Plasma-Treatments of Polymers by means of NH_3-H_2 RF Glow Discharges

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Abstract

The surface modifications induced on polymers by NH_3-H_2 fed RF Glow Discharges have been investigated. Actinometry and ESCA, supported by a derivatization reaction for -NH_2 groups, have been respectively utilized as plasma and surface diagnostics. Correlations between density of active species in the plasma and relative amount of surface-grafted -NH_2 respect to other N-containing groups, *i.e.* the treatment selectivity, have been obtained. Treatment kinetics have been proposed.

Introduction

Plasma-treatments in NH_3 [1], PE-CVD of amines [2], crosslinking and grafting of amine-surfactants by Ar plasmas [3] have been attempted for providing polymers with surface-grafted -NH_2 groups to be later utilized as reaction sites for immobilizing biomolecules *via* conventional chemistry, or for modifying the interactions of polymers with biological media. NH_3 fed RF- and corona discharges have also been studied for improving polymer-polymer or polymer-metal adhesion [4].

Even though the chemistry of NH_3 glow discharges has been investigated [5], direct correlations between the active species detected in the plasma and the resulting surface chemistry have never been really attempted. In our study the relative density of the species detected in NH_3-H_2 discharges have been correlated with the chemical modifications induced on the surface of polyethylene (PE). Treatments of polyethylene-terephtalate (PET) samples have also been performed.

Experimental

The polymer substrates have been modified in a home-made quartz parallel-plate reactor [6]. 13.56 MHz radiofrequency has been utilyzed for sustaining the discharges between the external (RF) and the internal (grounded) electrodes of the reactor. NH_3-H_2 mixtures, with inclusion of small constant amounts of Ar and He for performing actinometry [7], have been utilized as feeds. Constant total flow rate (11 sccm) and pressure (500 mtorr) have been utilized. Different experimental conditions in term of NH_3/H_2 flow ratio, RF power (2÷50 W), and substrate position (glow-afterglow) have been investigated. Actinometry has been performed with a JY HR320 monchromator equipped with a quartz fibre and an intensified multiarray detector. N_2 (3159 Å), NH (3360 Å, 3240 Å), and H (3653 Å) species have been detected in the plasma, along with Ar (7503 Å) and He (3889 Å). C1s, N1s, O1s, F1s detailed ESCA spectra of as-it-is, treated and treated-derivatized PE substrates have been acquired with a Perkin Elmer 5300 PHI ESCA spectrometer. Non monochromatic MgKα X-rays have been used, and a take off angle of 45°. Oxygen has been detected because of post-oxydation of treated PE samples exposed to the atmosphere. The N/C surface ratio of the substrates has been measured within an hour after treatment; duplicate samples have been derivatized with vapors of 4-trifluoromethyl-benzaldehyde (TFMBA, see ref. 6 for the procedure), then analyzed for measuring their $-NH_2/N$ ratio. Derivatization with TFMBA results in three F-atoms per grafted $-NH_2$ group, this allows to distinguish primary amines among other N-groups by ESCA. The N/C ratio directly obtained by treated PE samples has been taken as measure of the *process efficiency* in grafting all kind of N-containing groups; the $-NH_2/N$ ratio obtained by treated-derivatized PE substrates, instead, has been taken as measure of the *process selectivity* in grafting only $-NH_2$ groups [6].

Correlations of the relative densities of N_2, NH, and H species detected in the glow with N/C and $-NH_2/N$ surface ratios of PE samples have been utilized for highlighting the role of each specie in the surface kinetics.

Results and discussion

Changing NH_3/H_2 feed ratio and RF power results in changing the density of the excited species in the glow, hence the nature of the surface modifications changes as well. Certainly the positive-ion bombardment on substrates play also a role in the treatment, but its effects have not been investigated. Figure 1 shows the effect of feed ratio and RF power on efficiency (N/C) and selectivity ($-NH_2/N$) of the treatment on PE substrates.

Actinometric results obtained at different RF powers show a density increase of H-atoms in the plasma when the H_2 feed content is increased; at the same time N_2 and NH densities are decreased. According to ESCA data, the density change of plasma species results in lowering the N/C and incresing the $-NH_2/N$ surface ratios of PE samples, *i.e.* decreasing the grafting of all N-groups but $-NH_2$, and increasing process selectivity. A minimum power input, higher than 2 W in our system, is needed to obtain different $-NH_2/N$ ratios respect to pure NH_3 discharges, probably to trigger the plasma fragmentation of H_2 and the interactions of H-atoms with PE.

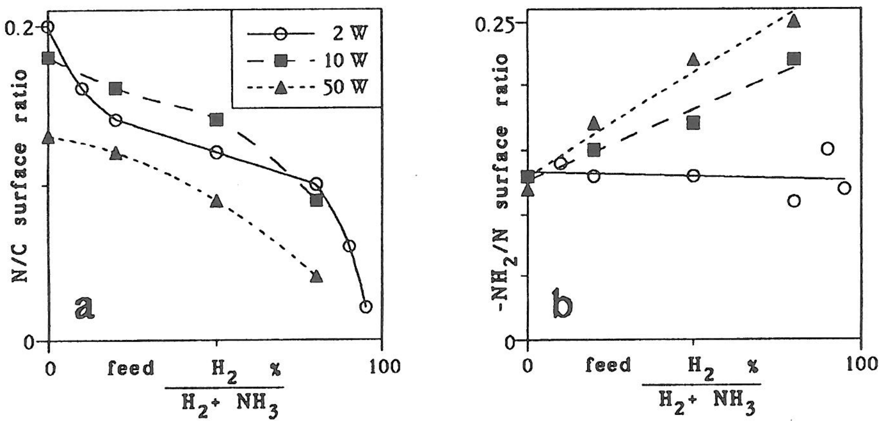

Fig.1 a) N/C and b) $-NH_2/N$ surface ratio of treated PE substrates as a function of the H_2 content of the discharges. The results have been obtained at 5 min treatment time.

Correlations between ESCA and actinometric data, shown in figure 2 for one particular set of experiments, allows to hypothesize the role of each of the plasma species in the overall kinetics. NH and N_2 relative plasma-densities are positively correlated with the N/C surface ratio of treated PE, while H atoms are negatively correlated; the situation is reversed when a correlation with the NH_2/N ratio is attempted. Other nitrogen species related to the above mentioned ones, *e.g.* N atoms, may be present and involved in the treatment, but are not detected in our conditions.

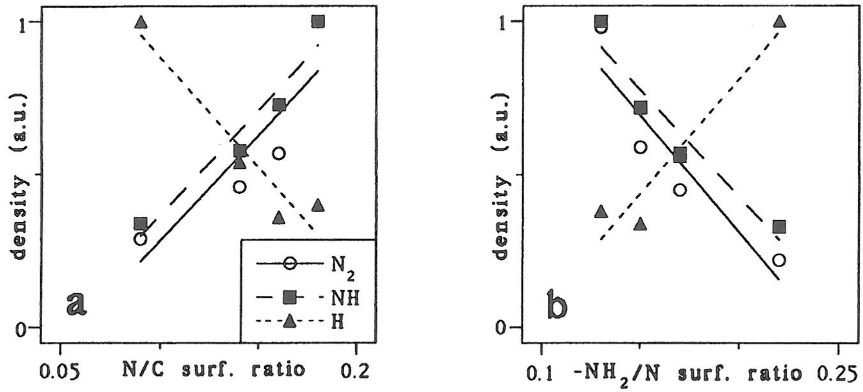

Fig.2 Relative density of the species detected in the plasma (10 Watt, variable NH_3/H_2 ratio, 5 min treatment time) as a function of a) the N/C and b) the $-NH_2/N$ surface ratio of treated PE samples.

The following kinetics scheme can be sketched:

A - NH_3 and H_2 are fragmented in the glow and produce reactive (excited) species, NH, N_2 and H among them, which reacts with PE surface.

B - Heterogeneous processes between N-species of the plasma and PE result in nitrogen groups (amine, imine, cyano, etc.) grafted on PE surface. Amides are also produced later, due to interactions (ageing) with air.

C - H-atoms produced in the glow transform grafted N-groups into $-NH_2$ by a reduction process. As a consequence, the selectivity of the process is increased. Exposition of 100% NH_3-treated PE to a 100% H_2 discharge confirmed this reduction process, which produces also NH_3 [6].

Treatment duration time and substrate position in the reactor have also been changed. Short treatments (seconds) in 100% NH_3 discharges result in increased selectivity ($-NH_2/N$ up to 0.4), but decreased efficiency. Afterglow treatments, characterized by a lower and different density of active species respect to the glow and by the absence of positive-ion bombardment on the substrate, result also in higher selectivity of the $-NH_2$ grafting ($-NH_2/N$ up to 0.75), as shown in figure 3.

The results presented so far deals only with surface treatment of PE samples, and have been obtained by analyzing the substrates soon after the treatment. Ageing occurs to some extent, starting hours after the treatment, but it has not been investigated yet.

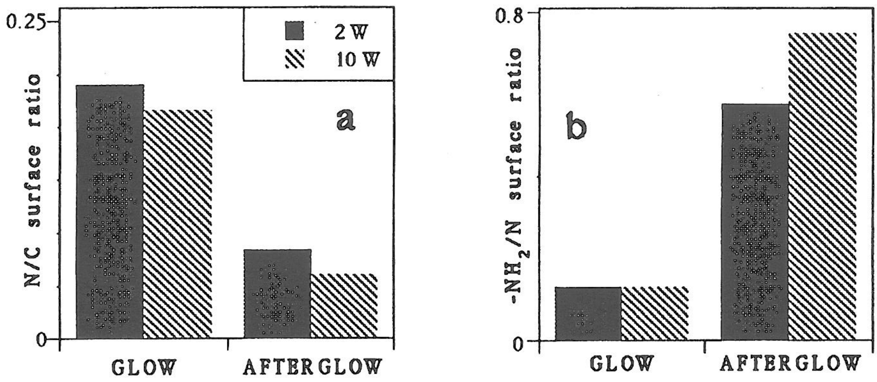

Fig.3 Differences in a) the N/C and b) the $-NH_2/N$ surface ratio of PE substrates treated in the glow and afterglow region of 100% NH_3 discharges at different power (5 min treatment time).

NH_3-H_2 plasma treatments have been attempted also on PET for improving its wettability and related biomedical properties. ESCA data confirm the surface production of both amine and amide groups, and show clear correlations between the water contact angle and the N/C and $-NH_2/N$ surface ratios induced on the polymer, as shown in figure 4.

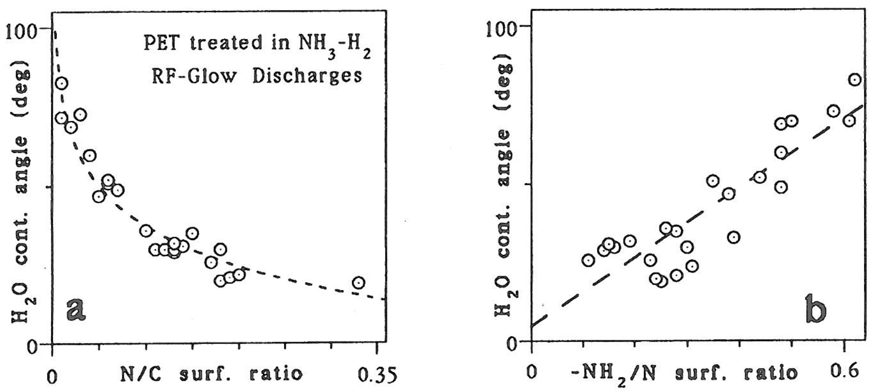

Fig.4 Water contact angle of treated PET samples, measured just after plasma-treatments performed in different conditions, as a function of a) the N/C and b) the $-NH_2/N$ surface ratio measured by ESCA.

Conclusions

Coupling actinometry and ESCA diagnostics in studying plasma-treatments allows to correlate the species present in the plasma with the chemistry of the modified polymers. This approach facilitates the understanding of the microscopic mechanism of interactions and of the effects of plasma parameters. Methods for enhancing the grafting selectivity of amine- *versus* other N-groups have been provided for NH_3-H_2 plasma-treatments of PE, which might turn useful also for surface-modifying different polymers.

References

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