

Grafting of Cellophane Films Using Magnetron-Enhanced Plasma Polymerization

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SYNOPSIS

The cellophane films were grafted with PAN for various time durations in magnetron enhanced air plasma. A magnetron-coupled plasma system was developed for the purpose. The rates of polymer deposition and etching were studied. The changes occurring in the angle of contact of water were studied. The attenuated total reflection–infrared spectroscopic studies confirmed the grafting of cellophane surface by polyacrylonitrile (PAN). The water vapor transmission rates through the grafted samples were also studied. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Polymerization and treatment of surfaces of materials using plasma have been recognized as very good process for the modification of surfaces. Glow discharge has the capability of producing sufficiently energetic species to cause the rupture of molecular bonds at the top layers (a few hundred Å) of the polymer surface. This allows both surface modification by treatment and polymer deposition.¹ The formation of thin polymer films in a high frequency glow discharge have been carried out over a wide variety of monomers and has been discussed in a number of research publications.^{2–8} It is well established that interfacial phenomena, such as wetting and adhesion, can be controlled and modified by introducing surface functional groups. Cellophane is an important material for packaging and as a battery separator. Grafting of cellophane film by ethyl acrylate monomer was carried out by Sakata and Goring⁹ with the help of corona discharge. Westerdahl et al. studied the effects of Rf gas plasma on the surface of cellophane film.¹⁰ The plasma polymerization of acrylonitrile is also a well-studied process.² In this paper, we report results of grafting the surface of

cellophane film by magnetron-enhanced plasma polymerization of acrylonitrile. The confinement of plasma using a magnetic field have been reported and have been used for sputtering and other applications.¹¹ The use of magnetron reduces the contamination of the other parts of the system and was needed to enhance the uniformity of deposition. Such treated films were then characterized using infrared–attenuated total reflection infrared (IR–ATR-IR) spectra, contact angle, and water vapour transmission rate (WVTR) measurements. Possible applications of such materials will be discussed.

EXPERIMENTAL

Materials

Cellophane films, obtained from M/s Kesoram Industries, Calcutta, India, of 25 μm thickness were used. Low density polyethylene (LDPE) films (40 μm) were used for comparison purposes. Acrylonitrile obtained from SD Fine Chemicals (AR grade) was used without further purification. Deionized double distilled water and CaCl_2 were used for determination of WVTR.

The Plasma Reactor

The plasma system used in the present study is shown in Figure 1. The entire system and the

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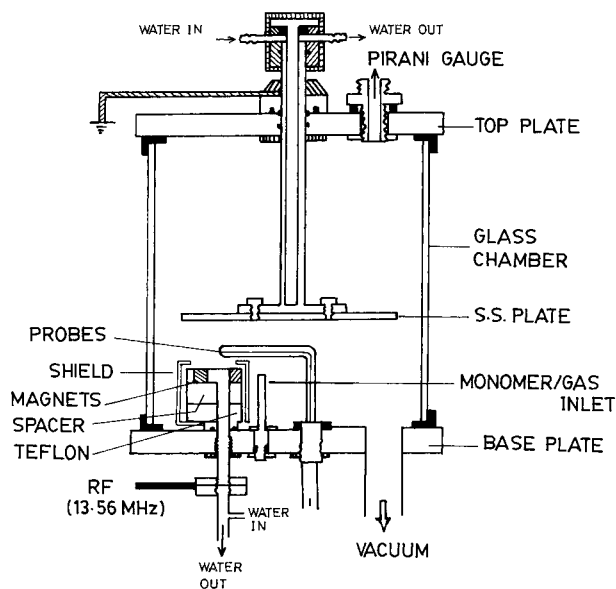


Figure 1 Plasma reactor.

magnetron were designed and fabricated in our laboratory. The system consists of a glass bell jar type reactor with the top and base plates made of stainless steel. The electrodes are capacitively coupled and are water cooled. The lower electrode consists of a magnetron consisting of circularly arranged beads of magnets with aluminium shielding and isolated from the base plate by a TeflonTM spacer. This electrode is coupled with Rf power generator (13.56 MHz) through a proper matching network. The upper electrode is grounded and is isolated from top plate by a TeflonTM Wilson seal. Two ports are available at the base plate for the introduction of monomer and gas in the chamber. The gas inlet is connected to a mass flow controller (UNIT model URS-100). The monomer flow is controlled with the help of a precision needle valve. The inter-electrode distance can be changed in vacuum. The vacuum system consists of a diffusion pump backed by a rotary pump through a single backing-roughing valve. The treatments were carried out at 0.15 torr and 12 W of power. The chamber was first evacuated to a pressure of 0.005 torr, and air flow was adjusted to set a pressure of 0.05 torr. Monomer was introduced until the pressure stabilized at 0.15 torr, and the polymerization was carried out for various time durations. The stabilized pressure during polymerization was 0.16 torr. In this reactor, the values found for air plasma characteristics from probe diagnostics are $N_i = 10^8 - 10^9/\text{cm}^3$,

and $T_e = 2$ to 5 eV. (N_i is the ion density, and T_e is the electron temperature.)

Deposition Rates

The rates of deposition were calculated using the percentage of weight change occurring in the substrate for various time durations.

$$\% \text{ weight change} = \frac{W_o - W}{W_o} \times 100$$

where W_o is the the initial weight of the substrate, and W is the the weight of the substrate after treatment.

IR-ATR-IR Spectra

The IR spectra were recorded using Hitachi Spectrophotometer. KRS-5 crystal with angle of incidence of 45 degrees was used for recording ATR spectra. The KBr pellet technique was used for recording transmission IR spectra. In addition, Fourier transform infrared-attenuated total reflection (FTIR-ATR) was also employed for getting well-resolved spectra of a few samples.

ESCA Studies

Electron spectroscopy for chemical analysis (ESCA) studies were carried out for recording of carbon, nitrogen, and oxygen spectra using a VG Scientific Co. ESCA-3 MK2 unit.

Contact Angle

The angle of contact of water on the surface of the film was determined by static sessile drop method. At least six readings were taken at two different positions for each film, and the average was found.

Water Vapor Transmission Rate

The WVTR were determined using a standard ASTM setup.¹² The films were sealed on a aluminium cup (film area 50 cm^2) containing desiccant material (CaCl_2), with the help of paraffin wax. The cups were placed in an 85% RH environment controlled by saturated KCl solution. The WVTR were allowed to reach equilibrium for one week, and the cups were weighed at regular intervals of 48 h.

RESULTS AND DISCUSSION

The aim of the present investigation was to graft acrylonitrile on the surface of cellophane film in the form of a thin layer. Chemical grafting and polymerization processes are not capable of giving a thin film of thickness 1 to 5 μm . Plasma processing, on the other hand, has a capability as a dry and quick process and is capable of giving a thin layer as low as few hundred \AA . However, the plasma process involves fewer molecules as the pressures are low. In addition, the rates of deposition on substrate depend on several parameters, such as diffusion, kinetic energies, molecular weight, etc. Since plasma consists of ionized species, the bombardment of surfaces by ions, electrons, and activated species leads to the phenomenon of etching. It has been observed that there is a competitive ablation and polymerization when plasma is struck in presence of monomer vapours. The rate of etching depends on the type of substrate, whereas the rate of deposition depends on the type of the monomer. The processes being opposite of each other, it is difficult to determine their rates very accurately. However, in the present investigation, an attempt has been made to determine this by using a standard LDPE film for which etching rates were observed to be negligible at the experimental conditions used.

Deposition Rates

If a monomer is not present in the plasma reactor and an inert gas or air is used, there is no deposition, but, largely, etching occurs. The loss of weight due to ablation process can be determined easily for various conditions of pressure of gas, power, etc. When monomer is present, deposition would occur simultaneously, and a net loss/gain in the weight of the sample will depend on which factor is predominant. It was observed during the course of experiments that the rate of etching of LDPE film was negligible in comparison to cellophane. It was, therefore, decided to use LDPE as a standard nonetchable substance and determine the net deposition rates. Figure 2 shows the results of these investigations, in which curve A shows the etching of the cellophane film, which seems to be increasing with increasing time of treatment. The observed change in weight of cellophane in presence of monomer is shown in curve B. Curve C represents only the deposition behavior of PAN on LDPE. Curve D represents the resultant deposition rates on cellophane, which are

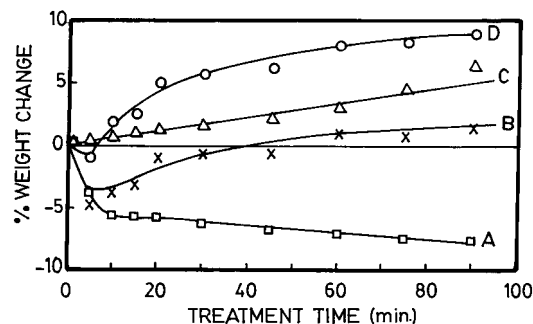


Figure 2 Percentage of weight changes with time of treatment: (A) air plasma treatment, (B) cellophane + PAN, (C) LDPE + PAN, and (D) calculated deposition on cellophane.

obtained from experimental values of curves A and B. Thus, it may be seen that the net or resultant deposition is quite high, though it could not be observed initially. It therefore seems that cellophane is a highly etchable substance, which is probably on account of amorphous nature of the film.¹³ The loss of weight can be accounted for by formation of oxygen reactive radicals in air plasma. Reaction of these with polymer surface leads to formation of oxygenated macromolecules, which ultimately form products of lower molecular weight and volatile products through chain scission reactions. Also, it can be concluded that as the PAN film grows on the surface of cellophane film, the etching phenomenon diminishes as the plasma-deposited PAN film is highly cross-linked and less etchable than cellophane film. The changes in weight percent were recorded four times for each type of treatment, and the average values are reported. The deposition observed on the surface was highly uniform.

IR-ATR-IR Spectra

In order to decide the extent and the type of deposition occurring on cellophane film, it was thought interesting to record the IR spectra. Since a very thin layer is expected, ATR spectrum is more appropriate and was, therefore, recorded. For the sake of comparison, IR spectra of the deposition observed on surrounding glass wall in the form of powder was recorded. Two of these typical spectra are reproduced in Figure 3. It may be seen that typical characteristic absorption band at 2250 cm^{-1} corresponding to ($-\text{C}\equiv\text{N}$) and 1640 cm^{-1} , corresponding to $-\text{C}=\text{N}$ are clearly visible. Similarly, strong absorption peaks in the region of 2950 cm^{-1} ($-\text{CH}$ stretching) and 1450 cm^{-1}

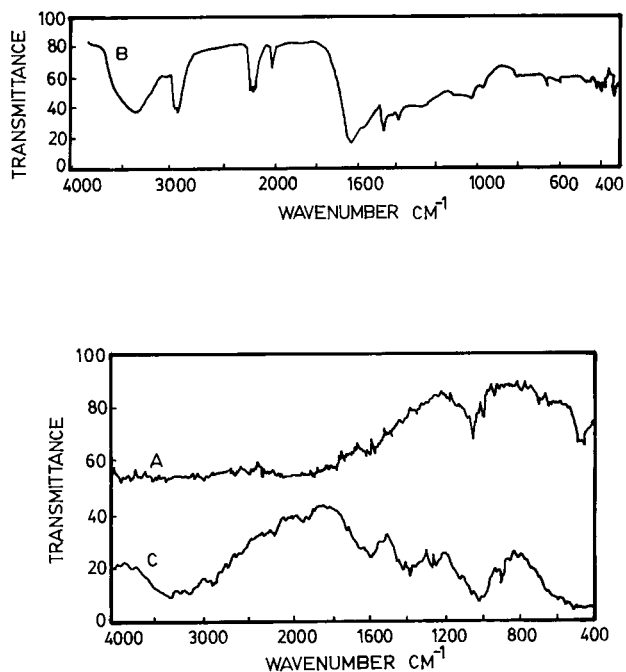


Figure 3 (A) ATR-IR spectrum of cellophane control film. (B) transmission IR spectrum of PAN. (C) ATR-IR spectrum of cellophane grafted with PAN.

(—CH bending) are visible. A broad absorption band corresponding to —NH stretching is also visible. It is seen that the intensity of peaks at 2250 and 1650 cm^{-1} increased with time of deposition of PAN. The ATR spectra for some samples showed that the characteristic peak corresponding to —C≡N has split sometimes into two peaks; but the transmission IR spectra of powder shows very clearly splitting at positions 2220, 2240, and 2260 cm^{-1} . This observation of having additional absorption peaks around 2250 cm^{-1} is due to the fact that —C≡N moieties are intermolecularly bonded in the structure. This can be understood because in plasma polymerization, very high crosslinking occurs. Such splitting of peaks at 2250 and 2230 cm^{-1} has been reported¹⁴ and have been assigned to the conjugation of —C=N and —C≡N. The peak corresponding to —C=N observed at 1640 cm^{-1} is found to get broadened and shifted towards the 1600 cm^{-1} , which may be on account of overlap of bands of substrate (—C=O) and deposited polymer. A careful analysis of PAN-grafted cellophane samples using FT IR reveals that an absorption band corresponding to C=O is present at 1635 cm^{-1} . On account of C—O groups present in the substrate film, there is an overlap of this absorption band with the one due to oxidation taking place during plasma poly-

merization. In order to see how effective this oxidation was, it was decided to carry out additional experiments by depositing PAN on polyethylene substrate. It may be noted that control polyethylene does not have any absorption band in the region of 1600 to 1700 cm^{-1} . Therefore, the resolution of peak and measurement of intensity is not hindered. It may be seen from Figure 4 that for PAN-deposited polyethylene, an absorption band appears at 1640 cm^{-1} and increases in intensity with the time of deposition.

Further, it was noted that there is increase in the intensity of the —NH band at 3330 cm^{-1} with increasing time of deposition. Thus, it seems that during plasma polymerization, C=O and —NH formations take place. Similarly, it may be of interest to visualize how and at what sites this bonding is formed. Recent work on the basis of solid-state nuclear magnetic resonance (NMR) studies of plasma polymerized PAN reported by Tajima et al.¹⁵ reveals strong possibility of the formation of —CO, —COO, —C—OH, and —CONH.

Thus, it seems that although plasma polymerization yields species of polyacrylonitrile, there are some modifications brought about due to the

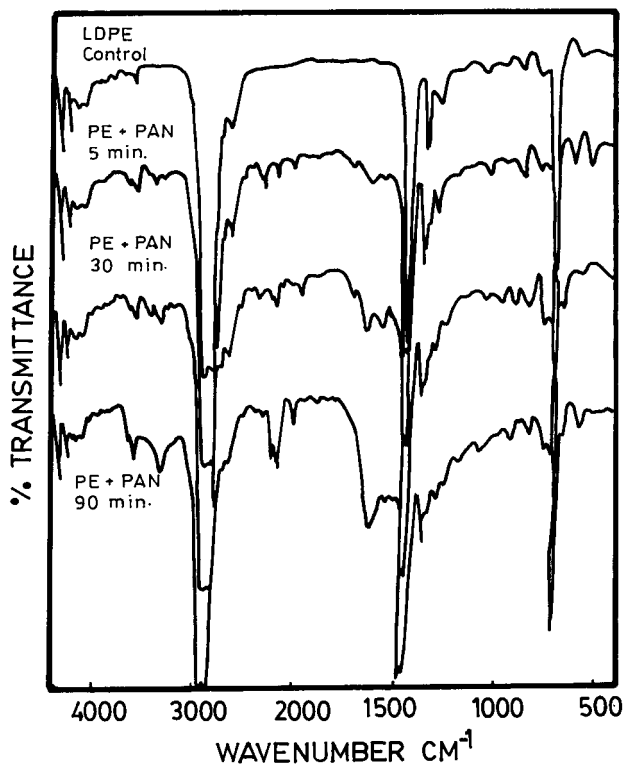


Figure 4 ATR-IR spectra of PAN-deposited polyethylene.

Table I Elemental Microanalysis for C, H, O, and N

Sample	Percent in the Sample of			
	C	H	O	N
Plasma PAN	61.6	3.8	12.7	21.9
Chemically polymerized PAN	61.3	5.3	9.6	23.8
Ideal (from mol formula)	67.9	5.6	—	26.4

incorporation of oxygen and hydrogen bonds. Such changes would give rise to a different mode of bonding and subsequent structure of the polymeric chain. That the deposited substance is close to PAN is evident from microanalysis of percentages of C, H, N, and O in the sample (refer to Table I).

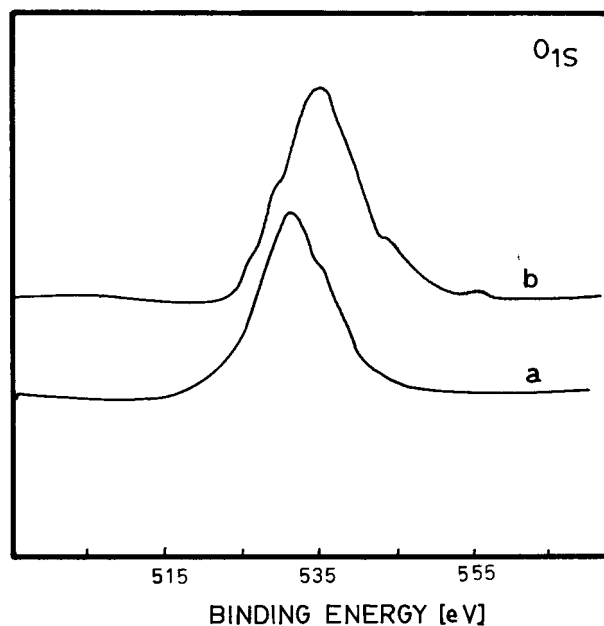
The transmission IR spectrum of PAN powder shows a band at 2030 cm^{-1} , which can be assigned to the ketone-imine linkage ($-\text{C}=\text{C}=\text{N}$) group.¹⁶ Such ketone-imine is more likely to be formed at low Rf power, and hence may have been visible in transmission IR spectrum of PAN powder.¹⁷ However in the ATR-IR spectra of the substrate, this band is not very well observed. This may be due to higher power being delivered at the substrate, rather than at the walls.

Analysis by ESCA

In order to determine the formation of new chemical species or bonds on the surface of cellophane film during the plasma treatment, it was thought of interest to carry out careful analysis using ESCA. C_{1s} , O_{1s} , and N_{1s} bands were scanned for control cellophane films. Illustrative spectra of O_{1s} are depicted in Figure 5. The binding energies of these levels are given in Table II. It can be seen that the slope, as well as the symmetry of the spectra changes, in particular, N_{1s} and O_{1s} spectra. It was also noted that width of all the peaks reduces. From the table, it can be seen that the N_{1s} binding energy increases from 399 to 401.5 eV when PAN deposition was carried out. Similarly, the O_{1s} binding energy increases by about 1.0 eV after deposition with PAN. These shifts indicate that $\text{C}=\text{O}$ is getting formed during the treatment.

Contact Angle of Water

The change in surface energy can be determined by observing the extent of wetting of a surface by

**Figure 5** ESCA spectrum for O_{1s} for (a) control cellophane and (b) PAN-deposited cellophane.

a solvent such as water. The angle of contact of water gives a direct measure of the modification of a polymeric surface, as wetting is a property that is governed by the top molecular layer of any surface. From this point of view, the angles of contact of water were determined on the surface of the cellophane films by standard static sessile drop method. The changes in the angle of contact of water with time of deposition are shown in Figure 6. From the graph, it can be seen that the angle of contact shows higher value (62 degrees) than the control film (43 degrees) for initial time duration of deposition. This may be due to the better uniformity of the surface achieved due to the initial deposition and may be also attributed to the surface property of PAN layer deposited. Here, the initial roughness of cellophane surface will decrease as crevices/rugosities get filled by

Table II ESCA Analysis

Sample	Binding Energy (eV)		
	C_{1s}	O_{1s}	N_{1s}
Cellophane (control)	285.0	529.0	399.0
Cellophane + PAN	285.0	532.0	401.5
Ideal	285.0	532.0	399.0

initial deposition of PAN. It may be of interest to point out that the angle of contact measured for chemically prepared control PAN film is 65 degrees, which is close to maximum value obtained here. Further treatment for larger duration of time will have the competitive ablation/etching, leading to the creation of some roughness in the surface. In addition, during the deposition of PAN, some charged species may be created on the surface. Both these effects would try to lower the angle of contact and has indeed been observed in the present investigation. In order to confirm that this lowering of the angle of contact is due to the effect mentioned above rather than any other phenomenon, it was thought interesting to measure the angle of contact for PAN-deposited glass plates. This would avoid complication due to effects of the substrate as glass substrate is inert towards plasma. The measurements show that the angle of contact for such PAN-deposited plates is 50 degrees, which is in agreement with the value obtained in these studies. The contact angles measured after aging of the films for two months show an increase in overall contact angles measured. This may be due to dying down of the activated charged species formed at the surface with time and subsequent decrease in surface free energy. Such dying down of the charges has been explained as occurring due to inversion and migration of the polar groups on the surface.¹⁸

Water Vapor Transmission Rates

The main drawback of the cellophane film for its application as a packaging film is its high permeability to water vapor, although it shows good mechanical properties. Cellophane, being a highly hydrophilic material, shows unusually high

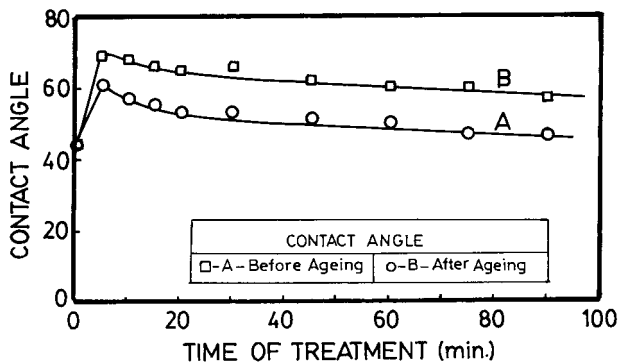


Figure 6 Changes in contact angle with time of treatment.

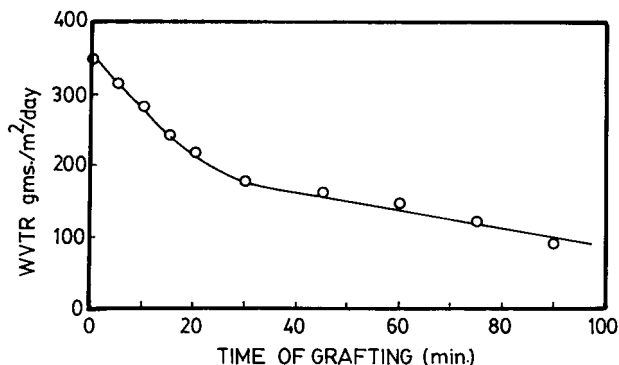


Figure 7 Changes in WVTR with time of treatment.

WVTR on account of swelling and high moisture absorption, although it shows low permeability towards dry gases. Also, it has been found to show high permeability for moist gases.¹⁹ From this point of view, it becomes important if one could improve its barrier property towards water. For this purpose, WVTR of the films were recorded. The results are shown in Figure 7. It can be clearly seen that the WVTR of the cellophane film decreases considerably with deposition time, and about 75% reduction in the WVTR can be obtained for high deposition of PAN. This may be due to the fact that PAN layer on the surface is highly crosslinked and, from contact angle measurements, is found to be slightly less hydrophilic than the cellophane film surface. This has been achieved without the loss of bulk properties of the cellophane substrate. Also, the plasma polymerized layers have been found to be highly inert (towards chemical attack).

CONCLUSION

Thus, these studies indicate that magnetron-enhanced plasma can be used for deposition of uniform thin layer of a commercial polymer on cellophane film to change the surface properties. The rates of deposition can be controlled by choosing the conditions of the plasma reactor. The formation of the thin layer of PAN on the surface of cellophane film decreases the WVTR. Further, the changes observed on treatment are not only durable with time but also show enhancement with period of aging. Thus, such films can find effective use as barrier films for packaging purpose.

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