etching.^{12–14} Such type of surface treatment not only changes the chemical composition but also the morphology of the surface.³ Of the above-mentioned methods low temperature plasmas have been widely used to modify polymer surface properties such as wettability and adhesion without changing the bulk

properties.^{15,16} Plasma technologies are successfully applied in the surface modification of polymers, either by surface activation of chemically inert polymer surfaces or by coating a substrate with a thin functional plasma polymer layer.¹⁷ The presence of reactive functional groups and surface roughening of the polymers enhances the adhesion of PE.³ A low-pressure plasma comprises a complex mixture of particles (ground-state and excited neutrals and ions, molecule and fragments and electrons) and a broad spectrum of electromagnetic radiation.¹⁸ The interaction of all these components with the polymer surface gives rise to multifarious reactions, resulting in a wide variety of different chemical structure in a shallow surface layer.¹⁹ Plasma modification is a very fast, clean, and environmentally safe (gas-dependant though) method and allows simultaneous uniform treatment of even complex 3D shapes. Moreover, it is possible to perform large-scale uniform modifications by plasma technology.²⁰

In the present investigation the surface of PE film was modified in air plasma with an aim of improving its adhesion and printability.

The samples were characterized using various methods such as electron spectroscopy for chemical analysis (ESCA), ATR-FTIR, atomic force microscopy (AFM), and contact angle to find out the surface energy of plasma-processed PE films. The adhesion of PE film before and after treatment was investigated by T-peel test method. Similarly, the printability was measured for different time of treatment by cross test method.

The mechanism of improvement in the above-mentioned surface-related properties of PE films are discussed.

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EXPERIMENTAL

PE films having a thickness of 40 μm were supplied by Reliance, India. Before treatment the films were cleaned with acetone in an ultrasonic bath for 6 min and then dried in air. PE films were partially crystalline in nature.

A typical bell jar type plasma reactor having a height of 30 cm and a diameter of 30 cm was used. The two electrodes were capacitively coupled to the RF source capable of giving power output up to 100 W. Various ports were fitted on the base plate for gas and monomer inlet. Pirani gauge was fitted onto the top plate. To confine the glow discharge to the specific volume, the magnetron was mounted on the base plate. Because of magnetron, the plasma confined to a volume of 500 cm^3 and the maximum sample that can be uniformly treated in our plasma chamber is 10 cm \times 10 cm. However, PE films of size 8 cm \times 8 cm were used in the present work. The working pressure was adjusted to 0.2 mbar and gas flow rate to 15 SCCM. The details of the plasma processing chamber has been reported else where.²¹

Weight loss

Weight loss is determined by the following formula:

$$\text{Weight loss} = \{(W - W_0)/W_0\} \times 100$$

where W_0 is the initial weight and W is the weight after treatment.

The surface energy (SE) was calculated by measuring the angle of contact using the sessile drop method. Contact angle (CA) was measured with reference to four different liquids, namely, water (W), glycerol (G), formamide (F), and ethylene glycol of known polar (γ_L^p) and disperse (γ_L^d) components. The SE was calculated from CA measurement using Fowkes' approximation. The detailed calculation is given elsewhere.²¹ At least 10 readings were taken at different places and an average value was determined. Contact angle measurements were done immediately after the plasma treatment. Samples used to study ageing effect were stored in desiccators.

To study the effect of plasma on adhesion, a standard T-peel test (ASTM D 1876) was carried out using Instron Instrument (model 1026) 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 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 centimeter of sample width (the

width of the sample was 2.5 cm.). Five samples were tested for one set and an average value was obtained, which is reported here. Printability was measured by Cross Test method (ASTM D 3359). Ink manufactured by Hindustan Inks and Resins was used. Average value for ten tests was obtained.

The ATR-FTIR spectra were recorded by using a Perkin-Elmer Paragon 500 FTIR spectrometer. A KRS-5 crystal with an angle of incidence of 45° was used for recording the ATR spectra. ATR spectra were recorded immediately after plasma treatment. For every ATR spectrum 64 scans were taken with a resolution of 4 cm^{-1} .

The morphology of the sample was observed using AFM. Nanoscope III manufactured by Digital Instruments was used for this purpose. The AFM was operated in contact mode with cantilever tip made up of silicon. Thermo VG Scientific MultiLab 2000 was used for ESCA recording and analysis.

Curve fitting: Lorentzian nonlinear curve fitting program of ORIGIN-6 software was used.

Principles of ESCA

Surface analysis by ESCA is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy of the ejected electrons. Monochromatic Mg K α (1253.6 eV) or Al K α (1486.7 eV) X-rays are usually employed as source of irradiation. When the sample is irradiated with such monochromatic X-rays, photoionization of the inner core electrons will occur. The resulting photoelectron will have a kinetic energy given by,

$$E_k = h\nu - E_B - \Phi_s$$

Here E_k is the kinetic energy of emergent electron, $h\nu$ is the energy of incident X-rays, E_B is the binding energy of core electron, and Φ_s is the spectrometer work function.

Since $h\nu$ and Φ_s are known, and E_k can be measured, E_B , i.e., binding energy of core electron, can be calculated. Because each element has a unique set of binding energies, ESCA can be used to identify and determine the concentration of the elements on the surface.²²

RESULTS AND DISCUSSION

Etching and weight loss study

It is believed that the interaction of ions, electrons, and energetic species of neutral atoms causes rapid removal of low molecular contaminants such as additives, processing aids, and adsorbed species, which is also called as "plasma cleaning." After plasma cleaning, ablation of polymer chains starts. Bombardment

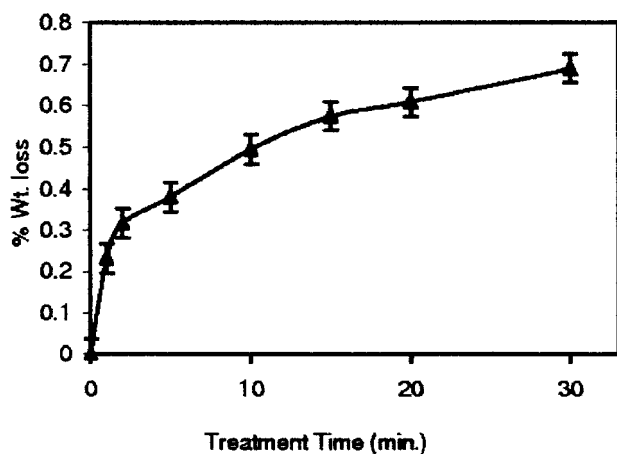


Figure 1 Percent weight loss of air plasma treated PE film.

by energetic particles, neutrals, VUV radiations, electrons, and ions results in etching of the surface. This is either due to the physical removal of molecules of fragments or due to the breaking up of bonds, chain scission, and degradation processes. The gases evolved in the reaction may be pumped out. This causes loss in the weight. In our studies we found that treatment under air results in loss of weight, which increases with time of treatment and is depicted in Figure 1. The etching process is predominant on the amorphous region of the surface than on the crystalline regions.²³ Therefore it is possible that the initial rates of etching are more rapid. Once all the etchable amorphous materials on the surface have been removed, the remaining crystalline and tightly bound amorphous material cannot be removed easily, causing decline in the etching rates.

Surface analysis of plasma-treated PE films using AFM

The morphology of the films was investigated using AFM. Figure 2(a) shows the surface of the control PE film which is very smooth. The AFM photomicrographs of plasma treated PE films are shown in Figure 2(b,c). It was found that the surface roughness increases as the treatment time is increased. Most of the amorphous portion is etched out in 15-min treatment time, as can be seen in Figure 2(c), resulting in a rough surface morphology. This results in an apparent increase in the surface area, causing improvement in wettability, bonding strength, and printability.

ATR-FTIR analysis of plasma-treated PE film

It is well known that treatment of polymer film in gaseous plasma incorporates hydrophilic functionality.²⁴ To see the changes in the chemical structure,

FTIR spectroscopy was employed. The FTIR spectra of untreated and air plasma treated PE film are shown in Figure 3. Table I shows the peak assignment of untreated PE film. When PE film is treated in air plasma the following changes take place, as shown in Figure 3(b,c). Bands at 1697–1700 cm^{-1} confirm the presence of $>\text{C}=\text{O}$ of $-\text{COOH}$ group and 1620–1622 cm^{-1} correspond to $>\text{C}=\text{O}$ group adjacent to an olefinic double bond or enolic $>\text{C}=\text{O}$ group. Peaks in the region 1700 and 1730 cm^{-1} correspond to $\text{C}=\text{O}$. Peak at 2200 cm^{-1} corresponds to $>\text{C}=\text{O}$ group. A weak maximum at 1400 cm^{-1} is related to COO groups. The IR spectra of 900–950 cm^{-1} show out of plane deformation carboxyl OH as well as a small peak of alkyl peroxide at 870 cm^{-1} .²⁴ The formation of new functional groups takes place in the remote regime. OH stretching bands are observed in the region 3000–3500 cm^{-1} . Various bands are observed in the

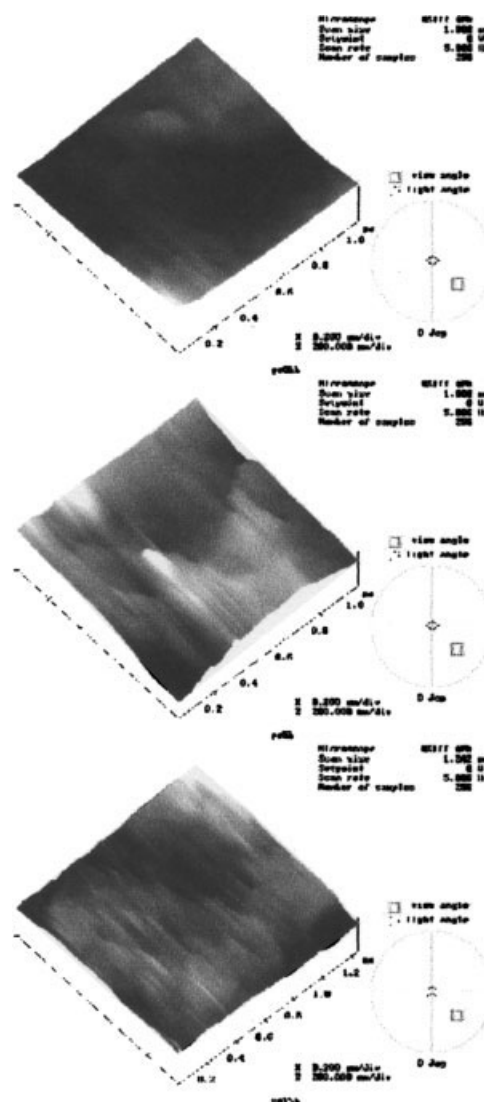


Figure 2 AFM photomicrograph of (a) control PE film, (b) PE film treated in air plasma for 5 min, and (c) PE film treated in air plasma for 15 min.

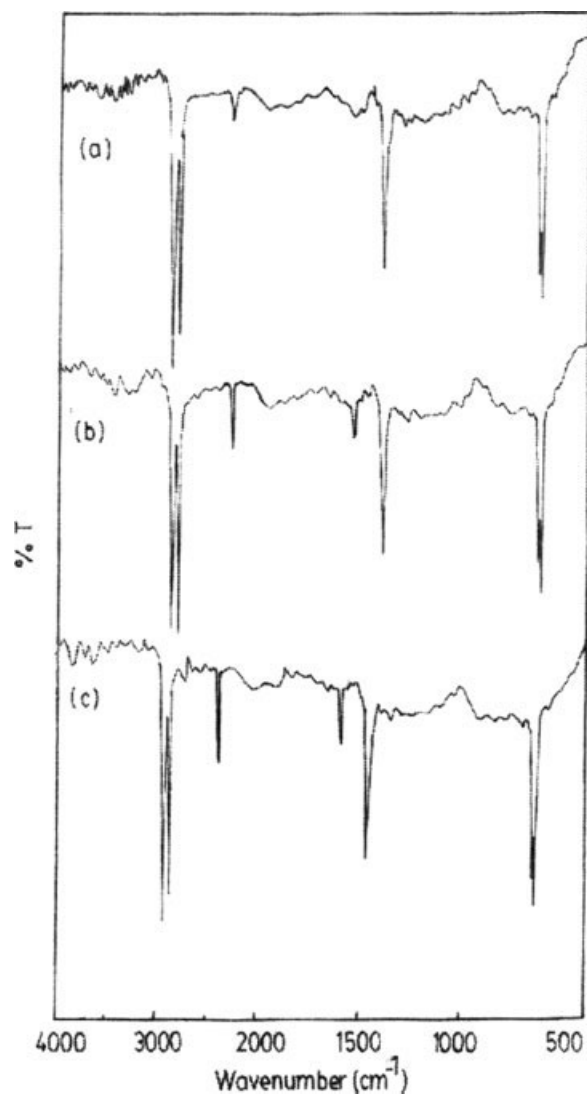


Figure 3 ATR-FTIR spectra of (a) control PE film, (b) PE film treated in air plasma for 5 min, and (c) PE film treated in air plasma for 15 min.

region between 1300 and 1000 cm^{-1} corresponding to C—O.²⁵

ESCA analysis of plasma-treated PE

Figure 4(a) shows C1s spectra of control PE film. Control PE film shows only one peak at 285 eV, which

TABLE I
Assignment for Absorption Peaks Observed in FTIR Spectrum of PE

| Band (cm^{-1}) | Peak assignment |
|---------------------------|----------------------------|
| 2900 | CH stretching |
| 2838 | CH ₂ stretching |
| 1467 | CH ₂ bending |
| 1370 | CH ₂ bending |
| 1290 | CH ₂ bending |
| 723 | CH ₂ bending |

corresponds to the carbon in CH₂. Figure 4(b,c) show C1s spectra of PE film treated in air plasma for 5 and 15 min. The first peak corresponds to C—C at 285 eV and the second peak corresponds to C—O at 286.2 eV which remains almost the same when the treatment time is increased from 5 to 15 min.²⁶ This shows that a large number of oxygen polar functional groups are introduced (from second peak) onto the PE surface when treated with air plasma. Plasma treatments are widely used to improve the wettability of polymeric films. Surface energy is an indirect measure of polar groups. The atomic concentration of C1s element decreased to 86.24% (Table II).

Figure 5(b,c) show O1s spectra of PE film treated in air plasma for 5 and 15 min. The O1s shows two peaks for air plasma treated PE film. First peak

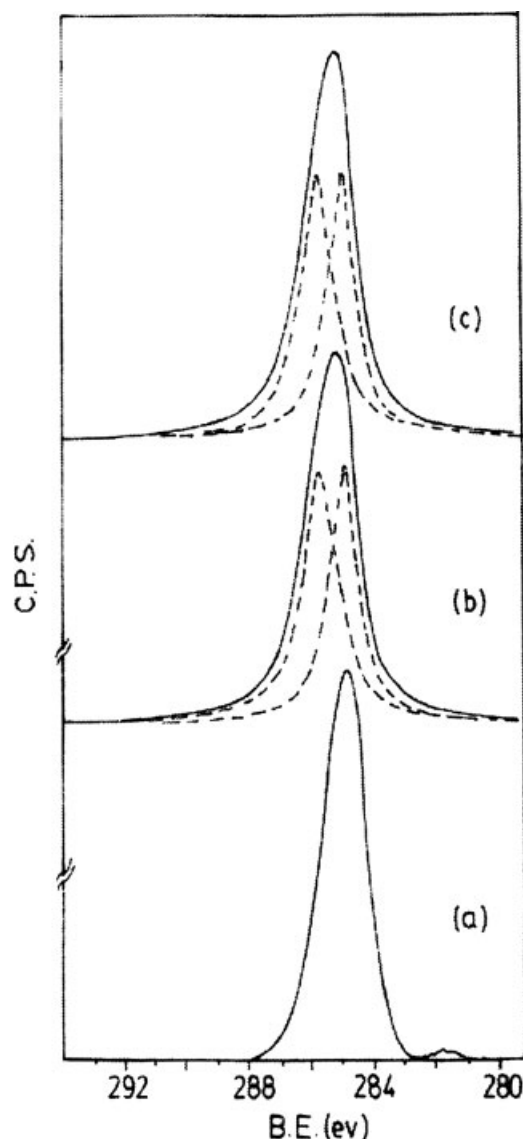


Figure 4 C1s spectra of (a) control PE film, (b) PE film treated in air plasma for 5 min, and (c) PE film treated in air plasma for 15 min.

TABLE II
Percentage Atomic Concentrations of Various Elements
in the PE Sample Subject to Plasma
Process Processed PE Film

| Sample | C1s | O1s | N1s |
|-----------|-------|-------|------|
| PE cont | 100 | — | — |
| PE 5 min | 87.26 | 11.93 | 0.81 |
| PE 10 min | 86.24 | 12.92 | 0.84 |

corresponds to O=C at 532.5 eV and the other one corresponds to O—C at 533.6 eV.²⁶ The incorporation of oxygen moieties onto the polymer surface is also due to the post plasma exposure of samples to atmosphere. This observation has been supported through our previous discussion of C1s spectra wherein it was indicated that contribution due to —O—C has increased. The atomic concentration of O1s element has increased to 12.92%.

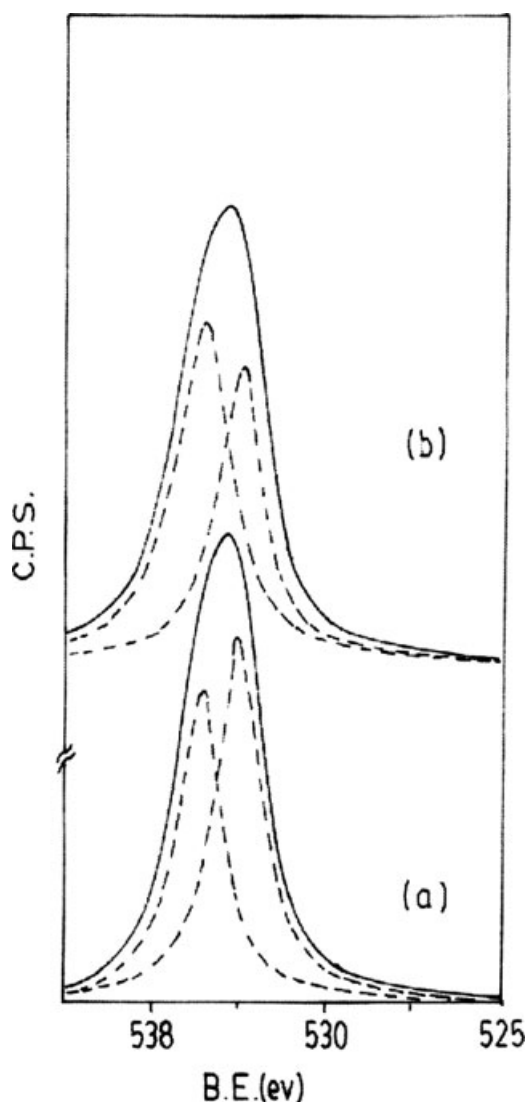


Figure 5 O1s spectra of (a) PE film treated in air plasma for 5 min, and (b) PE film treated in air plasma for 15 min.

N1s spectra of PE treated in air plasma for 5 and 15 min are shown in Figure 6(b,c) respectively. The N1s shows two peaks for air plasma treated PE film first peak corresponds to N=C at 400 eV and another correspond to N—C at 401.6 eV.²⁶ Since PE film was treated in air plasma, it is obvious that some nitrogen-containing group will be incorporated onto the surface. For control PE, there is no peak due to N1s spectrum, but for the air-treated, there appears to be a small peak. It means that nitrogen is getting incorporated onto the PE surface. The atomic concentration of N1s element has increased to 0.84% (Table II).

Surface energy measurements

One can observe a pronounced rise in SE (γ_s) over a short period of plasma treatment, as shown in Figure 7, and then steadily with the plasma treatment

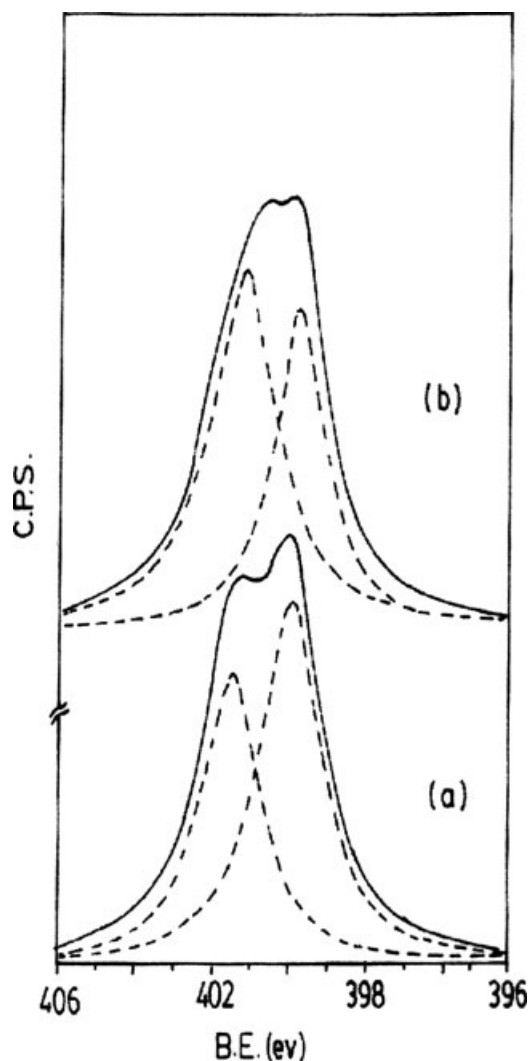


Figure 6 N1s spectra of (a) PE film treated in air plasma for 5 min, and (b) PE film treated in air plasma for 15 min.

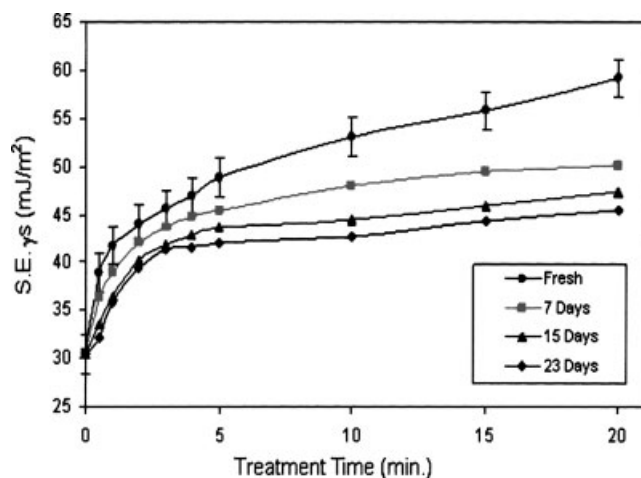


Figure 7 Variation of surface energy with time for air plasma treated PE films.

time. Similar kind of trend is observed in the increase in polar components (γ_s^p), as shown in Figure 8. It is mainly due to the incorporation of polar groups such as CO, COO, OH, etc.²⁷ However, there is a marginal change (± 3 units only) in disperse components (γ_s^d) up to 5 min of treatment time and then there is a decrease in its value for higher treatment time, as shown in Figure 9. Hence the increase in SE (γ_s) is mainly due to the incorporation of polar groups onto the PE surface. The wettability, and hence SE, of PE films is increased because of the interaction between the hydrogen bond and dipoles in the vertical direction of the interface.²⁸ The properties such as wettability, adhesion, printability, etc. strongly depend upon the SE.

Ageing behavior

It is often observed that the properties imparted by the treatment changes with time. This phenomenon is commonly called as ageing, which takes place possi-

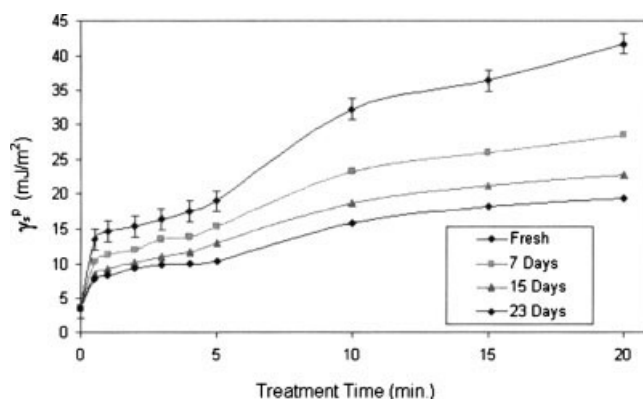


Figure 8 Variation of polar components of surface energy with time for air plasma treated PE films.

bly due to surface contamination, orientation of polar groups, blooming of additives, and absorption of ubiquitous contaminants. In many applications a hydrophobic polymer is converted into a hydrophilic one by suitable treatment and when a sample is stored in air, a driving force exists to restore the original structure or at least lower the SE of treated surface. As a result the high energy polar groups can be lost. It is shown that the hydrophobic recovery depends on the polymer and on treatment.²⁹ This ageing itself can be considered as one of the steps of the treatment in the sense that influences the outcome as determined by the properties imparted to the polymer surface.

In the present study, it was observed that the hydrophobic recovery (decrease in SE) is less for shorter treatment time. Similarly it can be observed that there is exponential relation between the hydrophobic recovery and period of ageing. A major recovery can be seen in the first 7 days of ageing. The hydrophobic recovery from 15 to 23 days is not very much when compared with the initial 7 days, as shown in Figure 7. It can be seen that there is a decrease in polar groups with ageing. Polar groups have major role in the SE and hence the nature of plots of SE is the same as that of polar groups, whereas the value of disperse components in all ageing and different times of treatment is ± 5 the value for untreated one. Though there is a decrease in SE because of ageing, it is clear from Figure 7 that the SE value of aged samples is still sufficiently high in comparison with the untreated one. Hence such films can be suitable for further applications.

Surface roughness

To control wettability and adhesion of polymers, numerous surface modification techniques such as exposure to flames, chemical modification, corona discharge, and low pressure gas plasma are used. In

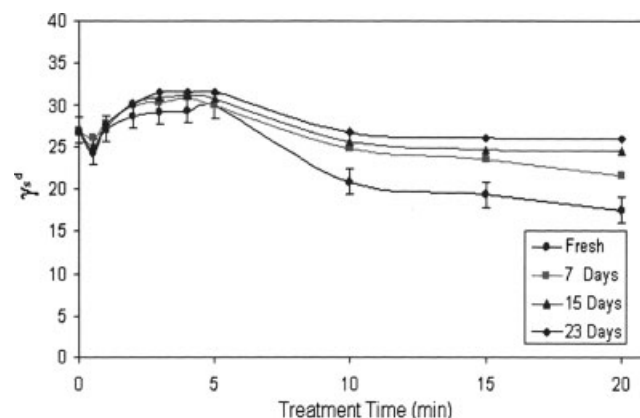


Figure 9 Variation of disperse components of surface energy with time for air plasma treated PE films.

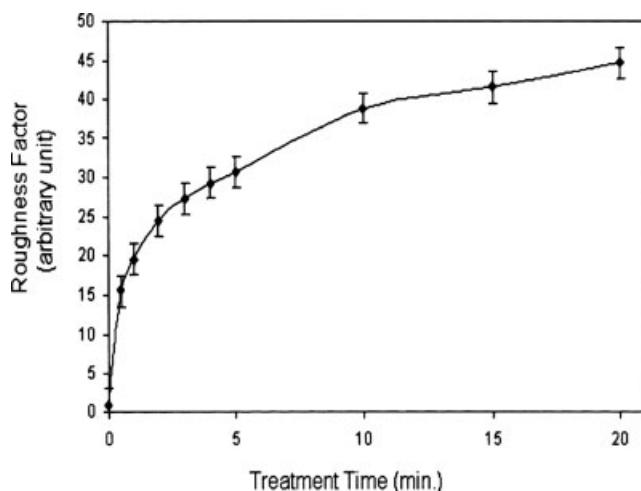


Figure 10 Variation of surface roughness with time for air plasma treated PE films.

many cases the wettability is regulated by changes in the chemical composition of the surface. But it has long been recognized that the surface roughness can be important for wettability. Wenzel's³⁰ equation (3) helps us to discover the influence of surface roughness on CA. He introduced the roughness factor R into the Young's equation because he argued that in case of solid surface, the interfacial tension γ_{SV} and γ_{SL} should not be referred to the geometric area, but to actual surface area, and thus

$$R = \frac{\text{True surface area}}{\text{Geometric surface area}} \quad (1)$$

or

$$R(\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \theta_w \quad (2)$$

For the CA on a rough surface, Wenzel obtained

$$R = \frac{\cos \theta}{\cos \theta^*} \quad (3)$$

where R is the ratio of the treated area to the untreated area. Based on the equation it can be predicted that roughness should have a major effect on CA and hence wettability of surface.

In the present study, the surface roughness was determined from CA measured with reference to water. From the Figure 10 it can be seen that surface roughness increases as treatment time is increased. This surface roughness can also be confirmed in Figure 2(b,c). The roughness was found to increase considerably with the plasma-exposure time. The surface roughness can enhance the mechanical interlocking, and this has relatively a strong influence on the adhesive properties.³¹

Adhesion

Adhesion is the joining of two different materials, whereas cohesion is the joining of different parts made by the same materials.³² A good adhesion can be guaranteed if the adhesive adequately wets the substrate of the two materials. Therefore, adhesion and wettability are two related properties.³³

Work of Adhesion

The CA data may be used to evaluate the work of adhesion between PE film and the substrate. The equilibrium CA for a liquid drop on an ideally smooth, homogeneous, and nondeformable surface is related to the various interfacial tensions by Young's equation.³⁴

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (4)$$

where γ_{LV} is the surface tension of the liquid in equilibrium with its saturated vapor, γ_{SV} the surface tension of the solid in equilibrium with its saturated vapor, and γ_{SL} the interfacial tension between the solid and the liquid.

Moreover, the work of adhesion W_{adh} is given by the following equation:³⁴

$$W_{adh} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (5)$$

Combining eqs. (4) and (5),

$$W_{adh} = \gamma_{LV}(1 + \cos \theta) \quad (6)$$

Work of adhesion was calculated from CA with reference to water and depicted in Figure 11. It is clear from the Figure 11 that there is a pronounced rise in the work of adhesion over a short period of plasma treatment and then steadily with the plasma treatment time.

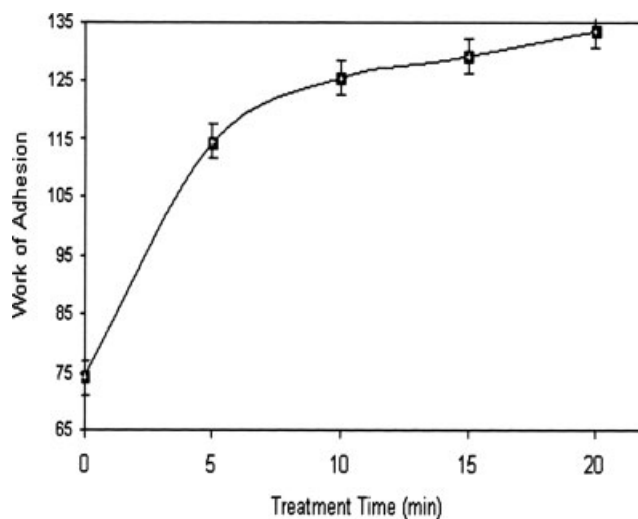


Figure 11 Variation of work of adhesion with time for air plasma treated PE films.

T-peel strength

Treatment of polymer film in plasma environment incorporates hydrophilic groups such as hydroxyl, peroxy, carbonyl, amine, amide, etc. These functional groups contribute for the increase in wettability and as a result adhesive layer spreads on the surface more easily. Moreover, when these functionalities come in contact with the adhesive material a weak bond is formed due to van der Waal's forces. This force of attraction between plasma-treated polymer surface and adhesive material contributes for the observed increase in bonding strength. To understand the effect of plasma treatment on bonding strength of PE films, treated films were subjected to standard T-peel test. The variation in the peel strength for samples treated in air plasma is shown graphically in Figure 12. It may be seen that the peel strength increases with time of treatment in plasma right up to 20 min of treatment time. This is caused on account of surface roughness and an increase in SE due to plasma treatment. As seen from the ESCA and ATR-FTIR studies, plasma treatment creates polar groups [such as $-\text{CO}-$, $-\text{COO}-$, $-\text{OH}$] on the surface as a result of which the CA of water decreases, showing that the surface is now more hydrophilic. Also from Figure 2(b,c) it can be seen that the surface becomes rougher and hence the effective surface area was found to have increased after plasma treatment. Thus the adhesion will be facilitated by all these factors.

Printability

It is well known that before printing is made, polymers are subjected to corona treatment.³⁵ This treatment requires very high power and the processing cost is also high. In the present study we have modified the surface of PE films using cold plasma to have a good printability and good adhesion to ink. The

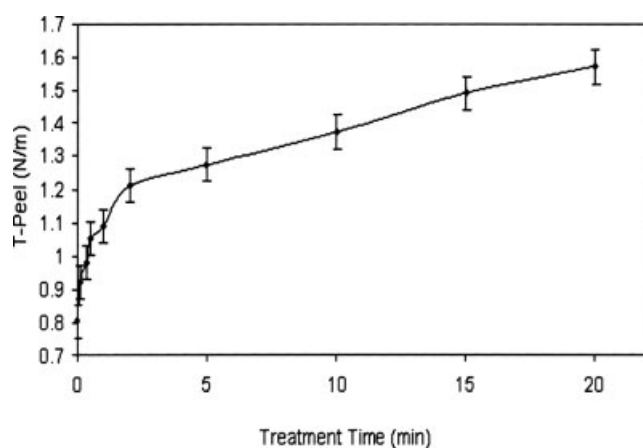


Figure 12 Variation of T-peel strength for air plasma treated PE films.

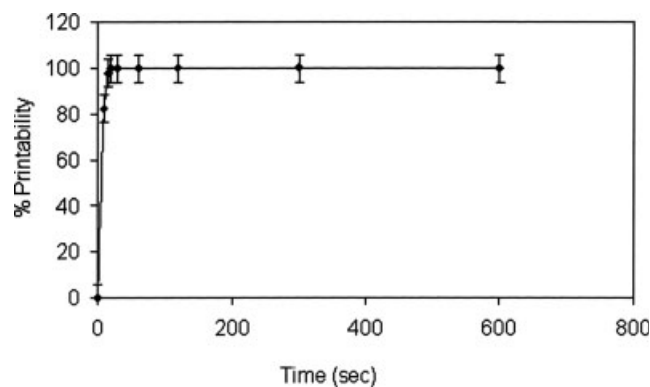


Figure 13 Changes in printability with time of air plasma treated PE film.

printability was measured using Cross Test method. This method offers a simple way to measure the degree of adhesion of the ink (coating) on a substrate.

The improvement in printability of air plasma treated PE films is shown in Figure 13. For control PE film the ink adhesion was almost 0%, which improved to more than 80% for a treatment time of 5 s only. This is a very sharp rise in the value of percent printability of plasma processed PE films. After 15 s, there is slow improvement in the value of percent printability and the increase continues up to 5 min.

Improvement in ink adhesion is generally observed after plasma treatment.²⁷ Such modifications are basically observed because of possible improvement in wettability due to incorporation of polar groups onto the surface and phenomenon of plasma etching in turn increases an effective area for contact for spreading of ink material. Both the processes contribute for improvement in ink adhesion. The incorporation of polar groups onto the plasma-processed surface is supported by ESCA and ATR-FTIR analysis. The AFM morphology shows that the surface becomes rough after plasma treatment. Anchoring of ink takes place at the rough surface, causing better adhesion.

CONCLUSIONS

Plasma treatment can greatly change the surface chemistry and the topography of PE films. Air plasma treatment incorporates polar functional groups onto the surface of the polymeric films, causing a rise in solid surface free energy. The effect of ageing (hydrophobic recovery) was found more prominent for longer treatment time.

The plasma processes generate wide range of reactive species in the treated system, which undergo consecutive chemical reactions, creating thus several oxygen based functionalities at the interface (carbonyl, carboxyl, peroxides, etc.). Simultaneously, the vigorous increase of the surface roughness was found as a result of the successful plasma etching. Mechanical

interlocking due to surface roughness and chemical interaction and bonding due to generation of active polar groups, as observed by ATR-FTIR and ESCA studies, are responsible for excellent surface-related properties such as autoadhesion, bonding strength, ink adhesion, etc.

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