

# Polymer deposition using atmospheric pressure plasma glow (APG) discharge

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## Abstract

A stable fluoro-polymer film was incorporated onto the inner surface of commercial poly(vinyl chloride) tube by atmospheric pressure plasma glow (APG) discharge treatment. A hydrophobic surface was obtained by polymerizing monomers like hexafluoropropylene (HFP) or tetrafluoroethylene (TFE) by the APG method and had high contact angle ( $\approx 98^\circ$ ) and peaks corresponding to fluorine functionalities (at about  $1200\text{ cm}^{-1}$ ) on Fourier transform infrared (FTIR) attenuated total internal reflection (ATR) spectra. The structural differences of the polymers deposited by HFP/He or TFE/He APG treatments were observed on X-ray photoelectron spectroscopy  $C_{1s}$  spectra: upon TFE/He APG treatment,  $CF_2$  was the main component of the deposited polymer, but upon HFP/He APG treatment, approximately equal amounts of CF,  $CF_2$  and  $CF_3$  were present in the deposited polymer. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Atmospheric pressure plasma glow discharge; Hexafluoropropylene; Plasma polymer deposition

## 1. Introduction

The energy level of the different active species in plasma discharge is high enough at 0.5–20 eV to dissociate all of the chemical bonds in organic compounds. Hence it is widely used in applications such as film deposition or surface modification by plasma polymerization and etching [1–6]. Most of such processes are conducted at low-pressure of a few Torr, and therefore it is difficult to apply plasma discharge for large scale objects, especially by continuous treatment. Application of low-pressure glow plasma is limited due to the need of vacuum system, and hence, cannot be used to treat powder and high vapor-pressure materials. Since the vacuum system required for industrial processes is very expensive, corona discharges, which are filamentary discharges at atmospheric pressure, are widely used. A limitation of corona discharge is that they lack uniformity because it is very difficult to control the spatial repartition and energy of each individual discharge canal. It is, thus, very important to achieve a stable, homogeneous glow discharge in plasma processes at atmospheric pressure.

Atmospheric Pressure plasma Glow (APG) discharge has been developed by Okazaki and coworkers since 1988 [7,8].

A stable glow discharge at atmospheric pressure requires: (i) the use of helium as a dilution carrier gas; (ii) the use of a source frequency of 1–20 kHz; and (iii) the insertion of a dielectric plate (or plates) between the two electrodes. This technique is useful in modifying materials by way of surface treatment, deposition, and surface etching similar to low-pressure glow plasmas [9,10].

We report the application of APG discharge to fluorinate the inner surface of commercial poly(vinyl chloride) (PVC) tubes to enhance biocompatibility for a blood circulating tube. A fluoro-polymer layer on the inner surface of PVC tube increases its blood compatibility and suppresses the bleeding of plasticizers present in the commercial PVC. Furthermore, it is so difficult for the conventional low-pressure glow plasma to coat the inner surface of soft tubular structures due to the pressure differences between the tube inside and outside which will distort the walls.

## 2. Experimental

### 2.1. Plasma treatment

Fig. 1 is a schematic representation of the system we used for the plasma polymer deposition. The special electrode used for APG discharge was insulated, and consisted of two electrically conductive parallel structures—two copper

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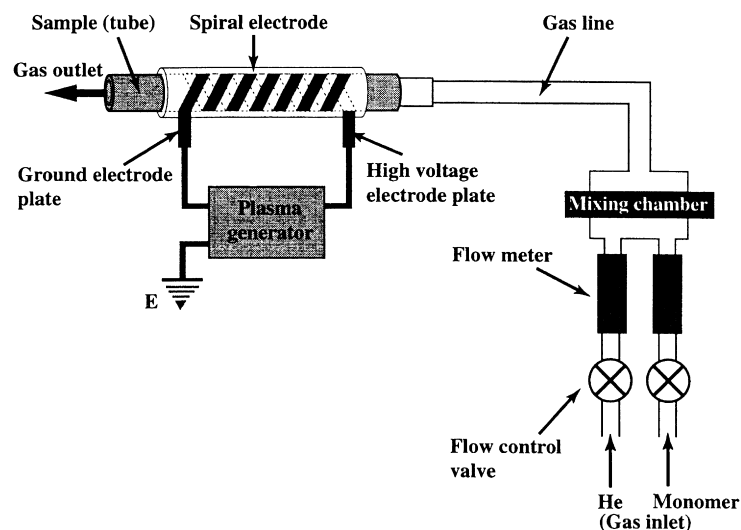


Fig. 1. Schematic representation of the APG Treatment system.

plates, each  $\approx 3$  mm wide—helically wound around a cylindrical glass. This was embedded in a plastic jacket and the space between the electrode and jacket was filled with silicone oil, an insulator. The plastic jacket was sealed at both ends with the copper leads protruding at each end. The high-voltage and ground leads of the power supply were connected to the copper electrode leads. A high-voltage alternating current with a frequency of 20 kHz was applied across the electrode. The sample PVC tube was inserted into the glass tube of the electrode. The carrier gas which is helium and the monomer—tetrafluoroethylene (TFE) or hexafluoropropylene (HFP)—pass through flow meters before being introduced into the mixing chamber, and then flow directly at atmospheric pressure into the PVC tube, thereby APG discharge is limited in the inner surface of the PVC tube. The standard conditions of treatment used to deposit the fluorocarbon layer are: the voltage is 5 kV and the frequency 20 kHz unless otherwise indicated. The frequency range is very different from that of the low-pressure plasma which is in the order of MHz (radio-frequency) or GHz (micro-wave).

## 2.2. Materials

The monomer gases used, TFE and HFP, were obtained from PCR Inc. (Gainesville, FL). Both molecules have a double bond between two carbons. Their chemical compositions are  $C_2F_4$  and  $C_3F_6$ , respectively. Commercially available soft PVC tubes having internal diameter 6.5 mm and outer diameter 8.4 mm were used as received.

## 2.3. Surface analysis techniques

X-ray Photoelectron Spectroscopy (XPS) analyses were performed within a few days after plasma treatment with an ESCALAB 220i-XL XPS (VG instruments), using an aluminum  $K_{\alpha}$  monochromatized X-ray source. The binding

energy shift from the surface charging of the polymers was compensated with an electron flood gun set at 4 eV.

The compositions of the surface were determined, in terms of chemical functionalities, with a Janssen Micro FT/IR-200 with ATR attachment (JASCO corporation, Tokyo, Japan).

The contact angles were measured by the sessile-drop technique. Briefly, a 2  $\mu$ l droplet of redistilled water was placed onto the surface to be studied by a syringe with a micrometer driven plunger. The contact angles were then measured with a contact angle meter (*FACE* Contact Angle Meter, Kyowa Interface Science Co., Ltd, Tokyo, Japan). Contact angles were measured before and just after treatment on PVC tubes exposed to HFP/He or TFE/He APG plasmas for different treatment periods while all other parameters—flow rates, plasma frequency and plasma power—were kept constant. Angles were averaged for 25 measurements (five essays at five different sites on a tube).

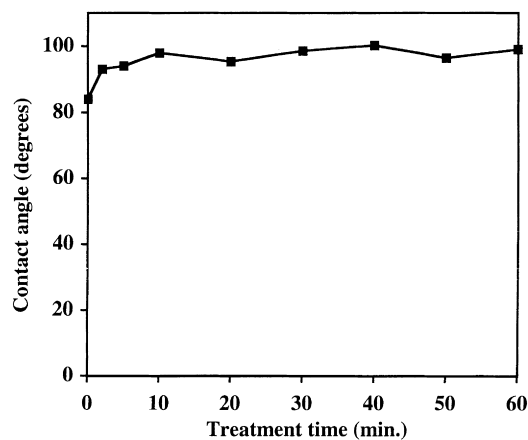


Fig. 2. Contact angle as a function of treatment time. He flow rate: 1000 sccm; HFP flow rate: 2 sccm.

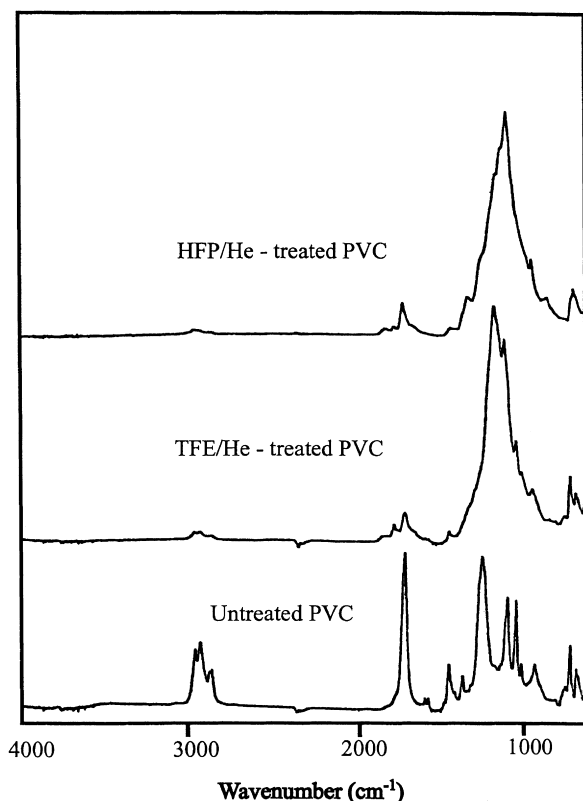


Fig. 3. FTIR-ATR spectra of untreated and treated PVC. Upper spectrum: HEP/He APG treated PVC; gas flows: 1000/2 sccm; treatment time: 40 min. Intermediate spectrum: TFE/He APG treated PVC; gas flows: 600/2 sccm; treatment time: 20 min. Lower spectrum: untreated PVC.

### 3. Results and discussion

The change in contact angle on treatment with HFP/He APG plasma is presented in Fig. 2 (He flow rate: 1000 sccm; HFP flow rate: 2 sccm). It is observed from this figure that a layer of hydrophobic polymer, i.e. fluoro-polymer, is deposited rapidly on the PVC surface. The contact angles increased significantly in the first 3 min of plasma treatment. As treatment continued, the thickness of the layer increased but the degree of hydrophobicity of the outer surface remained the same. The contact angle of untreated commercial PVC tube was  $\approx 90^\circ$  and after helium plasma (i.e. etching processing without monomer) it was decreased to  $\approx 75^\circ$ .

The contact angles of the surface after APG plasma treatment were about  $98^\circ$ , not as high as pure polytetrafluoroethylene (PTFE,  $132^\circ$ ). The contact angles after each experiment were constant along the tube or within the same section, indicating a homogeneous deposition. The results after TFE/He APG discharge also showed a similar trend (data not shown). The change in contact angles from  $\approx 75^\circ$  to about  $98^\circ$  in the absence and presence, respectively, of the fluorine containing monomers showed that the hydrophobic behavior of the plasma-treated PVC is entirely due to the fluorinated monomers.

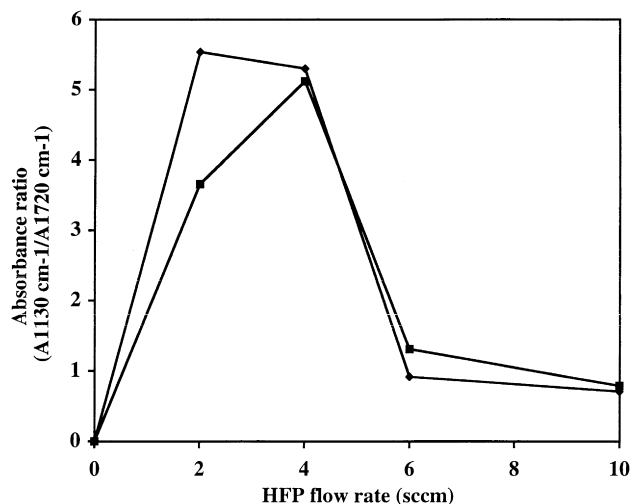


Fig. 4. FTIR-ATR absorbance ratio as a function of HFP flow rate. ◆ 40 min treatment; ■ 20 min treatment.

The Fourier transform infrared (FTIR) attenuated total internal reflection (ATR) spectra (FTIR-ATR) of untreated PVC tube (Fig. 3, lower) showed an absorbance peak at about  $1720\text{ cm}^{-1}$  which is due to carbonyl groups (C=O) in additives such as plasticizers present in the commercial PVC. The peaks due to C–C1 bonds occurred at about  $650\text{--}700\text{ cm}^{-1}$ . After both HFP/He (Fig. 3, upper) and TFE/He APG (Fig. 3, middle) plasma treatments, the carbonyl peak due to plasticizers decreased significantly. Since the analysis depth of the FTIR-ATR is about  $1\text{ }\mu\text{m}$ , the thickness of the deposition was assumed to be very close to this value. We also observed a very intense absorption at about  $1200\text{ cm}^{-1}$  due to fluorine-containing functional groups.

The FTIR-ATR spectrum of the treated PVC tube which had undergone TFE/He APG plasma treatment, resembled that of the HFP/He APG plasma treated PVC tube. However, the main peak of the TFE/He APG treated PVC surface was at  $1200\text{ cm}^{-1}$ , while that of the HFP/He-treated PVC surface was at  $1130\text{ cm}^{-1}$ , indicating that the structures of fluorine-containing plasma-deposited polymers differ slightly from each other. As to the TFE/He APG plasma treated PVC, the main peak consisted of two different absorbance bands from  $\text{CF}_2$   $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  modes. The separation of these two absorbance bands indicates a rather linear polymer [11].

We calculated the ratio of absorbance of peaks typical of polymer deposition (at about  $1200$  or  $1130\text{ cm}^{-1}$ ) to that of the carbonyl peak (plasticizer) typical of the commercial PVC tube to study the degree of polymer deposition. Fig. 4 shows the absorbance ratio of the PVC surface after HFP/He APG plasma treatment with different HFP flow rates for treatment times, 20 and 40 min. All other plasma treatment parameters (voltage, frequency, He flow rate (1000 sccm)) were kept constant. As the HFP flow rate was increased from 0 to 4 sccm, the deposition of fluoro-polymer was increased. However, as the percentage of HFP in the gas

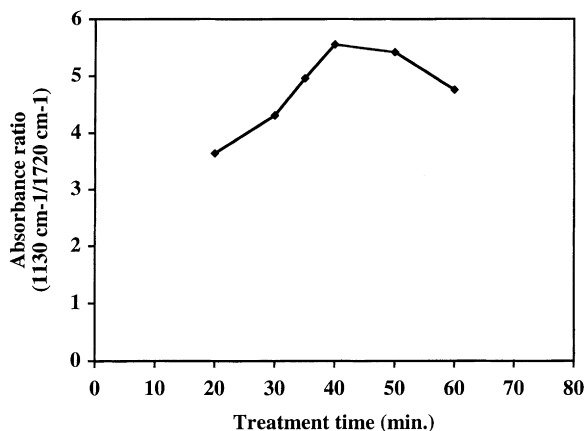


Fig. 5. FTIR-ATR absorbance ratio as a function of treatment time.

mixture was increased further, the fluoro-polymer deposition was decreased. At a flow rate of HFP greater than 6 sccm, the absorbance ratio was reduced to that of an untreated sample, i.e. there was hardly any deposition. When the monomer flow rate is very low, deposition is limited by the monomer supply (the so-called “monomer-deficient region” [12]). Deposition behavior at high monomer flow rates is related with APG discharge stability; that is, a large HFP/He ratio decreases the stability and efficiency of the APG discharge, and thus decrease the number of active species capable of effecting the polymer deposition.

PVC tube was subjected to HFP/He APG treatment for different time intervals between 20 and 60 min at optimum gas flow conditions (2 sccm of HFP with 1000 sccm of helium). The absorbance ratios are shown in Fig. 5. During the first 40 min of treatment, the ratio increased showing an increase in polymer layer thickness. The absorbance ratio reached a maximum at a treatment time of 40 min and then decreased in further treatments exceeding 40 min. The APG discharge is composed of numerous energetic species

(atoms, radicals, molecules, photons, etc.) and polymer degradation and deposition are continuous processes. During the first 40 min of APG treatment, polymer deposition is stronger than degradation; in PVC tubes treated for longer than 40 min, degradation seems to be more significant than polymer deposition.

The optimum gas flow rate and treatment time for polymer deposition with TFE/He APG plasma discharge (i.e. 2.5 sccm of TFE with 600 sccm of helium for 20 min) have been investigated and reported earlier [13].

XPS is widely used for the analysis of polymer surfaces and especially plasma-treated or plasma-deposited polymers. With this technique we can obtain information on the chemical content of the surface upto a few nanometer depth of the polymer. Wide scan spectra of XPS were used to determine to identify and to estimate the amount of the elements present on the surface, and the high-resolution spectra of XPS were used to reveal the element-bonding environment. The XPS wide scan untreated and treated PVC are presented in Fig. 6. The untreated PVC XPS spectrum Fig. 6(c) showed a C<sub>1s</sub> peak at about 285 eV. Cl peaks appear at 199 and 201 eV for Cl<sub>2p</sub>, and 272 eV for Cl<sub>2s</sub>. The weak intensity of the Cl peaks and the presence of the O<sub>1s</sub> peak at 532 eV confirm the presence of plasticizers and other additional products in commercial PVC.

In the XPS spectra of PVC tubes subjected to HFP/He APG treatment and TFE/He APG treatment, an intense peak occurred at 688.8 eV, corresponding to F<sub>1s</sub>, with no trace of Cl peaks (Fig. 6a and b). The absence of Cl atoms at the surface of APG-plasma treated PVC is due to: (1) etching of chlorine atoms (the XPS wide scan spectrum of the He only plasma treated-PVC shows a decreased intensity of the Cl peaks— not shown); and (2) concealment by polymer deposition. The weak O<sub>1s</sub> peak, which indicates the presence of a small amount of oxygen at the surface (about 3% of the atomic composition), is mainly due to post-plasma reactions

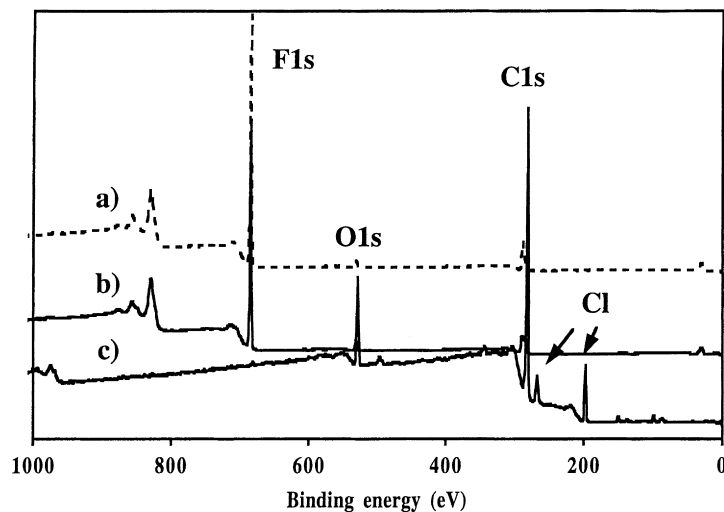


Fig. 6. XPS wide-scan spectra of untreated and treated PVC. (a) TFE/He APG treated PVC; gas flows: 600/2 sccm; treatment time: 20 min; 4 KV; 20 KHz. (b) HFP/He APG treated PVC; gas flows: 600/2 sccm; treatment time: 20 min; 4 KV; 20 KHz. (c) Untreated PVC.

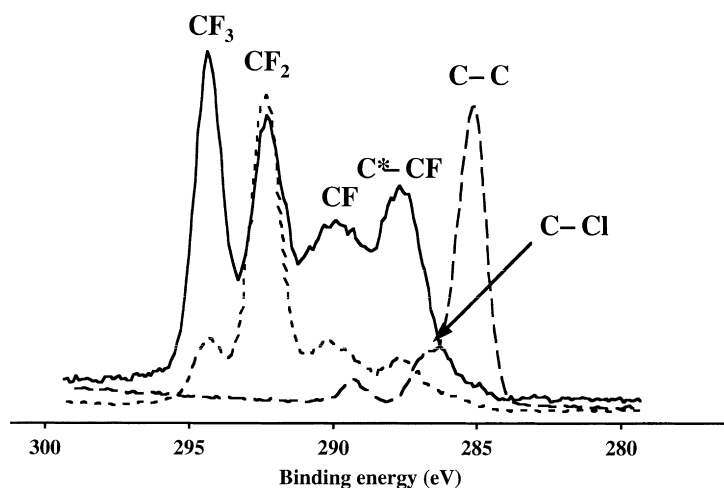


Fig. 7. XPS C<sub>1s</sub> peaks of untreated and treated PVC. — — — Untreated PVC; ··· TFE/He APG plasma treated PVC; gas flows: 600/2 sccm; treatment time: 20 min; 4 KV; 20 KHz; — ··· HFP/He APG plasma treated PVC; gas flows: 600/2 sccm; treatment time: 20 min; 4 KV; 20 KHz.

between oxygen from the air and the freshly prepared and still-reactive surface. These reactions occur after plasma treatment and before XPS analysis.

The XPS C<sub>1s</sub> high-resolution spectrum of untreated PVC (Fig. 7) confirms the presence of plasticizers in commercial PVC. This is shown by the smaller than expected contribution from C–Cl bonds (in the spectra of pure PVC, C–Cl and hydrocarbons would have same contributions) as well as the contribution of oxidized carbons around 288 eV.

On the XPS C<sub>1s</sub> high-resolution spectra of PVC tube subjected to HFP/He APG plasma discharge treatment for 20 min, the hydrocarbon peak had completely disappeared showing that the PVC surface is completely covered by the fluoro-polymer. The molecular formula of the starting monomer, HFP, is CF<sub>2</sub>=CF–CF<sub>3</sub> and the three contributions of CF, CF<sub>2</sub>, and CF<sub>3</sub> can be observed in the spectrum. They have roughly the same area (Table 1) suggesting that the HFP molecules, which are the film precursors, are added to the deposited polymer without major rearrangement and the plasma-deposited polymer retains the chemical characteristics of the building blocks.

After TFE/He APG plasma discharge treatment, the main contribution to the C<sub>1s</sub> peak is from CF<sub>2</sub> (57.1% of total carbons), as expected, but small contributions from CF and CF<sub>3</sub> which arise from secondary reactions or to degradation of the newly deposited polymer, are also observed (18.6 and 11.3%, respectively, of total carbons). Nevertheless, these contributions (CF and CF<sub>3</sub>) remain weak, as does the C\*–CF contribution indicating a rather weakly cross-

linked surface. This is in contrast with fluorocarbons deposited by low-pressure plasma treatments which show a highly cross-linked surface. The weakly cross-linked surface is mainly due to the characteristics of the APG plasma: the ion bombardment, which enhances cross-linking in low-pressure plasmas [1], but can be neglected due to the decrease of ion velocity [14].

As with HFP/He APG treatment, the PVC surface after TFE/He APG plasma is completely covered by the fluoro-polymer [13] (i.e. hydrocarbons no longer contribute to the spectra), but chemical compositions and structure of the two deposited polymers are slightly different from each other.

Though plasma treatment is an effective way of developing surface-specific novel materials, the experimental conditions of conventional low-pressure glow discharge treatment limits the nature and size of the materials to be modified. Continuous treatment, uneven materials, selectivity of treatment area etc. are some of those limitations. Even though plasticized PVC is commonly used for biomedical purposes, the presence of plasticizers (mainly di-2-ethyl hexyl phthalate (DEHP)) is of much concern to the biological system. Hence we attempted in this study to develop PVC supported biomaterials with fluoro-polymer surface coating by the APG treatment of monomers like HFP and TFE onto the inner surface of PVC tubes.

The selected specific conditions (as listed earlier) for developing the APG plasma influence the stability and sustenance of the plasma at atmospheric pressure. Yokoyama et al. [8], proposed that the stability of APG

Table 1  
F/C ratio and relative percentages of the chemical functionality groups in APG plasma-deposited polymers

Monomer	F/C	–CF <sub>3</sub> (%) 293.80 eV	–CF <sub>2</sub> (%) 291.75 eV	–CF (%) 289.45 eV	C–CF (%) 287.05 eV	CH (%) 285.00 eV
HFP	1.46	26.0	25.6	22.7	26.6	–
TFE	1.70	11.3	57.1	18.6	13.0	–

plasma is maintained by the following important processes. The insulated electrode enables a buildup of charge and the resulting opposite voltage halts its discharge, generating a pulsed discharge. A suitable frequency causes the discharge to show a micro-discharge on the electrode, enabling several pulse currents every cycle that cut off discharge before transition to an arc discharge. The use of helium, which has a low breakdown voltage and long transition time, is also important. The high-energy metastable state of helium atoms may help to extend micro-discharge points because high-energy helium ionizes mixed molecules. The combination of all of these processes prevents the discharge from attaining an arc formation, stabilizing plasma glow at atmospheric pressure [8,13]. The characteristics of fluoro-polymers obtained using APG treatment were similar in nature to those of other fluoro-polymers obtained by radio frequency glow discharge [15–17] as reported earlier.

#### 4. Conclusion

APG plasma treatment is a simple, inexpensive process that is useful in a wide variety of applications including the coating of the inner surface of commercial flexible PVC tubes with a PTFE-like polymer formed from HFP or TFE gaseous monomer. The deposition by APG is homogeneous and its thickness is about 1  $\mu\text{m}$ . This deposited fluorinated polymer layer can suppress the bleeding of plasticizers which are present in commercial PVC tubes. Small structural variations between HFP-treated surfaces and TFE-treated surfaces were clear from XPS and FTIR/ATR results. The APG-derived fluoro-polymers were similar to the conventional low-pressure plasma fluoro-polymers in properties even though the APG plasma is moderate in energy

characteristics. To elucidate the unique features of the APG plasma we are currently studying the gas phase with mass spectrometry and optical emission spectroscopy.

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