

Generation of Teflon-like layers on cellophane surfaces under atmospheric pressure non-equilibrium SF₆-plasma environments

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Summary

In this contribution a novel atmospheric pressure SF₆-cold-plasma method is suggested for the conversion of cellophane surfaces into perfluorinated layers. This approach takes advantage of the efficiency of SF_x (x<6) species generated in the discharge for oxygen extraction, dehydro-fluorination and fluorination reaction mechanisms. It was shown that relative surface atomic concentrations as high as 58% can be created under relatively short treatment times (5 minutes), and that CF₂ groups are the dominant components of the plasma-generated surface layers. Surface morphology analysis by atomic force microscopy (AFM) and scanning electron microscopy (SEM) indicate that SF₆-discharge environments selectively interact with the amorphous and crystalline zones of cellulose. Contact angle evaluations of plasma-exposed cellophane surfaces show an intense hydrophobic character, with contact angles as high as 120°. Potential applications of perfluorinated cellophane layers are suggested.

Introduction

Highly fluorinated thin surface layers, resembling poly(tetrafluoroethylene) (PTFE), should exhibit properties such as chemical inertness, thermal stability, low coefficient of friction, low dielectric constant, low surface-energy, and low oxygen and water permeation characteristics. Conventional PTFE technologies do not allow the deposition of thin layer structures due to the insolubility and infusibility of PTFE. High-CF₂-content thin macromolecular layers were synthesized under cold-plasma environments in several laboratories; however, none of these attempts resulted in the deposition of exclusively CF₂-based structures [1-4]. In addition, these plasma layers usually have a network nature based on branched and/or cross-linked macromolecular structures, which often incorporate trapped free radicals generated by the discharge. As a result, some of the desired “Teflon” characteristics, including reduced adhesion and slipperiness, are not associated with the plasma-generated fluorinated layers. Conventional wet-chemistry techniques do not offer solutions for efficient surface modification of polymers. These organic chemistry technologies are complex and usually require the use of large quantities of toxic solvents, which causes the need of additional stages in order to turn them into environmentally friendly processes. As a consequence they become commercially unattractive.

In this contribution, a novel process for surface fluorination of cellophane under atmospheric pressure non-equilibrium SF_6 -plasma environments is discussed. The suggested fluorination technique takes advantage of the special properties of SF_4 species generated by the discharge, which simultaneously promote oxygen-extraction and dehydro-fluorination/fluorination surface reaction mechanisms. It is known that SF_4 species convert $-\text{C}=\text{O}$ and $-\text{COOH}$ into $-\text{CF}_2$ and $-\text{CF}_3$ groups, and metal oxides into fluorides, which usually are in the same oxidation state [6]. The de-oxygenation/fluorination reactions of cellophane surfaces were carried out using a ceramic plasma tool, where the thin-plasma-layer is initiated and sustained, at atmospheric pressure, on the top of a flat ceramic plate.

Experimental

Sulfur hexafluoride was purchased from Aldrich Chemical. The relative surface atomic composition of cellophane samples were evaluated by electron spectroscopy for chemical analysis (ESCA) using a Perkin-Elmer Physical Electronics 5400 small area ESCA system (Mg source; 15 kV; 300 W; takeoff angle 45°). Carbon, oxygen, and fluorine atomic concentrations were evaluated, and the nonequivalent positions of carbon linkages were analyzed. In order to correct surface-charge-origin binding energy shifts, calibrations were performed based on the well-known C–O (286.7 eV) C_{1s} peak of cellulose.

Plasma-induced modifications of surface morphologies of cellophane substrates were evaluated by contact-mode AFM using a Digital Instruments Nanoscope III, and by electron microscopy with a LEO 1530 Field Emission SEM.

Contact angle tests were performed by the projected sessile droplet method with deionized water (5 μL), using a Ramé-Hart NRL C.A. goniometer. A sustaining 60 seconds contact angle was measured.

Plasma treatment of cellophane substrates:

All SF_6 -plasma-enhanced modification of cellophane surfaces were carried out using a custom designed atmospheric pressure 10 kV and 1 kHz flat-plate plasma installation presented in Figure 1. Similar atmospheric pressure plasma installations have been designed earlier [7]. The plasma-reactor is composed of a $105 \times 105 \times 6$ mm ceramic plate, which locates a comb-type, 1 mm diameter brass-wire, double electrode assembly. One of the electrodes is connected to the high voltage, high frequency power supply, while the second electrode is grounded. The electrodes are located at the bottom of grooves, which are machine-tooled into the ceramic plate, and are isolated from the plasma environment by a 0.8 mm thick ceramic layer. The grooves are filled with a dielectric material (e.g. PTFE, epoxy resin, silicon rubber, etc.), which insulates the electrode assembly from the atmosphere. When the high voltage, high frequency field is dissipated to the electrodes, a planar discharge (up to 3-mm thick) is initiated and sustained at the top of the ceramic plate (Figure 2). It should be mentioned that various electrode designs and assemblies can generate such surface discharges, including double-spiral electrode arrangements. By confining a small volume in a 0.5 to 5 mm narrow gap between the “plasma-generating ceramic plate” and a dielectric or conductive flat surface, such as glass, quartz or metal sheets, which are separated from the ceramic reactor by a dielectric spacer (e.g. silicon rubber O-ring), a very efficient plasma-reactor can be developed.

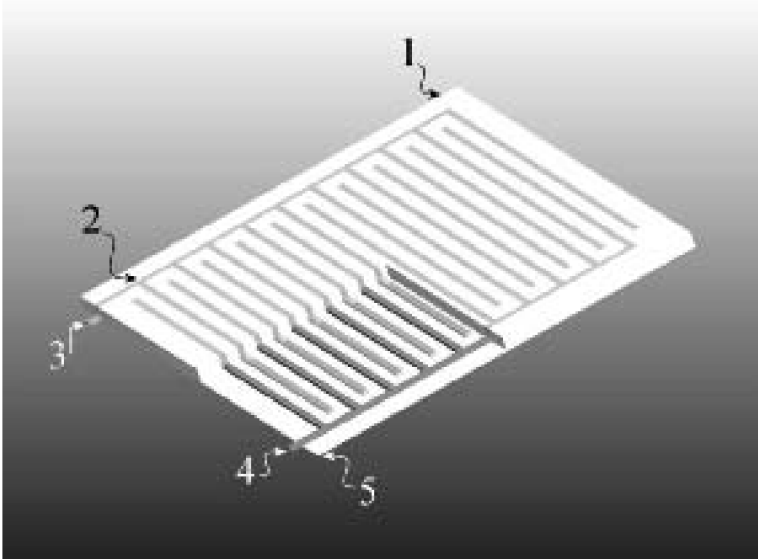


Figure 1. Ceramic Plate Reactor: (1) 6 mm thick ceramic plate, (2) electrode-enclosing-grooves filled with dielectric material, (3) charged electrode, (4) grounded electrode, (5) 0.8 mm thick ceramic layer.

The main advantage of this plasma-reactor is that the whole electrode system is embedded in one ceramic plate. This configuration allows initiation and sustaining of the atmospheric pressure discharge without constraints on the thickness of the substrate, since the reactor can be placed on top of the surface to be treated, whereas a parallel plate barrier discharge assembly requires a narrow gap between the plates to initiate and sustain the plasma. In addition, the reactor can be built in different shapes in order to accommodate any form or profile of the surface to be treated.



Figure 2. Ceramic plate reactor discharge.

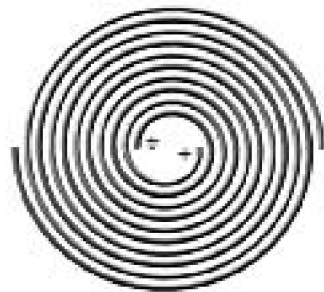


Figure 3. Spiral Electrode Configuration.

This atmospheric pressure plasma reactor opens up very attractive, novel ways for surface-modification of materials, using “ironing-type” plasma technologies, including functionalization, deposition, and surface disinfection/decontamination processes.

Results and discussion

Carbon and oxygen ESCA spectra of untreated and SF₆-plasma-treated cellophane are presented in Figures 4 and 5. All C_{1s} binding energy peak assignments have been made according to model-compounds. The following model-compounds were considered for the assignment of nonequivalent C_{1s} binding energy peaks: cellulose, perfluorofullerenes, poly(tetrafluoroethylene), poly(vinyl fluoride), poly(vinylidene fluoride), poly(vinyl trifluoroacetate), poly(trifluoroethyl acrylate), Viton ATM, and Fomblin YTM [8,9].

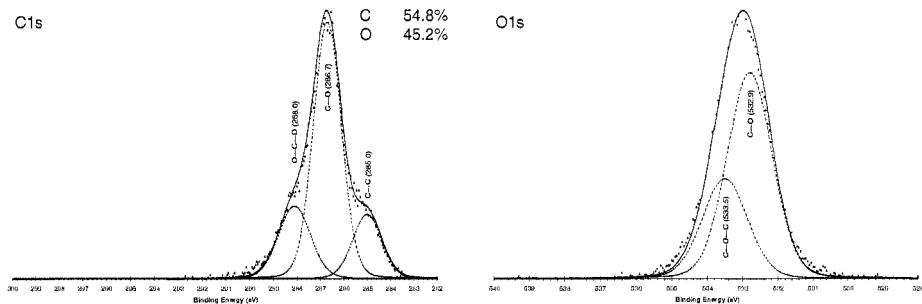


Figure 4. Carbon (C_{1s}) and oxygen (O_{1s}) ESCA spectra of untreated cellophane.

The C_{1s} ESCA spectrum of untreated cellophane shows, in addition to the characteristic C–O (286.7 eV) and O–C–O (288 eV) peaks, the presence of a relatively intense C–C (285 eV) peak, which is generally found in all cellulose-based samples, and its origin is not fully understood. As a result of the presence of this peak, the relative surface atomic composition of cellophane films is slightly different from the theoretical values for cellulose (Figure 4). The O_{1s} spectrum of untreated cellophane exhibits only the characteristic binding energy peaks associated with cellulose: C–O (532.9 eV), and C–O–C (533.5 eV).

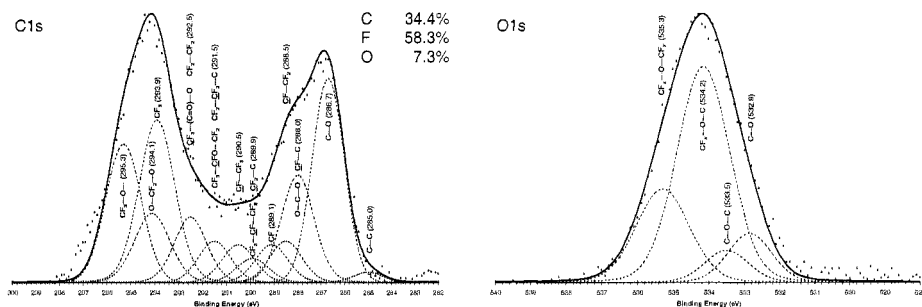


Figure 5. Carbon (C_{1s}) and oxygen (O_{1s}) ESCA spectra of SF₆-plasma-treated cellophane.

The C_{1s} ESCA spectrum of SF₆-plasma-exposed cellophane (Figure 5) shows, in addition to the characteristic peaks of cellulose, large area $\underline{\text{CF}}\text{-C}$ (288.0 eV), $\underline{\text{CF}}\text{-CF}_2$ (288.5 eV), CF (289.1 eV), $\text{CF}_3\text{-}\underline{\text{CF}}\text{-CF}_2$ and $\underline{\text{CF}}_2\text{-C}$ (289.9 eV), $\underline{\text{CF}}\text{-CF}_3$ (290.5 eV), $\text{CF}_3\text{-}\underline{\text{CFO}}\text{-CF}_2$ and $\text{CF}_2\text{-}\underline{\text{CF}}_2\text{-C}$ (291.5 eV), $\text{CF}_3\text{-C(=O)-O}$ and $\text{CF}_2\text{-CF}_2$ (292.5 eV), CF_3 (293.9 eV), $\text{O-CF}_2\text{-O}$ (294.1 eV), and $\text{CF}_3\text{-O-}$ (295.3 eV) peaks. The very high fluorine and relatively low oxygen surface atomic concentrations indicate that oxygen

atoms were efficiently extracted from the surface layers of cellophane by the plasma-generated SF_x species and replaced, during the plasma treatment, for CF_x ($x < 4$) functionalities. The presence of C–O and O–C–O peaks in the plasma-treated samples, suggests that the SF_6 -plasma-enhanced surface-modification reaction mechanisms affected only a depth of about 100 Å of the surface structure of cellophane. The O_{1s} spectrum of modified cellophane surfaces (Figure 5) also indicates that, in addition to the presence of C–O (532.9 eV) and C–O–C (533.5 eV) bonds, CF_x –O–C (534.2 eV) and CF_x –O– CF_x (535.3 eV) linkages are present in the plasma-modified surface layers.

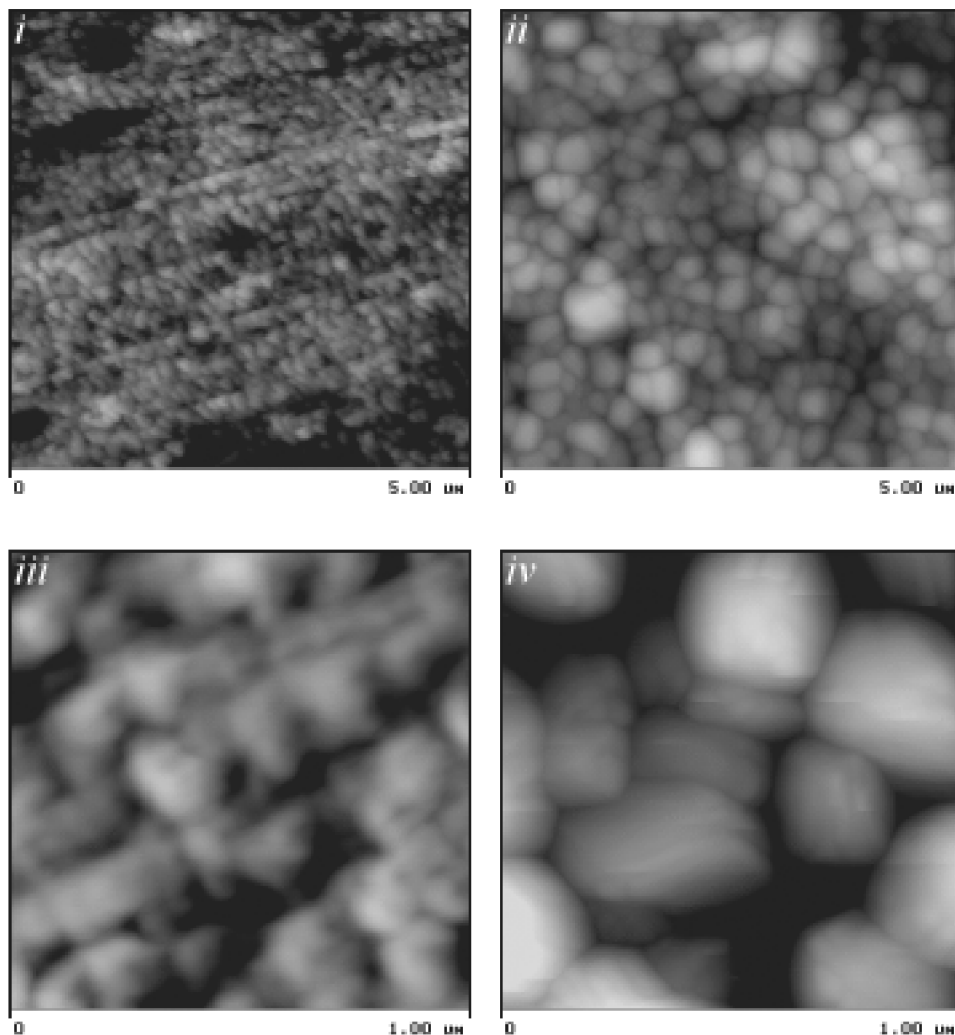


Figure 6. AFM top view images: (i) and (iii) untreated cellophane, (ii) and (iv) SF_6 -plasma-treated cellophane.

AFM and SEM images collected from unmodified and plasma-treated cellophane substrates (Figures 6-8) show significant surface-topography changes, generated as a

result of the interaction of SF_6 -plasma-species with cellophane. Top and trimetric views of the height AFM images clearly indicate that a hazy, granular surface structure of cellophane was transformed to larger, more clearly defined, ordered morphologies. These significant surface-topography changes can be explained by a selective etching, by the SF_x -plasma-species, of amorphous and crystalline zones of the cellulosic structure. As a result of the plasma-enhanced etching mechanisms, the more ordered crystalline domains will be exposed in the top cellulose layers. SEM micrographs (Figure 8) substantiate the AFM results. A distinctive granular (ordered) surface topography with larger-dimensions characterizes the modified substrates.

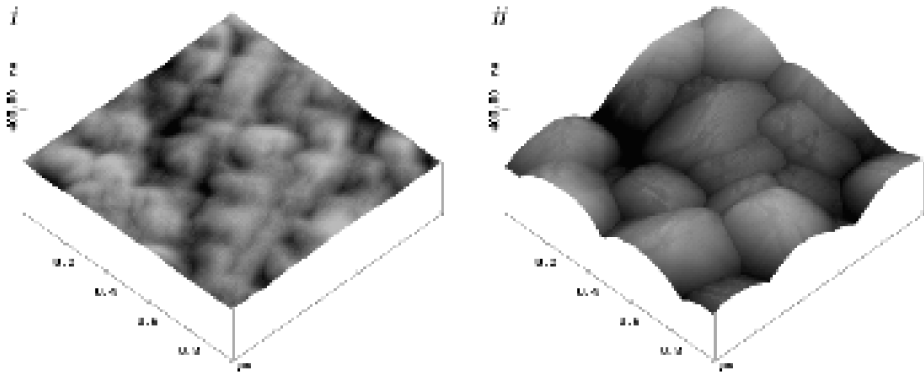


Figure 7. AFM trimetric images: (i) untreated cellophane, (ii) SF_6 -plasma-treated cellophane.

Contact angle evaluations performed on the cellophane surfaces, show that the low contact angle values characteristic of cellophane, become higher than 120 degrees for the SF_6 -plasma-treated cellophane. It is noteworthy that contact angle measurements performed after a 2 week period did not indicate noticeable changes.

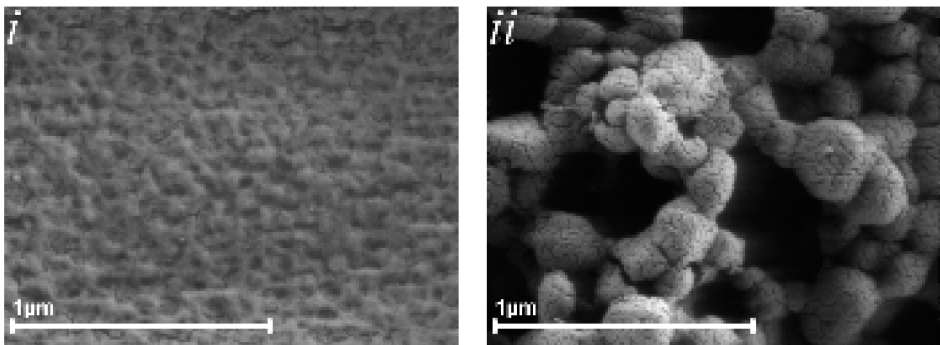


Figure 8. SEM images: (i) untreated cellophane, (ii) SF_6 -plasma-treated cellophane.

Conclusions

It has been shown that the atmospheric pressure “surface-plasma” system considered in this investigation is an efficient tool for surface-modification of cellophane. Efficient oxygen-extraction and fluorination SF_6 -plasma-enhanced reaction mechanisms were developed in the surface layers of discharge-exposed cellophane.

Stable contact angle values of 120 degrees were achieved as a result of the plasma treatments. It was demonstrated that the SF_x plasma-generated-species interact selectively with the amorphous and crystalline domains of the cellulose structure. This investigation opens up novel ways for the synthesis of renewable and biodegradable films with potential application in membrane and food-packaging technologies.

References

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