OPTICAL EMISSION SPECTROSCOPY OF TETRAFLUOROMETHANE PLASMA AS A DIAGNOSTIC OF SURFACE MODIFICATION OF POLYMER

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Fuorocarbon have been widely used, because of the resulting hydrophobic properties and their ability to promote polymer modification or etching. In the present work, on one hand, the fluorocarbon plasma is studied by an in-situ method, such as optical emission spectroscopy to identify excited species in the plasma. The evolution of CF, CF_2*, and F* emissions has been followed during the treatment of an organic surface, a n-alkane the hexatriacontane. Hexatriacontane has been used as a model of high density polyethylene because it provides a very flat substrate with a regular and simple atomic structure, thus enabling all potentialities of surface analyses such as AFM microscopy. On the other hand, hexatriacontane surface treated in different plasma conditions has been investigated by atomic force microsocopy (AFM) and surface tension measurements. Moreover, some relationships have been established between the behavior of the excited species in the CF_4 plasma and the properties of the treated surface.*

Introduction

Fluorocarbon plasma treatment of polymers is a powerful tool to modify their surface properties because of the hydrophobic property given to the polymer and of its ability to promote polymer etching. The interactions of plasma and a *n*-alkane (HTC

hextratriacontane, model of high density polyethylene [1-3]) surface are discussed on the basis of studies by optical emission spectrometry, atomic force microscopy and surface energy measurements. Some relationships have been established between the behaviour of the excited species in CF_4 plasma and the properties of the treated surface.

Experimental part

Thin films were prepared by melting the HTC (Aldrich) on aluminium sheets as described in [4,5]. The microwave plasma apparatus and the process are described in [4,5]. The sample substrate can be moved in or out of the plasma volume. Z corresponds to the distance between the bottom of the excitator and the substrate. Emission spectroscopy was performed with a Jobin Yvon HR 320 monochromator with a focal length of 32 cm equipped with two 1200 grooves/mm gratings and a Hamamatsu R928 photomultiplier whose spectral response ranges from 185 to 950 nm. The surface energies of the sample were estimated from the contact angles with distilled water, glycerol and diiodomethane using the classical method of Young-Dupre [6-7] and Fowkes [8]. Atomic force microscopy (AFM) experiments were carried out with a Nanoscope III (Digital Instruments, Santa Barbara, USA).

Results and Discussion

Excited species in tetrafluoromethane plasma

Emission spectrum of tetrafluoromethane plasma with 2% of argon was recorded from 200 to 710 nm. The CF_2^* emissions (A^1B_1 - X^1A_1) are easily observed between 240 and 280 nm. The strongest one is observed at 251.6 nm. Underneath these bands is a continuum emission from other states of CF_2 assigned by d'Agostino [9] to an electronic transition for the CF_2^+ ion from the $4b_2$ state to $6a_1$ state. The CF^* emission ($B^2\Delta$ - $X^2\Pi$) is also easily observed (strongest CF^* peaks at 202.4 nm [(0, 0) transition] and 208 nm [(0, 1) transition]). The fluorine atomic emissions were observed at 685.6 nm, at 690.2 nm and at 703.7 nm. The fluorine atom emission is much weaker than CF^* and [CF_2^*+ CF_2^+] emissions. In addition, the argon atom emissions at 420.4 nm and at 416.4 nm were also detected.

With the use of the actinometric technique [9-13], the relative concentrations of reactive species in the plama were estimated. The recorded intensities, for all emissions, decrease with the distance Z from the plasma source. The reactive species are much more concentrated in the discharge than outside.

Quantitative changes are observed when the sample is introduced into the plasma. $CF^*$and [CF_2^* + CF_2^+] emission intensities are enhanced by HTC, while the

emission of atomic fluorine is reduced. It results first in a jump in CF^* and [CF_2^*+ CF_2^+] emission intensities. Then, these intensities increase progressively and stabilize after about 3 minutes. The increase is about 20% for CF^* and 40% for [CF_2^*+ CF_2^+]. An opposite kinetics is observed for the F^* emission at 685.6 nm, and the process is faster. The relative decrease is about 25%.

The increase of [CF_2^*+ CF_2^+] and CF^* radicals in the presence of HTC is a signature of the catalytic recombination in the gas phase as described in the following scheme proposed in [14-16]

$$F + CF_{n-1} + M \rightarrow CF_n + M \quad (n = 2...4)$$

where *M* stands for a third body (gas species, reactor walls or HTC film).

Fluorine atoms should also be incorporated in the HTC surface where they form the fluorinated groups responsible for surface modification or degradation.

Surface energy modification of hexatriacontane

Cold plasma modification of organic materials results in functionalization and degradation of the surface [17]. On one hand, the fluorination which creates the fluorinated groups leads to a modification of the surface energy of hexatriacontane. On the other hand, the degradation induced by fluorine atoms bombardment changes the morphology of the surface. The investigation of modifications in surface energies and morphologies should help the understanding of the interactions between hexatriacontane surface and plasma phase.

As described previously [5], the CF_4 plasma treatment leads to a decrease in surface energy. This decrease is more important in the discharge than in the post discharge. Moreover, the polar term increases slightly with the substrate distance Z for a short treatment time, especially in the post discharge. This means that in the post discharge a short plasma treatment produces an incomplete fluorination of the HTC surface, but in the discharge it appears that a fluorinated layer was formed all over the surface even after 10 seconds treatment. HTC treated in the discharge presents a very low surface energy (~9 mJ/m^2) due to the formation of fluorinated oligomers or small fluorinated molecules on the HTC surface.

Additional informations can be obtained from the comparison of surface energy data and emission intensities of reactive species in the plasma phase (Fig. 1). The surface energy decreases with the quantum yield (normalized relative intensities times the treatment duration) of reactive species which include both CF_x radicals (CF and CF_2) and F atoms. CF_x in the gas phase represents key species in plasma deposition,

forming a fluorinated layer but F atoms can also react with HTC molecules leading to the formation of fluorinated groups on the HTC surface. Both actions result in a decrease of the surface energy. The surface energy decreases rapidly with the quantum yield at the begining, then remains constant, probably due to a saturation effect but also to an equilibrium between degradation and fluorination. A similar surface energy can be obtained either by a long treatment time with a weak emission, or by a short time with a strong emission. The emission intensity of reactive species can be used to quantify the changes in surface properties for a given plasma configuration.

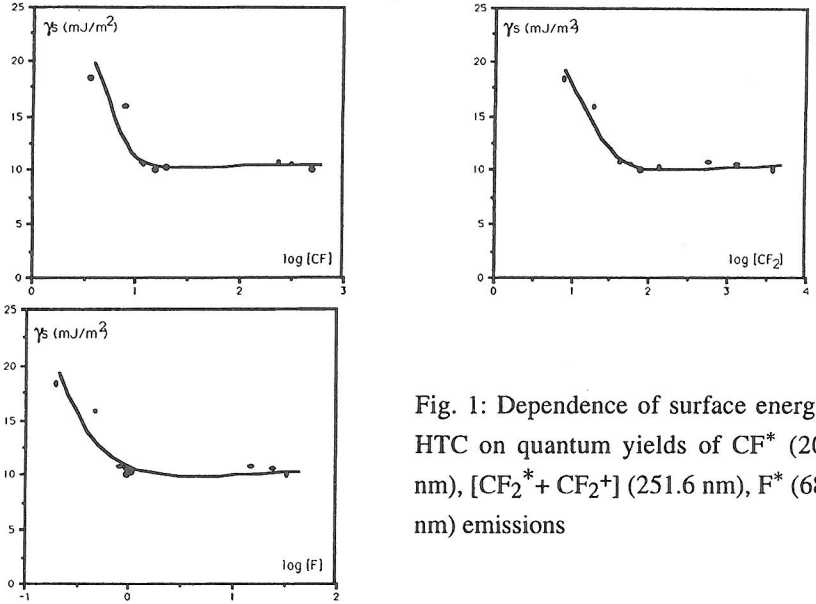

Fig. 1: Dependence of surface energy of HTC on quantum yields of CF^* (202.4 nm), $[CF_2^* + CF_2^+]$ (251.6 nm), F^* (685.6 nm) emissions

Plasma treatment and surface morphology modification

The effect of plasma treatment on the surface topography has been investigated in previous works [18]. The fluorine containing plasma appeared to lead at a microscopic scale to no significant degradation of the surface, even building a smooth surface [4,18]. In the present work, the plasma treated HTC surfaces are investigated at a nanometer scale by atomic force microscopy. An increase of surface roughness is observed. At a nanometer scale, untreated HTC shows a perfectly smooth surface and the high resolution observation shows the arrangement of HTC molecular chains. After treatment, the surface becomes rough, and a nodular structure appears on the film surface as for polypropylene treatment [19]. This is more obvious in the discharge than in the post discharge. The size of nodules increases with the treatment time. In addition,

the arrangement of molecular chains is perturbed by plasma treatment and explained by the formation of a non crystal material with an imperfect arrangement.

To evaluate quantitatively the effects of the plasma treatment on the surface morphology, surface roughness R_a was determined [20]. The results are presented as the surface roughness versus the quantum yield of [CF_2^*+ CF_2^+], CF^* and F^* (Fig. 4). The curves have the same shape for the three kinds of reactive species. In mild plasma conditions, the change in surface roughness is small. However, the strong plasma exposure either in discharge or in post discharge for a long time leads to a large increase of the surface roughness. CF_x radicals and F atoms in the plasma phase are at the origin of plasma deposition and plasma degradation respectively. Both effects enhance the surface roughness, essentially the latter is more important. Consequently, the surface roughness increases with both the F atom and CF_x radicals concentrations. By comparing Fig. 1 and 2, mild plasma exposure can result in a great decrease of the surface energy, whereas the surface roughness only changes under drastic plasma exposure. It means that the chemical modification of HTC surface occurs in very light exposure conditions even in the post discharge far from the plasma source.

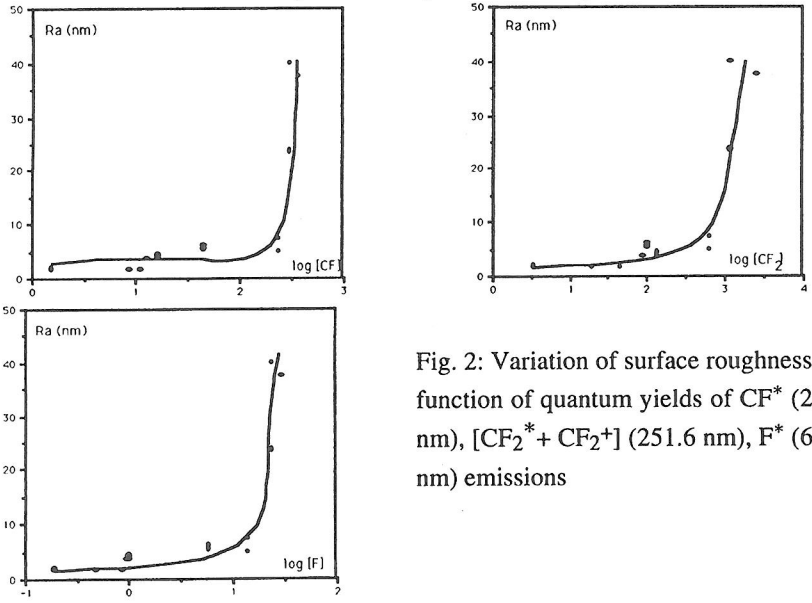

Fig. 2: Variation of surface roughness as a function of quantum yields of CF^* (202.4 nm), [CF_2^*+ CF_2^+] (251.6 nm), F^* (685.6 nm) emissions

Conclusion

The CF_4 -2%Ar plasma treatments lead to a fluorination of hexatriacontane surface, decreasing the surface energy, and result in surface roughness by both

degradation and deposition. The optical emission in plasma gas phase is not only an indication of the reactive species concentration, but also provides a measurement of the surface modification. The surface properties, such as surface energy and surface roughness, are correlated to the emission intensities of reactive species in the plasma gas phase.

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