CHEMICAL STRUCTURE OF PLASMA NITRIDED POLYMER SURFACES

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INTRODUCTION

Often, the existing surface properties of a polymer prevent its use in situations in which its bulk properties would make it an ideal candidate. This problem can frequently be remedied by modifying the surface properties in order to improve characteristics such as wettability, adhesion, friction, biocompatibility, etc. Plasma modification of surfaces presents a quick, efficient method to do so, and it is easily adapted to industrial needs.

We are interested in the surface chemistry and the structure resulting from various elements active on different polymer substrates /1/. Previous work on nitrogen-containing (NH_3, or N_2) plasmas has shown /2/ that the nitrogenated species formed on the polymer surface depend in large measure on the nitrogen source, and this has been confirmed in our laboratory. This paper considers N_2 as the nitrogen source, while the use of NH_3 is considered elsewhere /3/. The substrate used in this study, linear low-density polyethylene (LLDPE), is chosen as a model hydrocarbon polymer.

In the present work, we study the effect of process variables such as pressure, flow rate, exposure time, etc., on the surface modification in terms of composition and the chemical structure. This study is confined to microwave (MW) glow discharges because this type of plasma produces higher concentrations of active species in the gas phase, due to a higher population of electrons in the tail of the electron energy distribution function /4/. This is revealed, for example, by optical emission spectroscopy (OES), where the spectra emitted from the MW glow discharge manifest a higher concentration of atomic nitrogen than in the radio-frequency (RF) plasma /5/.

EXPERIMENTAL

The plasma treatments were carried out in the large volume MW plasma apparatus previously described /1/, where the MW power (2.45 GHz) is applied using a periodic slow wave structure. Ultra high purity N_2 gas, at flow rates up to 100 sccm was used at pressures up to 700 mTorr. In the present case, the power level was kept constant at 100 W.

The LLDPE substrate was obtained from ESSO Chemicals Canada Ltd, Sarnia, Ontario. It was 12.5 μm thick and contained no additives, as confirmed by X-ray photoelectron spectroscopy (XPS). After plasma treatment, the samples were exposed to the atmosphere during their transfer to the surface analytical instrument. The XPS studies were carried out in a Vacuum Generators ESCALAB 3 Mark II instrument using Mg K_α radiation. Surface chemical composition was obtained from the intensities of C(1s), N(1s) and O(1s) peaks in broadscans of XPS spectra.

The presence of different chemical functional groups was determined from high resolution core level XPS spectra. After a Shirley background subtraction /6/, spectra were separated into their component peaks by a computer program developed in our laboratory. This program permits variations in the Gaussian-Lorentzian peak ratio and in the peak width; these parameters, as well as the peak positions, were fixed for each series of spectra. The goodness of fit for each spectrum was evaluated by a chi-squared convergence between the original spectrum and the composite peaks.

RESULTS AND DISCUSSION

A series of experiments was performed to investigate the effect of process parameters such as nitrogen flow rate, pressure, and treatment time on the amount of nitrogen incorporated onto LLDPE surface. Figure 1 shows the atomic concentrations of nitrogen (C_N) and oxygen (C_O) calculated from the intensities of C(1s), N(1s) and O(1s) peaks. For constant exposure times of 30s, C_N increases with pressure and flow rate, rising to a maximum value of 45 atomic %. The presence of oxygen most probably originates from reaction of free radicals on the plasma-treated polymer surface during exposure to atmosphere. The C_O value remains relatively constant (7-9 atomic %).

The evolution of different chemical functional groups was followed as a function of treatment time. Examples of C(1s) and N(1s) XPS spectra are shown in Fig. 2. Peak separations were based on suggested peak positions /3,7-9/, the inductive effect of substituent groups /10/, and a new compendium of values for these inductive effects /11/. These latter values permitted the precise prediction of expected peak positions for several nitrogen-containing species, something which could only be guessed previously.

The positions and assignments of C(1s), N(1s) and O(1s) peaks are shown in Table I. Nitrogen incorporation increases with exposure time, although its apportionment among the three N(1s) peaks suggests several nitrogen components, assigned to amine-N1, imine-N2 and amide-N3 /6/; however, specific chemical identification cannot be determined from the XPS spectra alone. The O(1s) peak assignments are straight-forward: O1-ether, O2-carbonyl.

The C(1s) peak assignments are far more difficult, since they are more complex. Figure 3 shows that the areas of peaks C2, C3 and C4 increase with increasing plasma exposure time, while the oxygen concentration remains constant. This indicates that the increase in the C2, C3 and C4 intensities must be due to nitrogen incorporation only. The surface nitrogenation appears to be completed after 30 s of exposure time (see Fig. 3), in agreement with Fig. 1c.

The surface chemistry was found to change during ageing in ambient atmosphere over a four month period. These changes have been attributed to (1) the addition of adventitious carbon to the surface, (2) reactions of chemical groups leading to structural rearrangements, (3) nitrogen loss, and (4) further oxidation. During the ageing process the intensity of peak C4 (amide and nitrile) remains constant; peak C2 (amine) decreases within the first five days before stabilizing. Only peak C3 has been found to decrease continually during the first two months. This may be attributed to the reaction of imine groups with the atmosphere. A more detailed study of the ageing phenomena is now in progress.

CONCLUSIONS

Up to 45 atomic % of nitrogen has been incorporated onto LLDPE surfaces under optimized MW plasma conditions. The progression of the various carbon-nitrogen containing groups was monitored as a function of treatment time. Ageing in plasma-treated polyethylene was reflected in the loss of nitrogen and an increase in oxygen concentration.

ACKNOWLEDGEMENTS

This work was supported in part by the Institute of Chemical Science and Technology (ICST), by the Natural Sciences and Engineering Research Council of Canada (NSERC), and by the Fonds Formation de Chercheurs et Aide à la Recherche (FCAR) of Québec.

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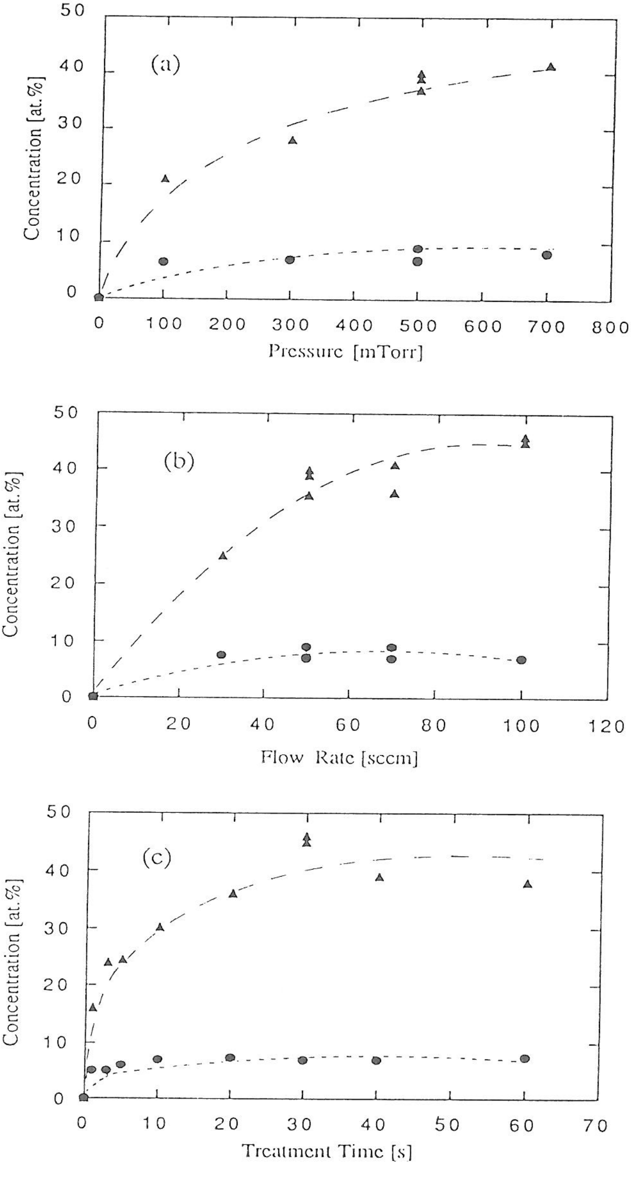

Fig. 1: Atomic concentration of nitrogen (▲) and oxygen (●) on LLDPE after N_2 plasma treatment as a function of a) pressure (flow rate 50 sccm; exposure time 30 s); b) flow rate (pressure 500 mTorr, exposure time 30 s); c) exposure time (pressure 500 mTorr; flow rate 50 sccm).

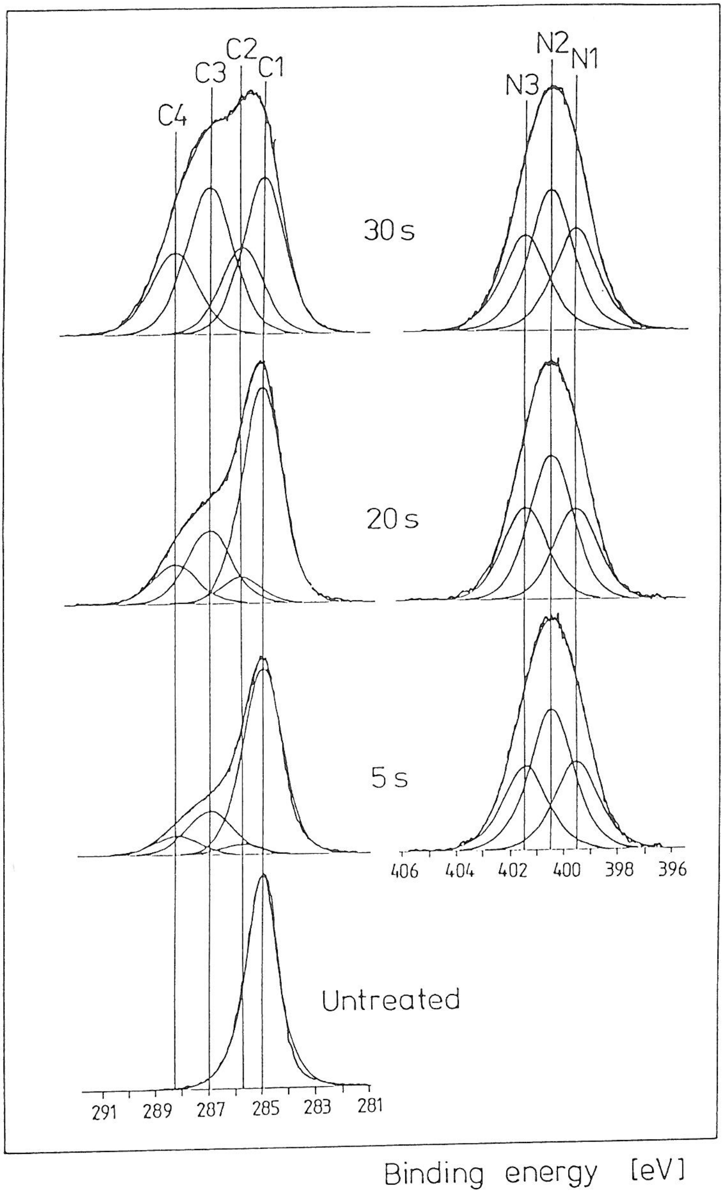

Fig. 2: C(1s) and N(1s) XPS spectra of LLDPE treated in plasma using different exposure times.

TABLE I

The Positions and assignments of deconvoluted C(1s), N(1s) and O(1s) peaks

Peak No.	BE [eV]	Assignment
C1	285.0	C-C , C-H
C2	285.8	C-N , $\underline{C}$-C-OH , $\underline{C}$-C-CHO
C3	287.0	C=N , C-OH, C-O-CH_3 , $\underline{C}$-CHO , $\underline{C}$-N=C=O
C4	288.3	C≡N , N≡C , N-C=0 , C=0
N1	399.7	NH_2
N2	400.6	C=N
N3	401.5	N-C=0
01	532.4	=0
02	533.6	-0-

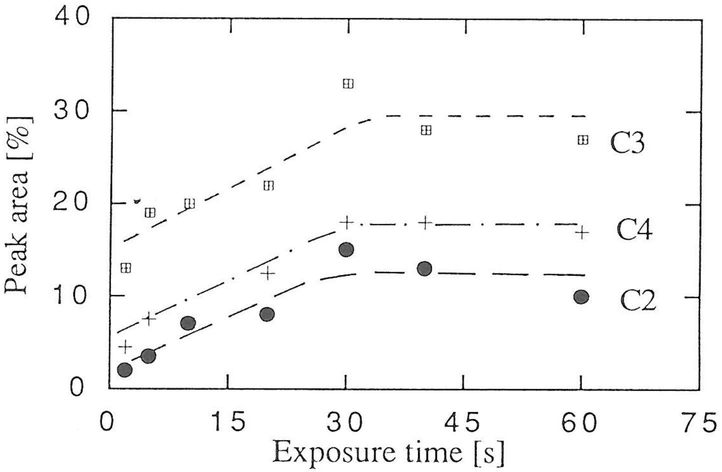

Fig. 3: Intensities of C2, C3 and C4 peaks as a function of exposure time.