Plasma-Induced Surface Modification and Adhesion Enhancement of Polypropylene Surface

N. V. Bhat, D. J. Upadhyay

Applied Physics Division, University Department of Chemical Technology, Matunga, Mumbai-400 019, India

ABSTRACT: Unoriented (UPP) and biaxially oriented (BOPP) polypropylene films were treated under radio frequency plasma of air, nitrogen, oxygen, and ammonia. Surface modification of polypropylene films was investigated by using surface energy measurement and attenuated total reflection (ATR)-FTIR spectroscopy. Surface energy of air and nitrogen plasma-treated polypropylene film increased for shorter treatment time and then decreased and attained an equilibrium value. Such changes in surface energy were not observed for oxygen and ammonia plasma-treated polypropylene film, which increased to an equilibrium value. ATR-FTIR studies revealed characteristic differences in the absorption spectra for short-duration and long-duration treatments. From the relative intensity change in the C—H stretching vibration, the mechanism of surface chemical reaction could be inferred. Studies regarding the durability of surface modification due to plasma treatment were evaluated by investigating surface energy of samples aged for 2 months. Treated films subjected to peel strength measurement showed improvement in bondability for UPP and BOPP film by hydrophilic surface modification accompanied by surface crosslinking. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 925–936, 2002

Key words: polypropylene; plasma treatment; surface energy; ATR-FTIR; adhesion

INTRODUCTION

Polypropylene (PP), because of its strong hydrophobic nature, is difficult to adhere to many substrates. As PP is superior in quality in terms of gas permeability to conventional packaging materials,[1] it is essential to improve its bondability to improve its usefulness. Various techniques are available for surface modification such as chemical, flame, corona, and plasma treatment, etc.[2–5] Among the various methods, plasma is an important method for inducing hydrophilic modification and improving adhesive properties of polymeric substrates.[6–23] Plasma modification, being limited to the depth of a few microns, induces physical and chemical changes on the surface without affecting the bulk.

Gas molecules such as air, nitrogen, oxygen, and ammonia in a plasma reactor are activated by the collision with electrons, positive ions, and metastable species that subsequently attack on a polymeric surface.[8] Oxides and nitrides thus formed lead to accomplishment of surface hydrophilic modification. Therefore, which gas used for the plasma treatment is closely related to the hydrophilicity caused by plasma. Commonly used gases, which can incorporate hydrophilic group such as hydroxyl, carbonyl, carboxyl, peroxy, amine, and amide, are air, nitrogen, oxygen, and ammonia.[18–20] The activated species, which are generated during plasma treatment, interact with the surface and get deactivated by the mechanism of energy transfer. Since these species are sufficiently energetic to cause surface etching, Kim and Goring[24] and Badyal and Rayan[25] reported improvement in bondability by inducing surface roughening on PP film. The study carried out by Hansen and Schongorn[26] indicates crosslinking initiated by activated species of inert gas (CASING) as one of the reasons for improving surface cohesive bonding. Hudis[27] reported gelation of polyethylene (PE) and PP induced by hydrogen glow discharge, showing PE causes more crosslinking than PP. Seven adhesion theories were discussed by Chung,[28] showing bondability improves by intimate molecular contact and by inducing attractive force between the substrates. Molecular contact can be improved by inducing surface crosslinking, whereas attractive force between the substrates can be improved by surface hydrophilic modification. Treating the polymeric surface in a plasma condition satisfies both the criteria.

In the present investigation, PP films of two varieties [i.e., unoriented (UPP) and biaxially oriented (BOPP)] were subjected to treatment of air, nitrogen, oxygen, and ammonia plasma to make the surface hydrophilic. Along with the change in wettability by surface energy measurement, an increase in bondability by peel test is also investigated. UPP film was found to be 42% crystalline and BOPP was 81% crystalline, as observed from X-ray diffraction (XRD) measurements using the method of Weidinger and Her-

Correspondence to: N. V. Bhat (bhatnarendra@hotmail.com).

mans.[29] Because UPP in its less crystalline form is expected to give much better detail about surface chemical reaction, it was therefore thought important to carry out attenuated total reflection (ATR) analysis only on UPP films. Studies also include aging of treated films by investigating surface energy of samples 2 months after the treatment. To correlate plasma modification of UPP film, similar experiments were also carried out with BOPP film.

EXPERIMENTAL

UPP and BOPP films of commercial variety were obtained from Reliance Industries Ltd.; the thicknesses of the film were 85 and 18 μm, respectively. Both films were of isotactic variety. Prior to plasma treatment, films were washed in ultrasonic bath with acetone for 9 min and then dried in air. All chemicals used were of AR grade. Gases used for plasma treatment were of commercial variety. The plasma-processing chamber consisted of a Bell jar with a diameter of 30 cm and a height of 30 cm. The top and base plate has various ports. The magnetron was mounted on the base plate. Also, the inlets for the gas and the monomer were provided on the base plate. The gas inlet was externally connected to mass flow controller (unit model URS-100). The top plate consists of a port on which Pirani Vacuum Gage made by Hind High Vacuum Ltd. (Banglore, India) is mounted.

Two stainless steel parallel plates, inside the chamber, were capacitively coupled with radio frequency (RF) source. The frequency of the power source was 13.56 MHz and can deliver a power of 100 W. Treatment time of the sample varied from 1 to 20 min. Before plasma treatment, the chamber was purged four times with gas and evacuated to a pressure of 0.05 mbar. The working pressure was adjusted to 0.1 mbar when the flow of the gas was 10 standard cubic centimeters per minute (SCCM). % Weight loss due to plasma treatment was calculated by using a Mettler AE 240 five-digit balance. Films were weighed before and after plasma treatment, and an average of five readings was taken for each sample. The error in the measurement was 0.012%.

The surface energy was determined by measuring the dynamic contact angle by sessile-drop method. The liquids used for calculating surface energy are water, glycerol, and formamide of known γ^p (polar coordinate) and γ^d (disperse coordinate), because other commonly used liquids, such as benzyl alcohol and diethyl phthalate, give complete spreading on the polymer surface. A small drop of double-distilled liquid was placed on the polymeric surface with a microsyringe and observed through a microscope. The height (h) and radius (r) of the spherical segment were measured and the angle was calculated by[30]

$$\text{Contact angle} = \sin^{-1}[2hr/r^2 + h^2]$$

At least five readings were taken at different places and an average was determined. From the value of slope and intercept, surface energy of polymeric film was calculated using Fowkes approximation.[31] The error in the measurement of surface energy was ±1.80 mJ/m^2. Surface energy of treated films was observed immediately after the plasma treatment.

The ATR-FTIR of the film was obtained 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. To minimize possible shift of the IR band and also to get relative change in absorbance with respect to control (untreated film), for every plasma treatment, ATR spectra of control film was taken, and also, care was taken to align the film in same direction as used for control. UPP films were treated for 3 and 10 min for ATR analysis and spectra were recorded immediately after plasma treatment. For every ATR spectra, 350 scans were taken with a resolution of 4 cm^{-1}.

The adhesion test was performed by using an Instron tensile tester 1026. The standard T-Peel test was used with adhesive tape by using standard test method.[32] An area of 2.5×4.5 cm^2 was used for the test. For measurement of peel strength, samples were treated for 15 s to 15 min. For every treatment, three specimens were prepared for peel strength measurement and a mean value was taken. The error in the measurement of peel strength was $\pm0.25N$.

RESULTS AND DISCUSSION

Surface energy measurement of plasma-treated UPP and BOPP films

The contact angle is a measure of the wettability and surface roughening of a polymer surface. The extent of surface modification achieved because of plasma treatment can be evaluated by using the contact-angle measurement. Surface free energy for UPP films treated in air, nitrogen, oxygen, and ammonia plasma was measured by calculating the angle of contact for three liquids (i.e., water, glycerol, and formamide). Figure 1 shows the surface energy of various gas plasma-treated UPP films against the time of treatment. Surface energy of air and nitrogen plasma-treated PP film increased for shorter treatment time and then decreased to equilibrium with the time of treatment. Such changes in surface energy were not observed for oxygen and ammonia plasma-treated UPP film, which increased to equilibrium value, after the initial increase.

These observations reveal the following:

1. The surface modification reactions with air and nitrogen plasma proceed mainly in two stages. During a short treatment time of 1–3 min, hydrophilic modification is predominant and reaches a
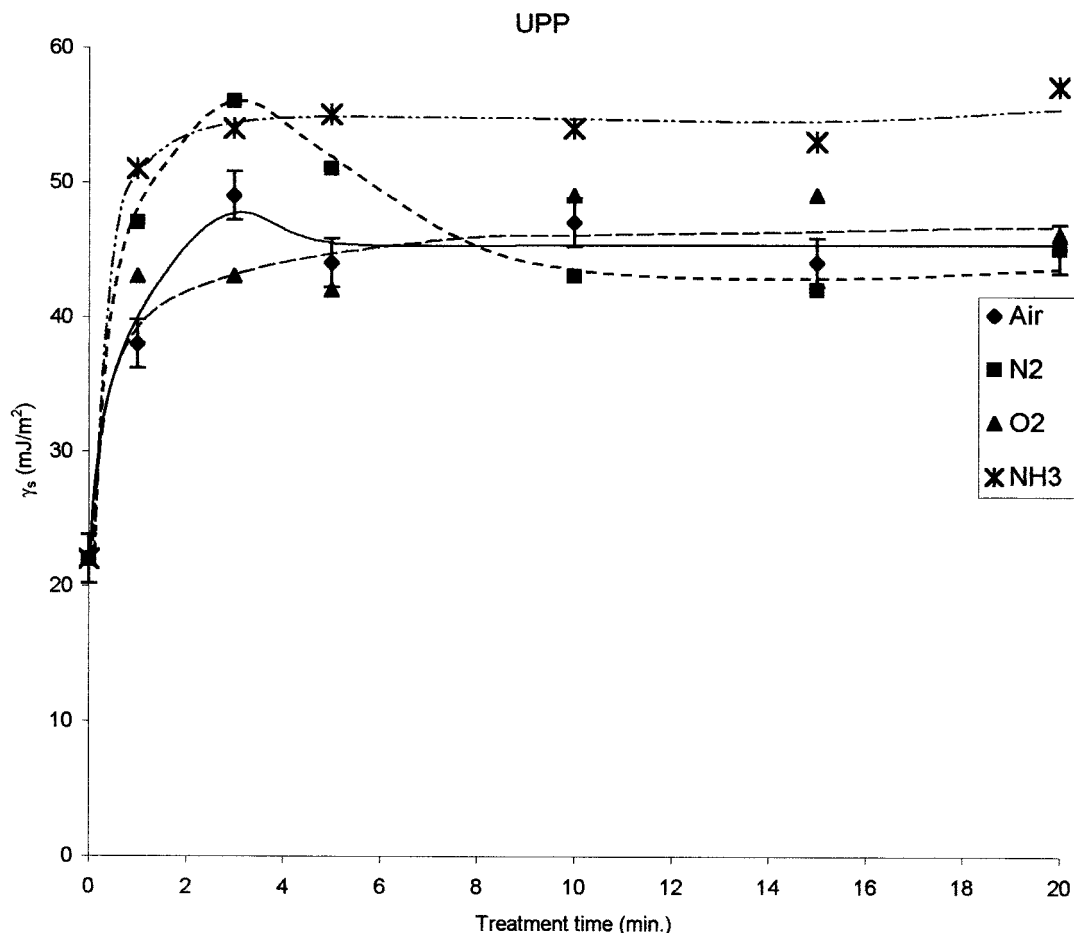
Figure 1 A plot of surface energy versus treatment time for plasma-treated UPP film in various gases.

maximum value at 3 min of treatment time. Further treatment (i.e., >3 min) leads to some surface reactions to decrease the hydrophilicity.

2. The surface modifications with oxygen and ammonia plasma proceed only with hydrophilic modification. The surface energy reached the maximum value for a short treatment time and then levels off.

Similar observations were reported by Marchant et al.,[21] where porous BOPP film was treated with nitrogen plasma. The induced hydrophobic modification for longer treatment time was not explained. However, such anomalous behavior of UPP film is attributed by the phenomenon known as CASING.[26]

When air and nitrogen are used in the plasma state for a treatment time of 1–3 min, it incorporates hydrophilic groups such as —OH, C=O, C—O—O—, NH$_2$, —NH, —NO$_2$, etc., predominantly making the surface more hydrophilic. This is also evident from a surface-energy plot showing a maximum value of 49 mJ/m^2 for air and 56 mJ/m^2 for nitrogen plasma-treated film.

As evident from Figure 1, the magnitude of decrease in surface energy, for nitrogen plasma-treated UPP film, is higher than that in air plasma, indicating that

nitrogen plasma gives more crosslinking than air plasma. Such an observation indicates that nitrogen is the one element that initiates crosslinking on the surface (known as the CASING phenomenon). Such a two-step reaction does not occur in the case of oxygen and ammonia plasma. Oxygen and ammonia, being reactive in nature, contribute mainly to incorporating groups such as —OH, C=O, —C—O—O and —NH$_2$, —NH, —NO$_2$, respectively. This can be observed from Figure 1, indicating an increase in surface energy to an equilibrium value for oxygen and ammonia plasma treatment. In the case of oxygen plasma treatment, it was observed that the surface energy increases and equilibrates in 5 min of treatment time. Also, it appears that oxygen and ammonia do not produce activated species having sufficient energy to create radicals having a long lifetime to interact within polymeric chain, and as a result, crosslinking is not initiated.

To relate surface modification with polymeric structure, similar treatments were carried out on BOPP film. Figure 2 shows the surface energy plot of air, nitrogen, oxygen, and ammonia plasma-treated BOPP film. BOPP also shows similar behavior, as is observed in the case of UPP. For air plasma-treated BOPP film, the maximum value of surface energy was observed at
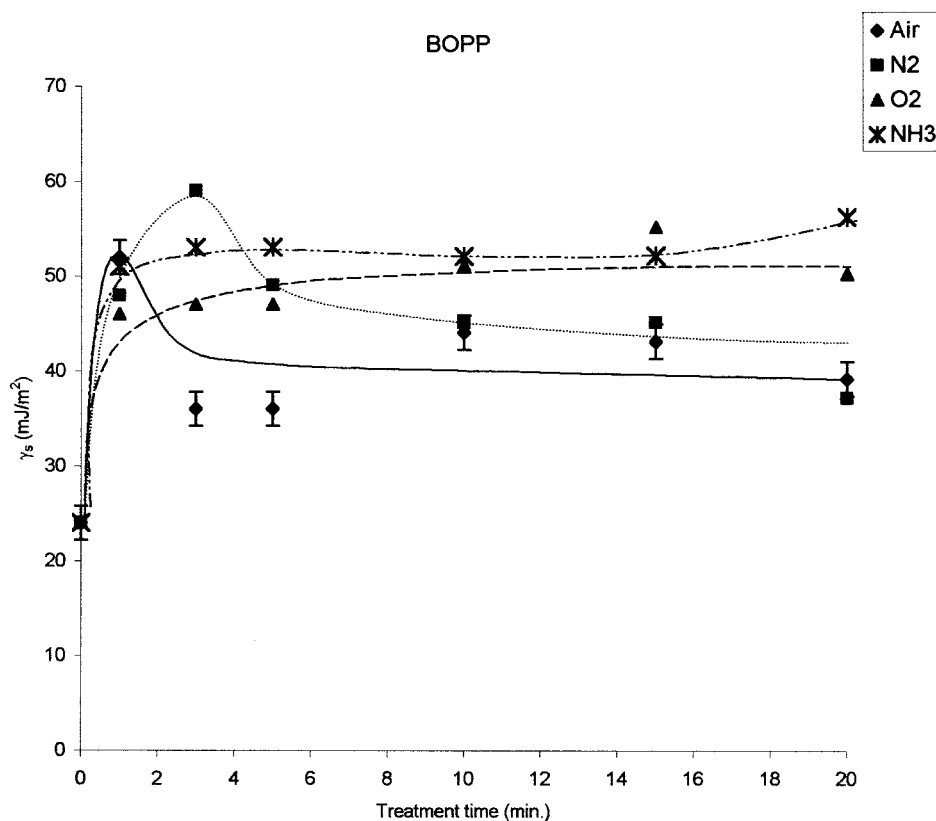
Figure 2 A plot of surface energy versus treatment time for plasma-treated BOPP film in various gases.

1 min; thereafter, it decreased to attain an equilibrium value. Nitrogen plasma-treated BOPP film showed an increase in surface energy until 3 min of treatment time; thereafter, it decreased to attain an equilibrium value. For BOPP film treated in air and nitrogen plasma, the magnitude of decrease in surface energy after achieving maxima is comparable. However, the magnitude of decrease in surface energy for BOPP film is much greater than UPP and may be due to phenomena of greater "plasma etching," as seen by a loss of weight measurements and by exposing the inner regions. Correlation of the surface energy data of UPP and BOPP film reveals that after plasma treatment BOPP films show a slightly higher value of surface energy than UPP for similar treatment time. Oxygen and ammonia plasma-treated BOPP film showed similar behavior as observed for UPP.

Surface energy measurement of UPP and BOPP film treated in air and nitrogen plasma shows a significant increase in polar coordinate of total surface energy until 1–3 min of treatment time; beyond that, there is an increase in the disperse coordinate, indicating a formation of crosslinked product on surface. PP films treated in oxygen and ammonia plasma show an increase in the polar coordinate as compared to a disperse coordinate, indicating the crosslinked product is not formed during plasma treatment. An increase in disperse coordinate for nitrogen plasma-treated UPP film is much larger than air plasma treatment, show-

ing that a degree of crosslinking is greater with nitrogen plasma treatment. In the case of BOPP, the disperse coordinate increases to a similar extent for air and nitrogen plasma treatment.

Loss of weight

Earlier studies show that gaseous plasma etches the polymer surface, and as a result, weight of the treated film is less than that of the untreated sample. Hence, it is important to study the weight loss of PP films due to plasma treatment. Figure 3 shows the % loss of weight for UPP films, which increases initially and then reaches an equilibrium value at a treatment time of 10 min for all gases except oxygen. In the case of air, nitrogen, and ammonia plasma treatment, there is a continuous increase in the weight loss after 10–20 min of treatment. Surprisingly, the weight loss for oxygen plasma increases quite rapidly and has maximum weight loss among the samples studied.

Figure 4 shows % weight loss of gaseous plasma-treated BOPP films. % Weight loss of BOPP reaches an equilibrium value until 10 min, followed by a continuous increase after 10–20 min in air and ammonia plasma. % Weight loss initially increases rapidly and reaches an equilibrium value at a treatment time of 10 min for nitrogen. Weight loss observed for oxygen plasma shows a continuous increase with time of treatment. Similar to UPP, BOPP films also show a
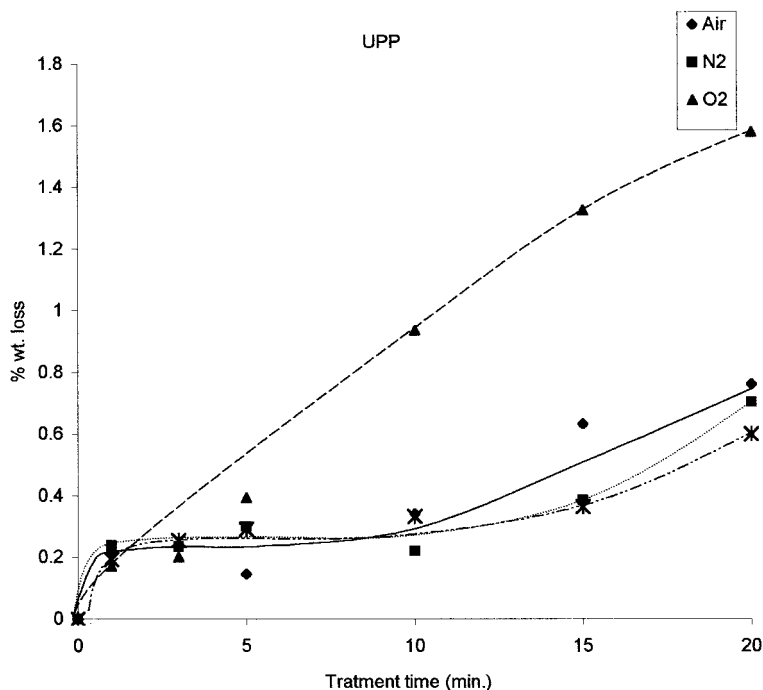
Figure 3 % Weight loss of plasma-treated UPP film in various gases for different times of treatment.

maximum increase in % weight loss for oxygen plasma.

The observed variation for air, nitrogen, and ammonia plasma-treated UPP and BOPP films has some similarities in that there is an increase and then saturation occurs at 10 min. This shows that the mechanism of interaction changes with time. It is believed that initially the interaction of ions, electrons, and energetic species of neutral atoms causes rapid removal of low molecular contaminants such as adhe-

sives, processing aids, and adsorbed species, which is also called as "plasma cleaning." After plasma cleaning, ablation of polymer chains starts. The etching process is more predominant on the amorphous region of the surface than the crystalline regions. Therefore, it is expected that the initial rate of weight loss is faster. It was observed that the initial rate of change of weight with time of treatment is faster and then it slowly reaches equilibrium. Figures 3 and 4 show that, after 3 min of treatment, equilibrium is reached (i.e.,
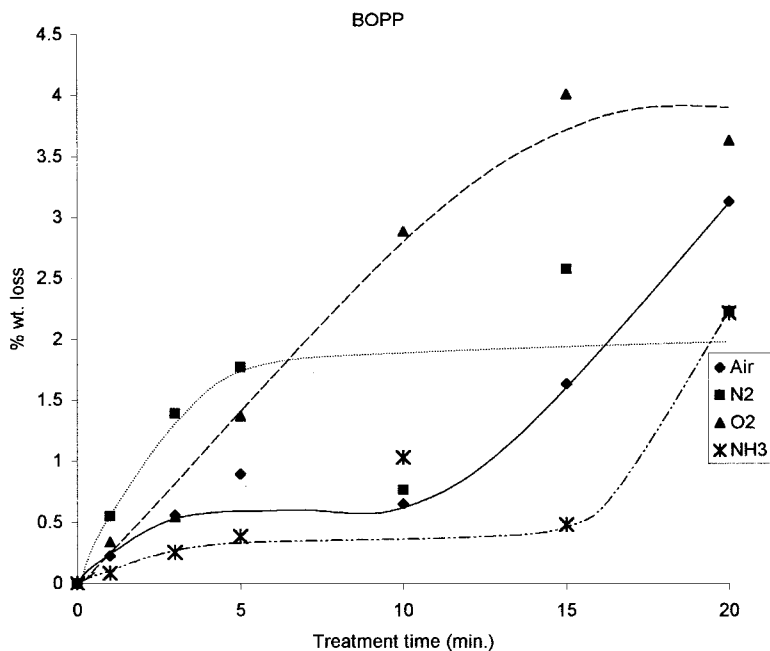

Figure 4 % Weight loss of plasma-treated BOPP film in various gases for different times of treatment.

TABLE I
Surface Energy of UPP Film Treated in Gaseous Plasma Before and After Aging

Treatment time (min)	Air γ_s (mJ/m^2)		Nitrogen γ_s (mJ/m^2)		Oxygen γ_s (mJ/m^2)		Ammonia γ_s (mJ/m^2)	
	Before	After	Before	After	Before	After	Before	After
1	38	34	47	44	43	38	51	37
3	49	45	56	48	43	40	54	42
5	44	40	51	46	42	36	55	39
10	47	46	43	42	49	44	54	42
15	44	42	42	39	49	43	53	45
20	45	43	45	43	46	35	57	48

between 3 and 10 min, the weight loss is very low). This indicates that the surface is not getting etched out during this time. On the basis of surface energy measurements, it appears that for air and nitrogen plasma-treated PP films, the surface is protected after 3 min, which is probably on account of crosslinking on the surface and becoming resistant to etching mechanism. Alternatively, on the basis of the amorphous-crystalline concept of polymers, it is believed that the amorphous part is removed initially up to 3 min and then the remaining crystalline parts are difficult to be etched out. However, for longer treatment time (15 and 20 min), the rate of etching again increases. This is probably due to the fact that now the etching of crystalline fraction is possible (as those get exposed to plasma and some additional effects take place).

It was observed that BOPP films showed a greater increase in % weight loss than UPP films, which may be due to ease of oxidation or ablation under stretched conditions. Rate of change of weight loss for BOPP films are also observed to be higher than the UPP films. Highest etching is in plasma of oxygen, which is due to comparatively higher molecular weight and its higher reactivity.

Effect of aging

It is well known that treatment with chemical, flame, corona discharge, and glow discharge of hydrophobic surfaces such as PE and PP increase the wettability of the surfaces. These processes are widely used on an industrial scale to increase the wettability of surfaces

that enhance the adhesion of resins and that of ink to yield improved printability. On the other hand, it is also well known that the wettability of surfaces introduced by these processes decays with time and may be almost completely lost. Although other factors such as contamination of surfaces, type of material, electrical properties, and others also may contribute to the overall decay process, it is the polar groups that play a major role in the decay phenomenon. Details of the phenomena of molecular mobility with storage time is discussed by Yasuda et al.[33] Recently Novak and Florian[34] reported the effect of aging on PP films treated in corona discharge, showing that storage of treated film > 30 days is not recommended for foil printing.

Treated UPP films were aged for 2 months and subjected to surface energy measurement. Values of surface energy before and after aging are given in Tables I and II. UPP film treated for 3 min in air plasma showed a decrease in surface energy by 4 mJ/m^2, whereas 10-min treated UPP film does not show much change in the surface energy value. Similarly for UPP, film treated in nitrogen plasma for 3 min showed a decrease in surface energy by 8 mJ/m^2, whereas film treated for 10 min does not show much change in surface energy value, which indicates that the effect of aging on samples treated for a longer time is not significant as compared to samples treated for a shorter time. The observed change in surface energy can be explained by phenomena of orientation of mobile group. For the shorter treatment time, hydrophilic groups are incorporated on the polymer surface, and as a result, surface energy shows improvement for

TABLE II
Surface Energy of BOPP Film Treated in Gaseous Plasma Before and After Aging

Treatment time (min)	Air γ_s (mJ/m^2)		Nitrogen γ_s (mJ/m^2)		Oxygen γ_s (mJ/m^2)		Ammonia γ_s (mJ/m^2)	
	Before	After	Before	After	Before	After	Before	After
1	52	46	48	44	46	40	51	42
3	36	31	59	47	47	43	53	42
5	36	35	49	45	47	42	53	38
10	44	38	45	38	51	44	52	36
15	43	43	45	43	55	46	52	45
20	39	38	37	34	50	38	56	40

freshly treated samples. However, for the samples stored for 2 months, hydrophilic groups start getting reoriented toward each other and also toward the interior. Because of this, hydrophilic groups do not face air–liquid interface and therefore the contact angle increases and surface energy decreases. When the treatment time is longer (10 min), the induced crosslinked surface may not allow the mobile group to reorient easily and the surface energy does not decrease.

It is now interesting to look at the results of aging for oxygen and ammonia treatments. Oxygen plasma-treated UPP film shows a decrease in surface energy by 3 mJ/m^2 for 3 min and 5 mJ/m^2 for 10 min of treatment time, whereas ammonia plasma-treated UPP film shows a large decrease in surface energy by 12 mJ/m^2 for 3 and 10 min of treatment time. Thus, both short and long duration of plasma treatment of film allow a decrease of surface energy on aging. Therefore, it is concluded that oxygen and ammonia plasma treatments induce only hydrophilic modification and do not induce any crosslinking.

It is now worth comparing similar studies of aging on BOPP films. After aging, BOPP film treated in air plasma shows a decrease in surface energy by 6 mJ/m^2 for 1 min and 10 min nitrogen plasma-treated BOPP film shows a decrease in surface energy by 12 mJ/m^2 for 3 min, whereas film treated for 10 min shows a decrease in surface energy by 7 mJ/m^2. These observations indicate that the long time of treatment does induce crosslinking in BOPP film in a similar fashion as for UPP. However, lowering of surface energy values indicates that the crosslinking may be weaker and on aging some reorientation occurs. Oxygen plasma-treated BOPP film shows a decrease in surface energy by 4 mJ/m^2 for 3 min and 7 mJ/m^2 for 10 min of treatment time. Ammonia plasma-treated BOPP film shows a large decrease in surface energy by 11 mJ/m^2 for 3 min and 16 mJ/m^2 for 10 min of treatment time.

It can be seen from the observed decrease in surface energy value that due to aging the degree of reorientation of mobile group in the case of BOPP film was found to be much more than UPP film, indicating that crosslinking induced in BOPP film by plasma treatment was not as strong as in the case of UPP film. This may be due to the fact that UPP is a semicrystalline material and possesses enough mobile chains to form a stable surface crosslinked product as compared to BOPP. On the other hand, in BOPP films, the drawing process orients the chains and crosslinking does not occur to give a stable product.

ATR-FTIR analysis of plasma-treated PP surface

To understand the extent and type of chemical modification on the surface because of plasma treatment, ATR-FTIR spectra of treated films were recorded.
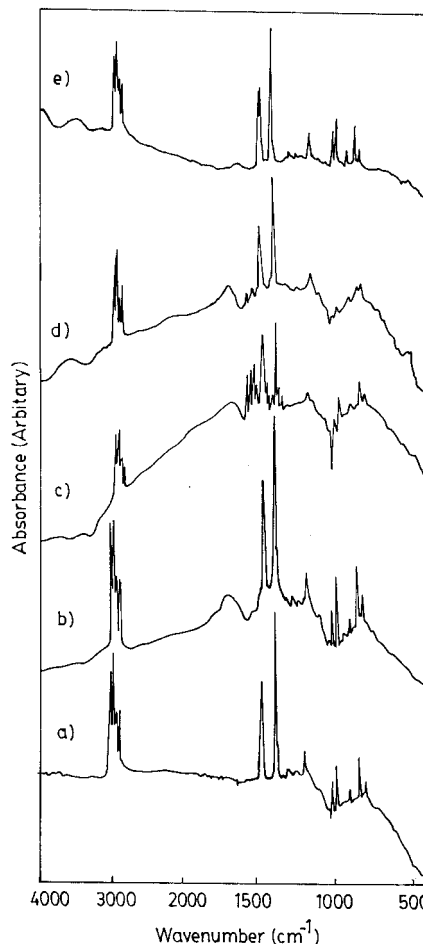

Figure 5 Full ATR-FTIR spectra of UPP film (4000–400 cm^{-1}). (a) Untreated UPP film; (b) 10-min air plasma-treated UPP film; (c) 10-min nitrogen plasma-treated UPP film; (d) 10-min oxygen plasma-treated UPP film; (e) 10-min ammonia plasma-treated UPP film.

Plasma modifies the surface of polymeric film to a depth of only 1 to 10 μm and does not affect the bulk properties. Hence, ATR-FTIR is a more appropriate technique than transmission spectra.

Figure 5 shows a full spectra of untreated and plasma-treated UPP film. It may be seen that the spectrum for 10-min air plasma-treated UPP film has developed weak and broad absorption bands at 1697 cm^{-1}, corresponding to C=O stretching vibration. Similarly, spectrum for 10-min nitrogen plasma-treated UPP film showed broad absorption bands at 1684 and 1541 cm^{-1}, corresponding to C=O stretching and —NO$_2$ asymmetric stretching. Weak absorption was also observed between 1330 and 1400 cm^{-1}, corresponding to —NO$_2$ symmetric vibration.[34] Oxygen plasma-treated UPP films showing broad absorption around 3500–3700 cm^{-1} was observed because of —OH stretching vibration. Bands corresponding to C=O and —NO$_2$ around 1654 and 1508 cm^{-1} are also observed after oxygen plasma treatment. Ammonia plasma-treated films show broad absorption bands near 3550 cm^{-1} because of the primary amine (—NH$_2$) and weak ab-

TABLE III
Changes in Relative Intensity for 3-min Plasma-Treated UPP Film in Various Gases

C—H stretch/Bands (cm^{-1})	Air		Nitrogen		Oxygen		Ammonia	
	Before	After	Before	After	Before	After	Before	After
2950 ν_{as} —CH$_3$(1°)	0.59	0.52	0.59	0.20	0.72	0.68	0.74	0.72
2917 ν_{anti}—CH$_2$(2°)	0.69	0.64	0.69	0.22	0.87	0.78	0.82	0.78
2906 ν CH(3°)	0.49	0.39	0.49	0.11	0.62	0.55	0.64	0.62
2875 ν_s —CH$_3$(1°)	0.34	0.23	0.34	0.04	0.48	0.42	0.52	0.52
2868 ν_s —CH$_3$(1°)	0.35	0.25	0.35	0.04	0.49	0.43	0.53	0.51
2836 ν_s —CH$_2$(2°)	0.37	0.26	0.37	0.05	0.49	0.44	0.54	0.52

sorption near 3300 cm^{-1} because of the amide group. Weak absorption due to C=O of the amide group was also observed at 1651 cm^{-1}.

To understand the site of attachment of hydrophilic groups and the plasma chemistry of surface modification, the spectra of treated films were analyzed by measurements of relative intensities. In the spectra of UPP films, C—H stretching vibrations were found to be intense and show the presence of three types of carbons (i.e., primary, secondary, and tertiary). Since C—H stretch bands are sensitive to chemical reaction occurring at 1° (primary), 2°(secondary), and 3° (tertiary) carbon atoms, ATR spectra in the region from 3000 to 2700 cm^{-1} need further scrutinizing. Spectra were analyzed by calculating the relative intensities of C—H stretching band with respect to chosen standard. Because the intensity of the spectroscopic band is directly proportional to the concentration of corresponding species, a decrease in relative intensity is indicative of a decrease in concentration of corresponding species. The experiment was repeated three times to check the reproducibility of the method and

was found to be sensitive enough to project the surface chemical changes. This type of analysis can project the most predominant surface chemical changes occurring on the polymeric surface.

The following IR bands[35–38] of PP were analyzed to understand surface chemical reactions. The C—H stretching vibrations used are as follows:

2950 cm^{-1} corresponds to ν_{as} of —CH$_3$ (1°),
2917 cm^{-1} corresponds to ν_{anti} of —CH$_2$ (2°),
2906 cm^{-1} corresponds to ν_{CH} (3°) appearing as a shoulder peak,
2875 and 2868 cm^{-1} doublet corresponds to ν_s —CH$_3$ (1°),
2837 cm^{-1} corresponds to ν_s —CH$_2$ (2°).

C—H bending vibration of the —CH$_3$ group corresponding to 1376 cm^{-1} was chosen as a standard for calculating relative intensities. To understand the site of attachment of the hydrophilic group on the PP surface, relative intensity changes of only symmetric bands were considered, because symmetric bands

TABLE IV
Changes in Relative Intensity for 10-min Plasma-Treated UPP Film in Various Gases

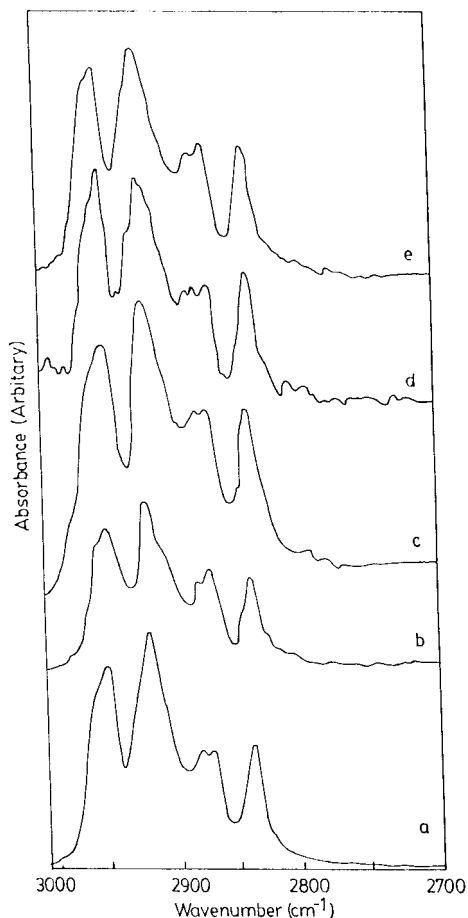| C—H stretch/Bands (cm^{-1})	Air		Nitrogen		Oxygen		Ammonia	
	Before	After	Before	After	Before	After	Before	After
2950 ν_{as} —CH$_3$(1°)	0.58	0.30	0.70	0.09	0.74	0.46	0.74	0.49
2917 ν_{anti}—CH$_2$(2°)	0.71	0.37	0.77	0.11	0.96	0.46	0.82	0.52
2906 ν CH(3°)	0.46	0.23	0.62	0.05	0.65	0.38	0.64	0.45
2875 ν_s —CH$_3$(1°)	0.31	0.12	0.52	0.01	0.47	0.31	0.52	0.37
2868 ν_s —CH$_3$(1°)	0.32	0.13	0.52	0.02	0.49	0.32	0.53	0.39
2836 ν_s —CH$_2$(2°)	0.32	0.14	0.53	0.01	0.48	0.33	0.54	0.38

Figure 6 ATR-FTIR spectra showing C—H stretching vibration bands of UPP film. (a) Untreated UPP film; (b) 10-min air plasma-treated UPP film; (c) 10-min nitrogen plasma-treated UPP film; (d) 10-min oxygen plasma-treated UPP film; (e) 10-min ammonia plasma-treated UPP film.

were rather more sensitive to chemical change than asymmetric or antisymmetric bands and give a true picture of the surface chemical changes.

It can be seen from Table III that analysis of the spectra of air and nitrogen plasma-treated UPP film indicates that for a short treatment time (i.e., from 1 to 3 min), relative intensity of bands corresponding to 2875 and 2868 cm^{-1} of ν_s —CH$_3$ decreases to a maximum extent, indicating 1° carbon is the site where proton abstraction and surface hydrophilic reaction occurs predominantly [as depicted in Reaction 1(a)]. Table IV shows that bands corresponding to 2906 cm^{-1} of ν_{CH} (3°) have developed a maximum decrease in relative intensity for 10 min of air and nitrogen plasma-treated film. This indicates the involvement of 3° carbon atom in surface crosslinking [Reaction 1(b)], although hydrophilic modification continues at 1° and the possibility of its involvement in crosslinking cannot be neglected. On the basis of these observations, it could be concluded that air and nitrogen plasma generates a metastable species having sufficient energy that can abstract proton mainly from 3° carbon atom, thereby inducing surface crosslinking.

In the case of oxygen plasma-treated UPP film, relative intensity decreased drastically for absorption band of 2950 cm^{-1} corresponding to ν_{as} of —CH$_3$ (1°) when treated for 3 min [Reaction 2(a)]. When the treatment was further increased for 10 min, the relative intensity of the band at 2906 cm^{-1} of ν_{CH} (3°) [Reaction 2(b)] decreased. This indicates that hydrophilic modification continues on 3° carbon atom after completion of reaction at 1° carbon atom. The positive ions generated are not sufficiently energetic, and as a result, hydrophilic modification occurs at 1° when treated for a short period of time, whereas for longer treatment time, they acquire sufficient energy to create radicals at 3° carbon atom. Although the lifetime of radicals generated are not significant enough to induce surface crosslinking, as a result, these radicals immediately decay by combining with hydrophilic groups formed in the plasma state.

As shown in Table III, in the case of ammonia plasma-treated UPP film, relative intensity of 1° carbon decreases the most, irrespective of treatment time [Reaction 2(a) and 2(c)]. These observations reveal that ammonia plasma treatment induces hydrophilic modification only at 1° carbon atom.

Figure 6 shows C—H stretching vibration bands of 10-min plasma-treated UPP film in air, nitrogen, oxygen, and ammonia. It can be seen from the figure that air, nitrogen, and ammonia plasma-treated UPP film has developed significant change in the absorption band of ν_s —CH$_3$ stretching vibration. C—H stretching vibration of oxygen plasma-treated UPP film shows a splitting of various bands, which may be due to the formation of low molecular oxidative product on the surface.[25]

On the basis of the relative intensity data, the most predominant surface chemical reaction is projected as follows. Hydrophilic group X can be —OH, —C=O, —C—O—O for air and oxygen plasma treatment and —NH$_2$, —NH, —NO$_2$ for nitrogen and ammonia plasma treatment. Possible intermediate steps are not incorporated in the reaction.

T-Peel strength of plasma-treated PP films

To understand the effect of plasma treatment on bonding strength of PP films, treated films are subjected to a standard T-Peel test. Figures 7 and 8 show variation in peel strength of UPP and BOPP film with respect to the time of treatment. To investigate the effect of plasma for short periods of treatment time, peel strength is measured for the samples treated for 15 s, 30 s, and 1 min. Peel strength measurement for films treated for shorter times (15 s–1 min) shows an unusual decrease and then increase irrespective of whether UPP or BOPP film is used and shows a similar trend in different gases. This is unusual in the sense that roughening of the surface was expected, which would lead to an increase in peel strength. As is
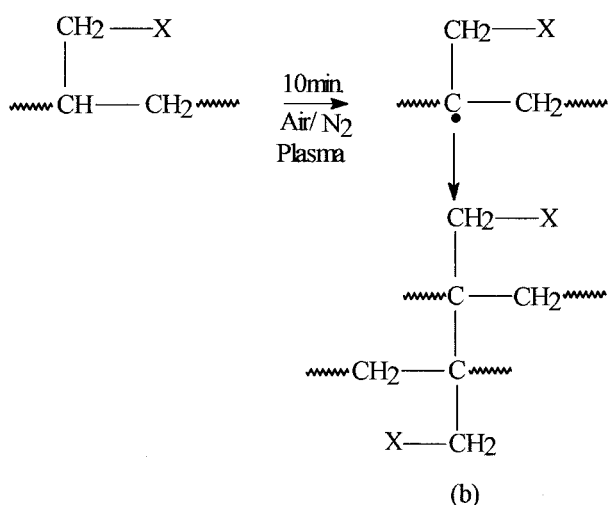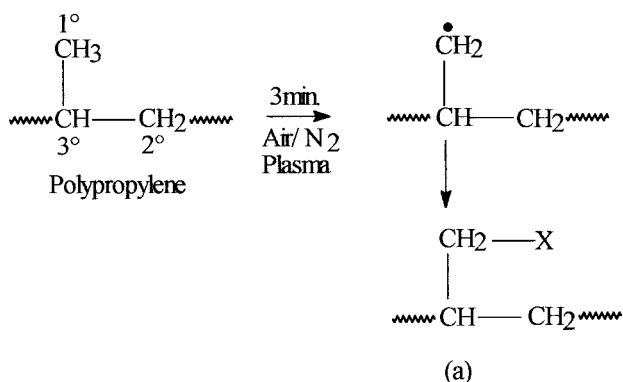
Reaction 1. Mechanism of surface crosslinking for PP when treated in air and nitrogen plasma.

well known, during commercial manufacturing, some contaminants or machine marks are present and, on short time treatments, a phenomena known as "plasma cleaning" occurs, leading to an observed initial decrease in the peel test.

UPP film treated in air and nitrogen plasma shows substantial improvement in the peel strength after only 5 min of treatment time, as seen in Figure 7. Similarly, BOPP films treated in air plasma show slow but steady improvement in peel strength (Fig. 8). Nitrogen plasma-treated BOPP films show a slight improvement until 5 min of treatment time, followed by a decreasing trend in peel strength value. BOPP films treated in oxygen and ammonia plasma show marginal improvement in peel strength and reach equilibrium value for both UPP and BOPP films.

The improvement in peel strength for air and nitrogen plasma is definitely expected to be high because of the phenomena of CASING, which produces the crosslinked surface as described earlier. This improves the cohesive bonding between the substrate and the adhesive. Improvements in peel strength due to ammonia and oxygen plasma are comparatively marginal, although these gases induce more hydrophilic-

ity. Thus, the presence of only functional groups is not sufficient to increase bonding strength.

From the intercomparison of Figures 7 and 8, it is evident that UPP film gives betterment of bonding strength than BOPP film. As explained earlier, once again it seems that this difference arises mainly because of the unoriented and semicrystalline nature of UPP. The chains can have many radical sites formed and are capable of having longer life and get crosslinked with each other. Thus, on the basis of results, it appears that the treatment of polymer film in a plasma environment incorporates hydrophilic groups such as hydroxyl, peroxyl, caronyl, amine, amide, and others. These functional groups contribute to the increase in wettability, and as a result, an adhesive layer spreads on the surface more easily. Moreover, these functional groups when in contact with the adhesive material form a weak bond because of Van der Wals' forces. This force of attraction between plasma-treated polymer surface and adhesive material contributes to the observed increase in bonding strength.

It was interesting to correlate the data of peel strength with that for the FTIR spectra. A systematic
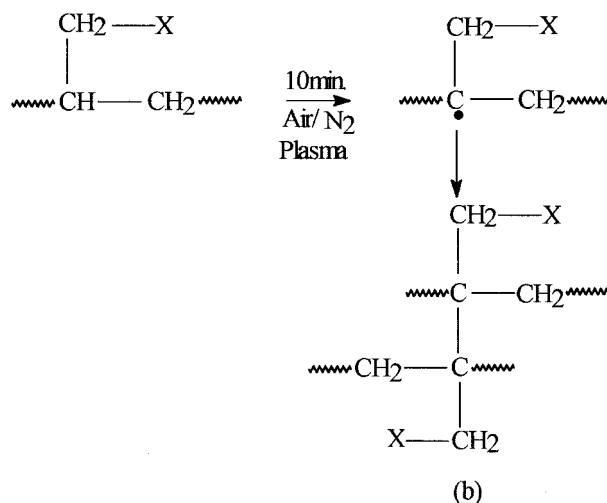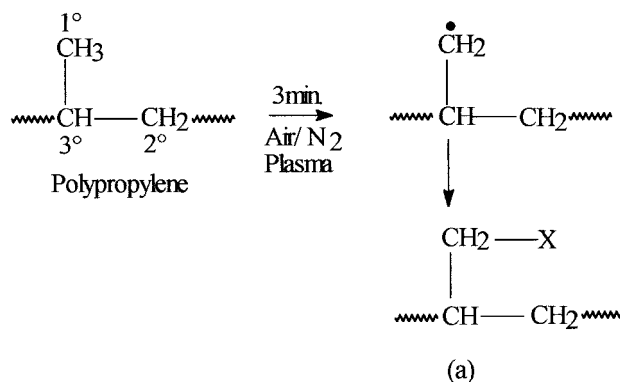
Reaction 2. Mechanism of surface hydrophilic modification for PP when treated in oxygen and ammonia plasma.
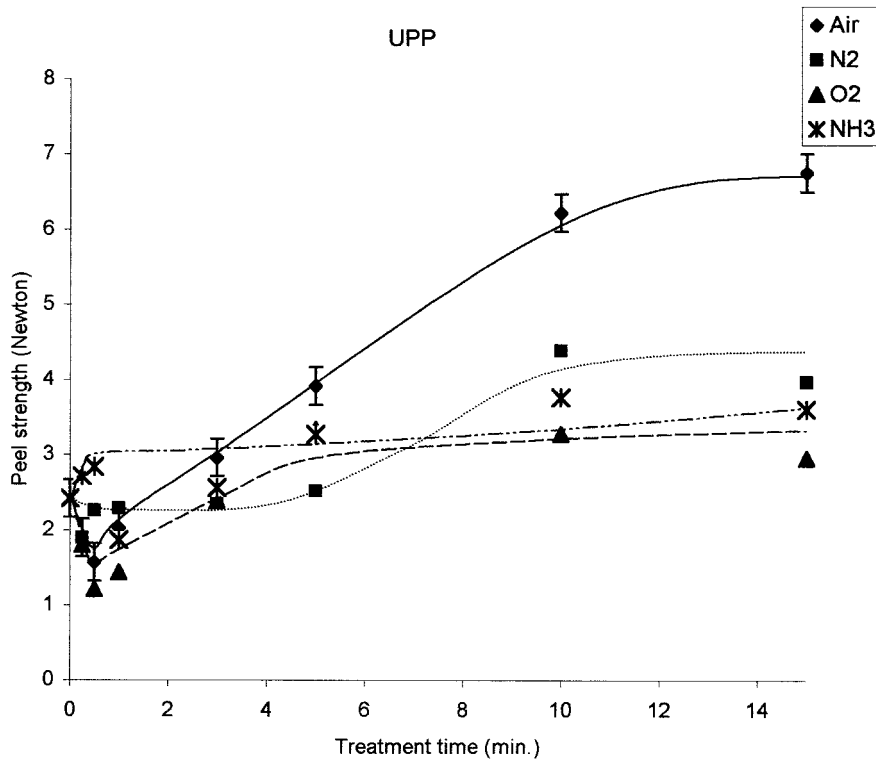
Figure 7 T-Peel strength of UPP film treated in plasma of various gases.

change in the intensity of IR bands corresponding to C=O was observed for UPP film treated in air and oxygen accompanied by an increase in peel strength (Table 5). Similarly, an increase in intensity of the IR band corresponding to the —NO_2 absorption band was observed for UPP films treated in nitrogen plasma
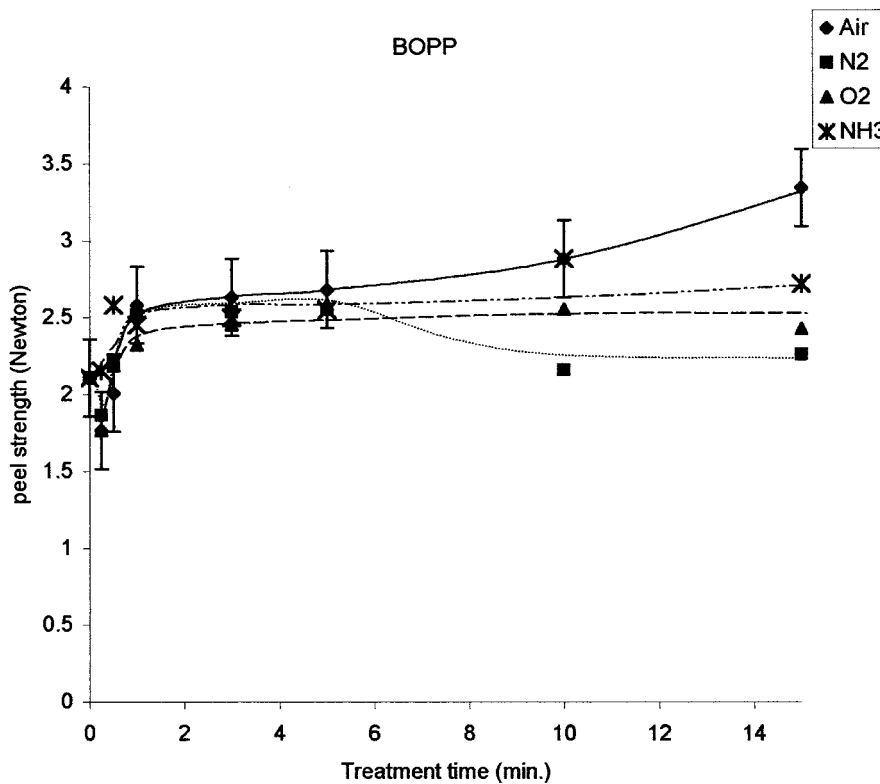

Figure 8 T-Peel strength of BOPP film treated in plasma of various gases.

TABLE V
Comparison of Band Ratio and Peel Strength
of Plasma-Treated UPP Film

	Band ratio	Peel strength (N)
Air plasma	(C=O/C—H)	
3 min	0.090	2.96
10 min	0.132	6.20
Oxygen plasma	(C=O/C—H)	
3 min	0.175	2.38
10 min	0.242	3.26
Nitrogen plasma	(—NO$_2$/C—H)	
3 min	0.086	2.40
10 min	0.821	4.37
Ammonia plasma	(—NH$_2$/C—H)	
3 min	0.287	2.56
10 min	0.334	3.75

and the —NH$_2$ absorption band when treated in ammonia, accompanied by an increase in peel strength (Table 5). It should be evident that improvement in peel strength is significant for air and nitrogen because of the formation of stable surface crosslinked product and hydrophilic modification. Thus, these correlations reveal that IR analysis may be a powerful tool to predict the peel strength of pretreated samples.

CONCLUSIONS

It can be concluded that maximum hydrophilicity can be achieved by treating PP film in plasma for a shorter duration and maximum bonding strength can be achieved by treating PP film for a longer time. BOPP film gives a high value of surface energy than UPP mainly because of more surface roughening, but the bondability achieved after treatment was less than that of UPP. The induced crosslinking in BOPP was found to be more than UPP film, but on aging, the induced crosslinking on the UPP surface was found to be more stable. To achieve good bonding strength for UPP and BOPP film, hydrophilicity and surface crosslinking are necessary criteria.

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