Nitrogen Plasma Treatment of Polyethylene and Polystyrene in a Remote Plasma Reactor

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Synopsis

The effect of a remote nitrogen plasma on polyethylene and polystyrene was studied. The gas flow rate, the dilution of reactant gas, exposure times, and reactor base pressure were all found to have a large impact on the efficiency of nitrogen incorporation. Optimum conditions caused 18 atom % nitrogen to be incorporated within 20 seconds for polyethylene and 10 seconds for polystyrene. Studying a remote nitrogen plasma treated polyethylene sample over a period of 1 month indicated that except for a drop in the % N on initial exposure to air the concentration of nitrogen on the surface remained steady within the experimental limits. Angle resolved photoelectron spectroscopy indicated that nitrogen is incorporated to a depth below the analysis depth of XPS.

INTRODUCTION

Methods of polymer surface modification by wet chemical and physical techniques have produced surfaces whose composition and structure differ from those of the bulk polymer.[1-6] This has enabled enhancement of polymer printability, adhesion, and wettability properties by altering their surface energy and surface chemical nature.

One method of surface modification is the use of a plasma glow discharge at or near the polymer surface. A polymer surface can be modified most effectively using a gas plasma which does not deposit material, but rather acts as to change the chemical and physical nature of the outer few monolayers of the polymer.[7-9] Plasma discharges in gases such as argon, helium, oxygen, nitrogen, ammonia, carbon monoxide, and fluorocarbons have previously been contacted with a variety of polymers.[7-14] The electronically and vibrationally excited species present in a gas plasma cause the modification of the polymer surface, regardless of the polymer's structure and chemical reactivity. By choosing the type and nature of gas to be used, it is further possible to choose the type of chemical modification of the polymer surface.

In this work the reactive species produced in a nitrogen plasma were reacted with polyethylene and polystyrene surfaces positioned downstream from the main plasma region. This is known as remote plasma modification,[15] the main application of which has so far been in manufacture of electronic devices. The rates of uptake of nitrogen on the surface of the polymers have been investigated as a function of exposure time, gas flow rates, dilution and reactor base pressure. The amount of nitrogen uptake and functionality was determined by X-ray photoelectron spectroscopy (XPS). Use of angle resolved X-ray photoelectron spectroscopy (ARXPS) allowed the depth of modification to be investigated.

A *remote* plasma reactor has been chosen as compared to a *direct* plasma reactor as this allows greater control over the number of unwanted reaction pathways and the substrate is not surrounded by the plasma, which can lead to sputter damage.[15] Thus, remote plasma treatment provides a much less destructive method for surface modification of polymers in comparison to direct plasma modification[16] and other more commonly used polymer modification methods such as corona discharge, ozone, and flame treatment.[17]

EXPERIMENTAL

The reactor, which has previously been described,[17,18] may be attached directly to the XPS spectrometer via the introductory/transfer chamber. The introductory/transfer chamber is turbomolecular pumped and a base pressure of ca. 8×10^{-8} Torr can be reached. From this chamber direct transfer is also allowed into the analysis chamber and the preparation/reaction chamber. Both these chambers are ion pumped and pressures of ca. 2×10^{-9} Torr are typically achieved. Thus, it is possible to transfer samples to and from the remote plasma reactor or any of these chambers without exposure to air or moisture. The analysis chamber houses a SSL SSX-100 XPS spectrometer, which utilizes a monochromatized Al $K\alpha$ X-ray source capable of being focused to a spot size of 150 μm. The analysis chamber also houses an electron flood gun for charge neutralization.

A nitrogen plasma is generated using ultra high purity nitrogen by a 2.45 GHz microwave discharge situated approximately 24 cm above the sample shelf. The excited species flow along a quartz transfer tube extended into the main reactor chamber to 4 cm above the sample. The system is pumped by a 512 L/min rotary pump. To achieve low initial reactor base pressures a 20 L/s ion pump is also attached to the reactor. Before reaction, the reactor was baked at 130°C for 12 h after which base pressures of 2×10^{-8} Torr could be achieved. Once such pressures were obtained, the samples were introduced into the reactor for reaction.

The low density polyethylene was supplied by Canadian Industries Limited (Toronto, Ontario) and the polystyrene by Polysar (Sarnia, Ontario), both in the form of small pellets. The pellets were ultrasonically washed in dichloromethane for a few minutes followed by drying in a vacuum desiccator. The washed and dried pellets were then placed into a small vice and mounted on special sample holders designed for the transfer of samples between the reactor and analyzer chamber.

XPS was used to determine the chemical changes occurring on the surface of the polymers. The experimental conditions used were an X-ray spot size of 150 μm and a pass energy of 50.0 eV for the high resolution core level spectra, and a spot size of 1000 μm, pass energy of 148.0 eV for the elemental analysis. The experimental parameters used minimized the full width at half maximum (FWHM) of the C 1s line to 1.2 eV. The use of XPS for the analysis of polymers surface has already been discussed in a number of articles and book chapters.[7,9,19–21] To control the charging of the polymer surface, the electron flood gun was utilized together with a metal screen placed 1 mm above the sample surface. This has in the past proven to be the most effective method of charge

neutralization[22] on insulating surfaces. ARXPS was performed by rotation of the polymer sample under the X-ray beam, thus allowing the angle between the sample surface and electron analyzer to be varied from 0 to 90°.

RESULTS AND DISCUSSION

Flow Rate

Initial studies were performed to investigate the experimental parameters required for optimum performance of the remote plasma system for the modification of polymer surfaces. One parameter is the flow rate of the gas through the reactor.

A series of experiments was performed where samples of low density polyethylene were exposed for 1 min to a remote nitrogen plasma using flow rates of 500, 1000, 1500, and 2000 standard cubic centimeters (sccm). Using the rotary pump to cause a continuous flow of gas, chamber pressures of 2.8, 3.4, 4.5, and 5.4 Torr have been achieved respectively during the experiments. The equipment utilized in this study did not allow the flow rate and chamber pressures to be varied independently, but steps are being taken to achieve this.

Figure 1 shows that as the flow rate is increased the amount of nitrogen detected on the surface increases gradually; even with a flow rate of 2000 sccm, the maximum nitrogen uptake does not appear to have been reached. The highest flow rate possible with the flow controller used was 2000 sccm and all further experimentation was performed using this flow rate. All samples indicate an uptake of approximately $6 \pm 2\%$ oxygen to the surface, which may originate from residual water vapour in the system, plasma reactions with the silica walls or adsorbed oxygen in the sample.
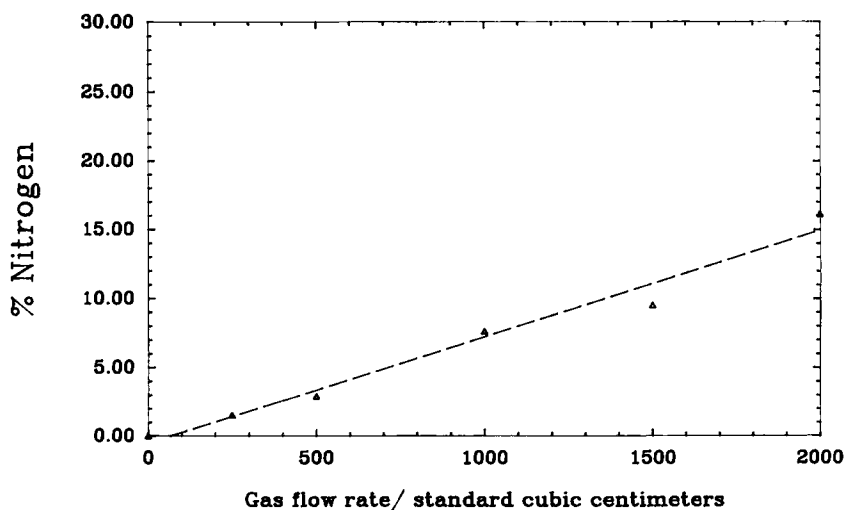

Fig. 1.   Percent nitrogen uptake by polyethylene in a remote nitrogen plasma using different gas flow rates, 1 minute exposures.

Remote Nitrogen Plasma Treatment of Low Density Polyethylene

Low density polyethylene samples were exposed to the remote nitrogen plasma for exposure times of 1, 5, 10, 15, 20, 30, and 60 s using a flow rate of 2000 sccm. As presented in Figure 2, it can be seen that even after a 1 s exposure of the polymer to the remote nitrogen plasma a significant amount of nitrogen (2.5%) is detected on the surface. With longer exposure times the amount of nitrogen increases steadily, reaching a steady state situation after 20 s with 18 ± 1 atom % nitrogen detected on the surface.

Most reports[12,14,24,25] on nitrogen plasma treatment of polymers have concentrated on the direct plasma treatment. Gerenser[14] has recently reported the reaction of a high voltage glow discharge nitrogen plasma with a polyethylene surface, reaching a steady state after 60 s, with the incorporation of 20 atom % nitrogen. Earlier studies[12,25,26,27] indicate much lower yields being achieved even after much higher exposure times (approximately 5% in 5 min[26]).

As the reaction of the remote nitrogen plasma with polyethylene proceeds, the photoelectron C 1s spectra, Figure 3(a), show a change in the type of functional group for exposure times longer than 20 s, even though the total amount of nitrogen is not increasing. In the spectra a peak 0.9 eV above the main hydrocarbon peak can be directly associated with the formation of $C-N$ single bonds on the surface. Since oxygen is also incorporated during the reaction, interpretation of the higher binding energy components is more difficult. Thus, the component at a binding energy shift of 1.9 eV may be associated with $C=N$, $N-C-N$ or $C-O$ groups on the surface. However, since this component increases with time, while the total oxygen and nitrogen do not, it is reasonable to associate part of it with $C=N$ groups. The highest binding energy peak at a separation of 3.7 eV from the hydrocarbon component is most likely to be associated with carbon bonded to three nitrogens as in $C\equiv N$.
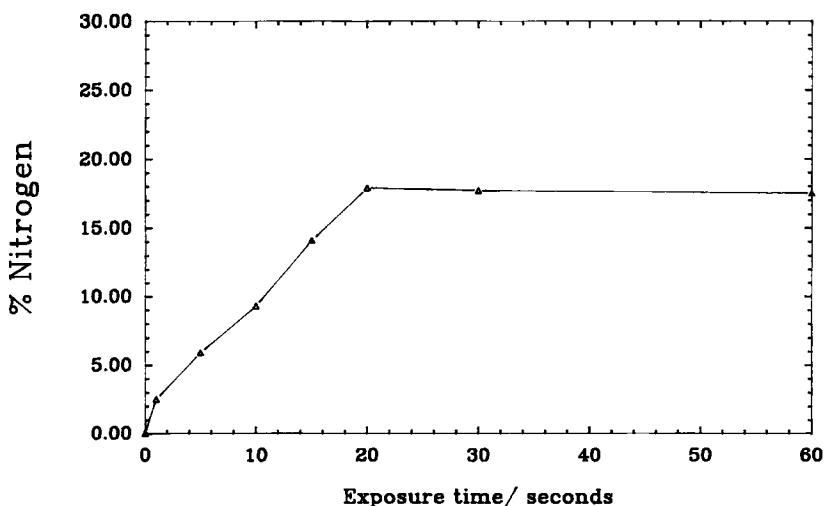

Fig. 2. Percent nitrogen uptake of polyethylene in a remote nitrogen plasma, flow rate 2000 sccm, 5.4 Torr.
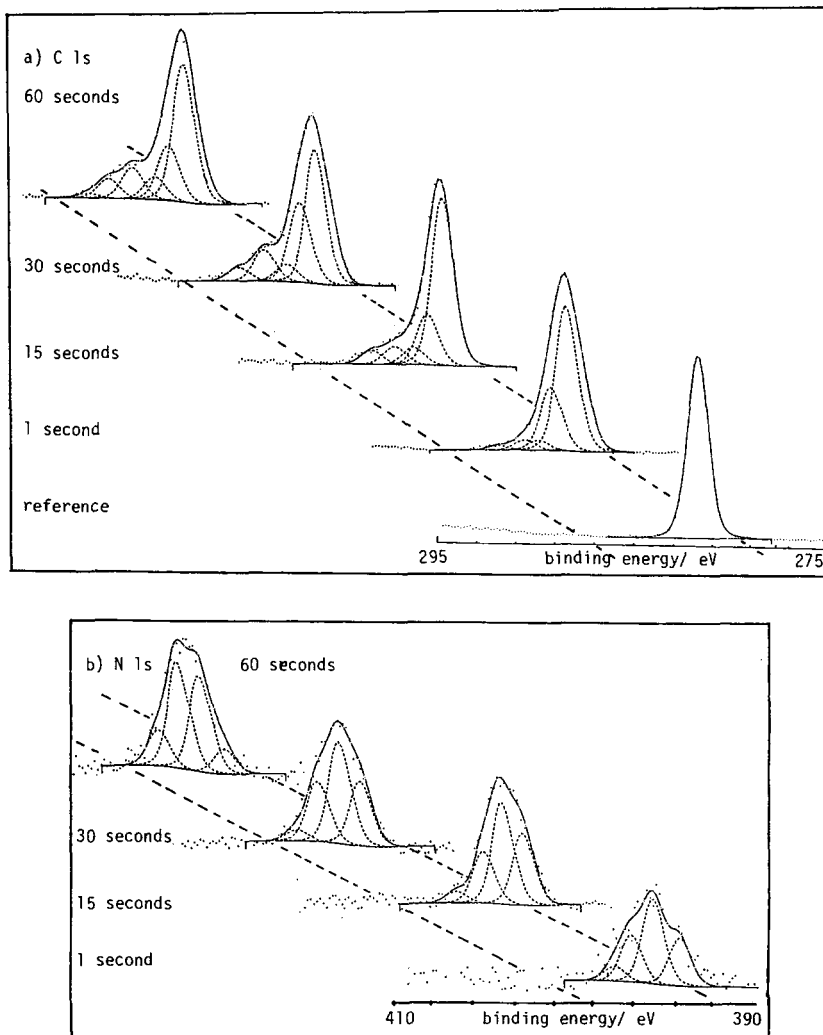
Fig. 3.   (a) C 1s and (b) N 1s spectra of polyethylene after remote nitrogen plasma treatment.

The nitrogen 1s spectra [Fig. 3(b)], are interpreted with more difficulty since very small energy shifts are observed with groups such as $C-N$, $C=N$, NH_2, $C-NH-C$ and C_2N-C. However, the peak at lowest binding energy is assigned to $C-NH_2$,[23] while the higher energy peaks are believed to represent $C=N$ and $C\equiv N$ groups. As can be seen from Figure 3(b), these latter peaks increase in relative intensity with higher exposure times, suggesting again that further exposure to nitrogen atoms results in the introduction of unsaturation in the form of $C=N$ and $C\equiv N$.

Thus the elemental data, the C 1s and N 1s data appear to be consistent with a process in which 18 atom % nitrogen is incorporated in the first 20 s, after which time no more nitrogen is incorporated, but instead $C-N$ single bonds are converted to $C=N$ double and $C\equiv N$ triple bonds by the abstraction of hydrogen atoms.

Remote Nitrogen Plasma Treatment of Polystyrene

Remote nitrogen plasma treatment of polystyrene was investigated for time periods of 1, 5, 10, 20, 30, and 60 s. Figure 4 shows that even at the very short exposure of 1 s, 5% of nitrogen is detected on the surface. This increases steadily, reaching a maximum of $17 \pm 1\%$ nitrogen after 10 s of exposure, after which time no further increase in the nitrogen concentration was observed.

The photoelectron carbon 1s and nitrogen 1s core level peaks (Fig. 5) show the change in the chemical nature of the surface. Before reaction the C 1s is a single line representing both the hydrocarbon chain and the aromatic ring structure of the polymer. Separated by approximately 6.2 eV from the main peak, another smaller structure is observed representing the $\pi - \pi^*$ shake up satellite, characteristic of aromatics and unsaturated systems. After exposure to the remote nitrogen plasma the principal peak shape is seen to alter and additional features are seen at the higher binding energy side. As was observed with polyethylene these higher binding energy features increase in relative intensity with longer exposure times, indicating the formation of $C=N$ and $C\equiv N$ groups on the surface of the polymer. However, since oxygen is also incorporated during the remote plasma treatment, completely unambiguous identification of the individual groups is not possible. From the C 1s spectra observed, no evidence is found for reactions of the remote nitrogen plasma with the aromatic ring system of polystyrene. As was the case with polyethylene, the nitrogen 1s spectra of polystyrene are seen to shift towards higher binding energy with longer exposure times, indicating that as the reaction proceeds $C=N$ and $C\equiv N$ are formed in preference to primary amines.

When comparing the reaction of polyethylene and polystyrene with a remote nitrogen plasma, it appears that, even though the rate of the reaction for the two polymers is different, the chemical species formed are similar. In both cases the nitrogen 1s spectra indicate a change from the single $N-C$ bond to groups
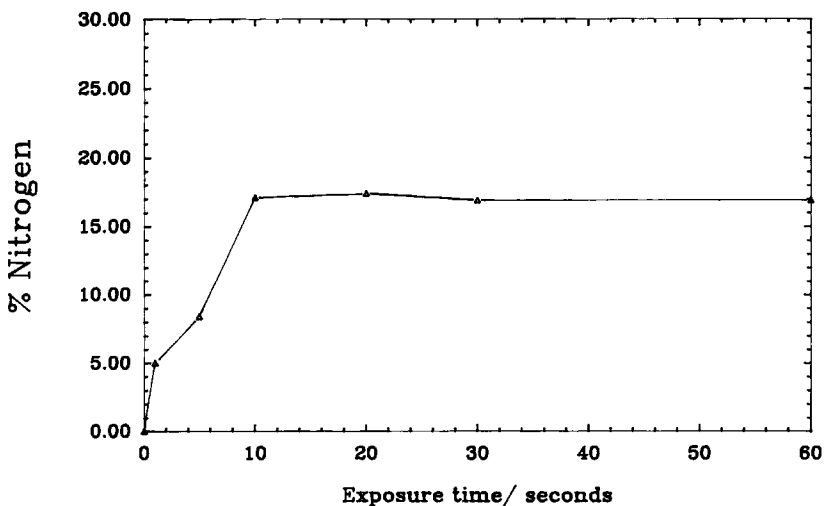

Fig. 4. Percent nitrogen uptake of polystyrene in a remote nitrogen plasma, flow rate 2000 sccm, 5.4 Torr.
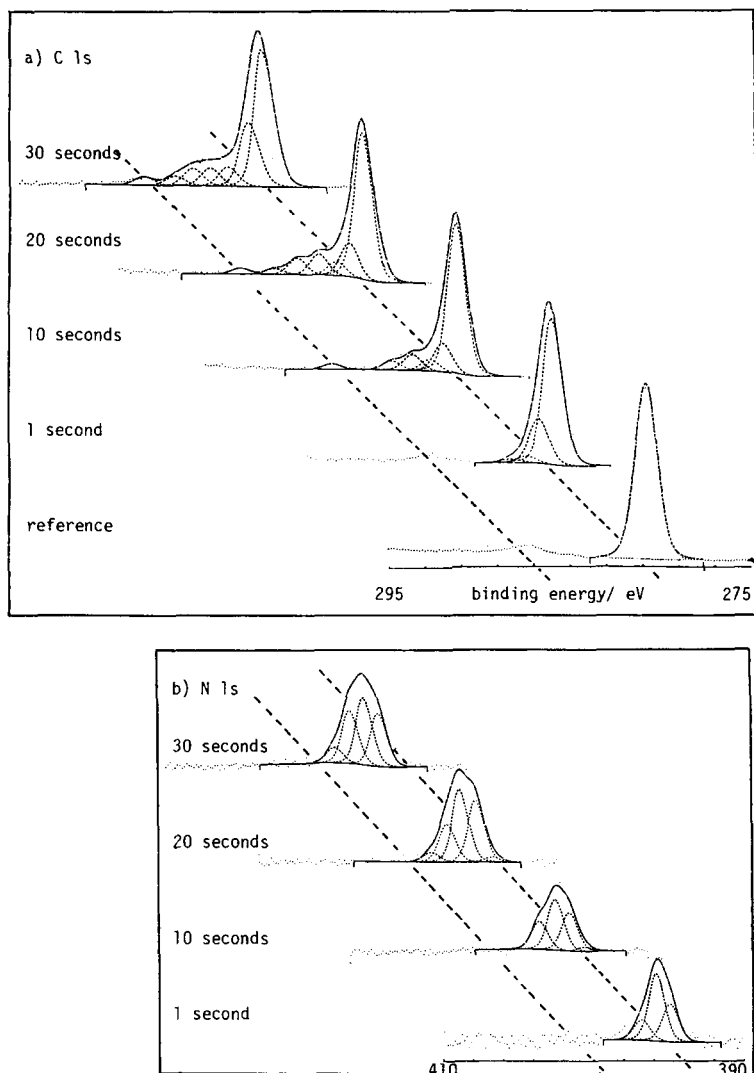
Fig. 5.   (a) C 1s and (b) N 1s spectra of polystyrene after treatment in a remote nitrogen plasma.

in which more than one nitrogen bond to carbon is formed. Furthermore, the maximum amount of nitrogen incorporated by both polymers is the same, i.e., approximately 18 atom % in both this work and other work,[14] such that at the steady state the C : N ratio is about 5 : 1.

One way to explain this is that initially the reaction of the nitrogen atoms with the polymers creates amines at certain intervals on the polymer chain. With longer exposure times, nitrogen atoms remove hydrogen at sites where nitrogen atoms are already present, thus forming C=N and C≡N.[27] This suggests that nitrogen adds to the polymer structure at only very specific sites, suggesting that the reaction with nitrogen atoms requires an "active" site on the polymer to initiate the reaction. Such a site may be a hydroxyl or carbonyl

group, since oxygen is always incorporated during remote nitrogen plasma treatment.

Dilution of Reacting Gas

Downstream from a remote nitrogen plasma the main reactive species are nitrogen atoms.[28] The recombination of nitrogen atoms is however in direct competition with the reaction between the plasma and the surface. Recombination is apparent as an orange/pink afterglow which normally extends down the plasma reactor towards the sample. In order to reduce recombination, dilution of the excited nitrogen with other gases has previously been suggested.[28-31] This was investigated by reacting polyethylene for 1 min and diluting the nitrogen flow with argon, keeping the total gas flow rate constant at 1000 sccm.

Table I shows the flow rates used for the two gases, the percent of nitrogen in the gas mixture entering the reactor and the amount of nitrogen detected on the surface by XPS. The results clearly indicate that as the percentage of nitrogen in the mixture decreases from 100 to 25%, the amount of nitrogen detected on the surface increases. Further dilution however, does not appear to increase the percentage of nitrogen on the polymer surface. Thus dilution of the nitrogen does appear to increase the extent of nitridation, yet there is an optimum ratio of $Ar : N_2$ which creates the highest uptake of nitrogen by polymers. This is in agreement with previous work[31] where the concentration of nitrogen atoms was determined in Ar/N_2 mixtures. Results indicated that the nitrogen atom yield increased with increasing Ar concentration, reaching a maximum at 3% nitrogen.

Dependence on the Reactor Base Pressure

The term "reactor base pressure" in this context describes the minimum pressure reached inside the reactor before reaction. Low pressures may be maintained by an ion pump directly connected to the reactor via a gate valve, or by the turbomolecular pump of the introductory/transfer chamber. In the former case pressures of 2×10^{-8} Torr have been achieved and maintained with extensive use of the reactor. In the latter case only base pressures of 4×10^{-7} Torr and above have been achieved, since it is necessary to break vacuum within this chamber for the introduction of samples.

TABLE I
Dilution of Reacting Nitrogen Gas by Argon, Relative Percentage Uptake
of Nitrogen by Polyethylene, 1 min Exposures

Flow rate N_2/sccm	Flow rate Ar/sccm	% N in mixture	% C	% N	% O
1000	—	100%	84.4	7.5	7.2
200[a]	500	45%	79.2	11.4	9.3
200	800	25%	74.2	18.9	6.9
10	1000	1%	74.1	18.9	7.0

[a] Lower total flow rate.

The availability of these two methods of pumping allowed a systematic study of the effect of reactor base pressure on the rate of reaction of the remote nitrogen plasma with polyethylene. For this study, samples of polyethylene were exposed to a remote nitrogen plasma for a series of different exposure times with base pressures of 10^{-8} Torr, 10^{-6} Torr, and 10^{-5} Torr. During the experiments a gas flow rate of 2000 sccm was used, giving a pressure inside the reactor of 5.4 Torr. Figure 6 shows that by far the highest percentage of nitrogen is taken up for the lowest base pressure of 10^{-8} Torr, with the reaction reaching a steady state after 20 s. As the pressure is increased both the rate and the percentage uptake of nitrogen decreases.

This clearly indicates the importance of low base pressures within the reactor for fast and efficient reaction. As the base pressure increases within the reactor a greater number of contaminating and scavenging molecules are adsorbed on the polymer surface including air, water, and small hydrocarbons. These act as to decrease the amount of nitrogen atoms reacting with the polymer itself and subsequently, the rate and amount of uptake of nitrogen by the polymer.

Depth of Modification

The depth of modification can be investigated using ARXPS.[7,26,32,33] In this work samples were also analyzed by attenuated total reflectance infra red spectrometry (FTIR-ATR) and surface sensitive Raman spectroscopy. Both of these methods probe deeper into the sample, reaching down to and below 1000 Å of the surface, thus also analyzing the bulk of the material. Nitrogen functional groups such as $-NH_2$, $C=N$, and $C\equiv N$ could not be detected by either method, not even by subtraction of the original LDPE spectrum.

ARXPS was performed on samples exposed to the remote nitrogen plasma for 1 s, 15 s and 1 min. Table II gives the $N_{1s} : C_{1s}$ intensity ratios for each of these samples at a number of angles. For the 1 s exposure sample, the maximum
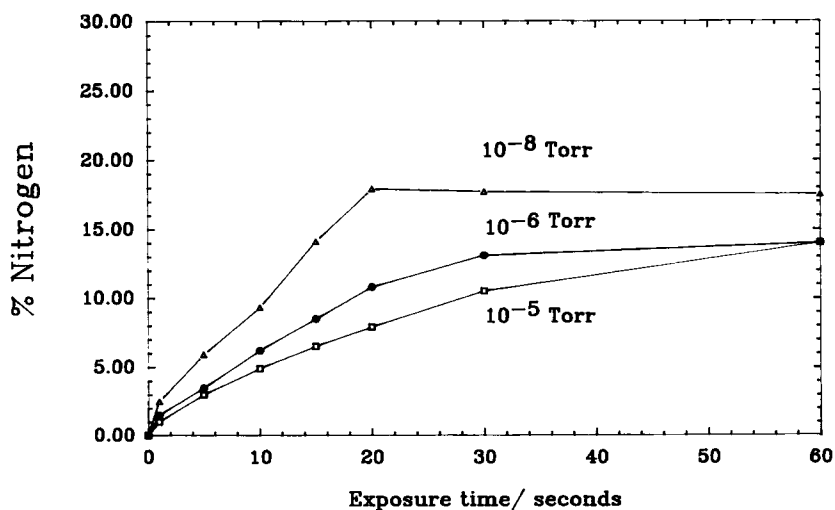

Fig. 6. Percent nitrogen uptake by polyethylene in a remote nitrogen plasma using different base pressures, 2000 sccm, 5.4 Torr.

TABLE II
$N_{1s} : C_{1s}$ Intensity Ratios as Determined by Angle Resolved X-ray Photoelectron Spectroscopy
for Remote Nitrogen Plasma Treated Polyethylene Samples

1 s N_2 plasma		15 s N_2 plasma		1 min. N_2 plasma	
Angle	$N_{1s} : C_{1s}$	Angle	$N_{1s} : C_{1s}$	Angle	$N_{1s} : C_{1s}$
15°	0.007	25°	0.069	15°	0.073
		45°	0.049	35°	0.071
65°	0.009	65°	0.053	65°	0.066
90°	0.005	90°	0.034	90°	0.067

amount of nitrogen detected is low enough that the changes in percentages detected may be considered to be at least equal to the error involved in the analysis. For the 15-s exposure sample, however, the analysis shows a definite trend, indicating a decrease in nitrogen with increasing angle, and therefore increasing sample depth. Thus, at the shallowest angle, sampling the very top atomic layers of the sample, the greatest amount of nitrogen was detected. Assuming an inelastic mean free path of 4 nm in polyethylene, the mean depth sampled at a take off angle 25° is 1.5 nm. For the 1-min exposed sample no trend is observed.

This suggests that after 1 min the polymer surface has been saturated with nitrogen to the sampling depth of the 90° analysis, while after 15 s this is not the case, and the rate of uptake of nitrogen into the polymer surface exceeds the rate of inward diffusion. After 20 s, which is described above as the point at which the maximum amount of nitrogen is incorporated onto the surface, a steady state is reached where the rate of diffusion of nitrogen groups into the polymer is equal to the uptake of nitrogen atoms by the surface and the amount of nitrogen detected remains constant. Eventually a point is reached where the surface, to the sampling depth of ARXPS, is saturated with nitrogen groups and no differences are observed at the various depths probed by ARXPS. Results indicate this to be achieved after 1 min.

Durability of Products

One major concern in determining the usefulness of a surface modification technique is the durability of the products formed by that technique. Ideally, the newly acquired functional groups formed on the surface will remain within the top monolayers of the substrate, either for its life time, or for the time period that it is to be in use. For example, in food packaging it is required that the modified polymer being used will maintain its surface physical properties for at least the expected life time of the food product.

In order to determine the effect of air on remote nitrogen plasma treated polyethylene, a series of experiments were performed over a time period of one month. A sample of polyethylene was exposed to a remote nitrogen plasma for 10 s using a flow rate of 2000 sccm. *In situ* XPS indicated 8 atom % nitrogen on the surface and 6 atom % oxygen. Figure 7 shows the percentage of nitrogen and oxygen detected on the surface observed for several days during the following month. It appears that the percentage nitrogen drops only when the sample is
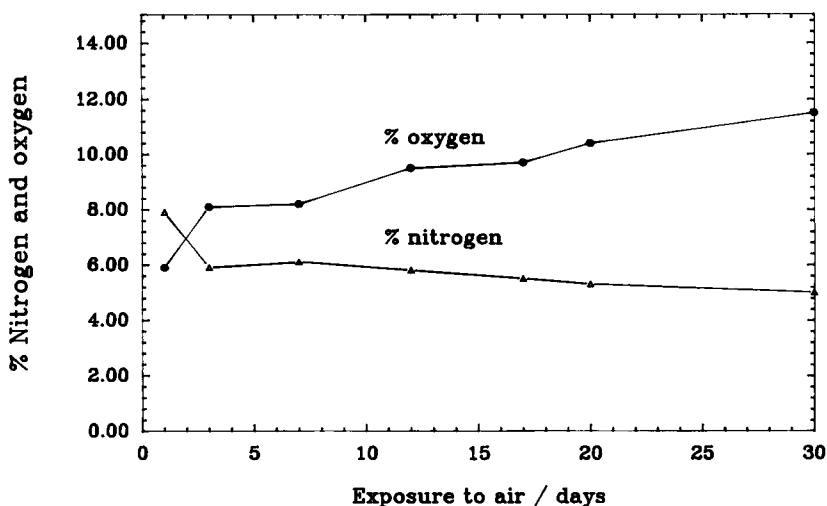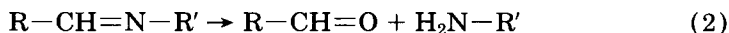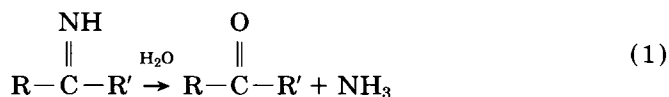
Fig. 7. Durability of remote nitrogen plasma treated polyethylene, change in oxygen and nitrogen content on exposure to air.

initially exposed to the atmosphere. All following experiments indicate an equal concentration of nitrogen of 5.8 ± 1 atom % on the surface. Oxygen, on the other hand, is seen to increase rapidly on initial exposure to air and then more slowly with time. On exposure to air, it thus appears as though there is a direct interchange between oxygen and nitrogen on the surface, with an equal amount of nitrogen being lost as oxygen is gained. An initial loss of nitrogen and the incorporation of oxygen could be understood if imines were present. Hydrolysis by atmospheric water could lead to fairly rapid replacement of nitrogen by oxygen (Eq. (1)) and slower incorporation of oxygen without loss of nitrogen (Eq. (2)).

$$R-\overset{\overset{\displaystyle NH}{\|}}{C}-R' \xrightarrow{H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + NH_3 \tag{1}$$

$$R-CH{=}N-R' \rightarrow R-CH{=}O + H_2N-R' \tag{2}$$

CONCLUSION

The formation of new chemical groups on polymer surfaces by the action of a remote nitrogen plasma has been investigated. The experimental parameters of the gas flow rate and pressure, the initial reactor base pressure, dilution of the gas and the depth of penetration of the nitrogen species within the polymer have been investigated. Results have shown that the best results can be achieved when a minimum base pressure is attained, and when the gas flow rate is at the maximum possible with the equipment used. Under our conditions a steady state situation is reached after 20 seconds for polyethylene and 10 s for polystyrene. The percentage of nitrogen detected on the surface was seen to be the same for both polymers. It is suggested that the reaction proceeds via an active

site on the polymer and that nitrogen atoms attach to the polymer surface at these active sites until no further insertion of nitrogen is possible; following this hydrogen abstraction occurs.

ARXPS indicated that even after a short exposure of polyethylene to the remote plasma, nitrogen is detected below the sampling depth of ARXPS. With longer exposure times, the amount of nitrogen detected at the greatest depth was equal to that at the immediate surface.

A study of the durability of the products of remote nitrogen plasma treatment of polyethylene showed that initial exposure to air caused a decrease in the surface nitrogen concentration, accompanied by an increase in the oxygen concentration. Sequential experiments over a period of one month indicated no further significant loss of nitrogen, yet an increase in the percentage oxygen on the surface perhaps due to hydrolysis by atmospheric water.

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