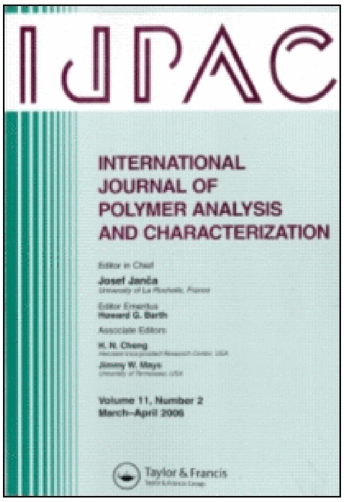

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Analysis and Characterization of Printed Plasma-Treated Polyvinyl Chloride

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Abstract: A number of polyvinyl chloride (PVC) applications require a modification of surface properties of the polymer. In the present work, the effects of plasma treatment on the resulting surface, including chemical composition, wettability, and roughness, were assessed using X-ray photoelectron spectroscopy, contact angle measurements, and scanning electron microscopy analysis. A significant alteration regarding the oxygen and carbon content as evidenced by the XPS data was observed after oxygen plasma treatment. Scanning electron microscope images revealed a drastic change of the topography of the treated surface. These changes correspond to improvement in the printability of the treated surface. Therefore, plasma modification in air is demonstrated to be a viable method to improve printability of PVC.

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Keywords: Plasma treatment; Printing; PVC; Pigment uptake; Surface modification

INTRODUCTION

Polyvinyl chloride (PVC) is frequently used in the medical field for production of blood storage bags, endotracheal and dialysis tubing, and intravenous catheters. Most medical grades of PVC have a hydrophobic surface.[1,2] Their bulk properties provide structural integrity and determine properties such as tensile strength and barrier characteristics. However, for the purpose of many applications, their surface properties often do not meet demands regarding adhesion, wetting ability, biocompatibility, printability, friction, chemical resistance, and physical corrosion.[2] As it is quite difficult to design biomaterials fulfilling all needs, a common approach is to fabricate biomaterials with the required bulk properties followed by special treatment to enhance the surface properties for a specific application. This helps to strike a balance so that a material can have both acceptable mechanical properties and surface properties.

Furthermore, the surface properties can be selectively modified to enhance the performance of the biomaterials. Hence, surface modification of artificial biomaterials is becoming an increasingly popular method to improve device multifunctionality while minimizing expenses and time to develop brand-new materials. It has become one of the key methods in biomaterials engineering. Usually, more than one approach can address these requirements, and the ultimate selection must take into account the process reliability, reproducibility, expenses, and time, among other considerations.[2]

In this regard plasma-surface modification is a viable, effective, and economical surface treatment technique for many materials and is of growing interest in biomedical engineering. The unique advantage of plasma modification is that the surface properties and biocompatibility can be enhanced selectively while the bulk attributes of the materials remain unchanged.[3] Plasma engineering is usually reliable, reproducible, relatively inexpensive, and applicable to different sample geometries and materials. Processing with plasma can provide sterile surfaces and can be scaled up to industrial production relatively easily.[4–7]

These techniques change the surface energy of the substrate by altering the electrical charge of the particles closest to the part's surface, giving them a hydrophilic nature.[8] Generally, conversion of polymers from being hydrophobic to hydrophilic improves the adhesion strength, biocompatibility, and other pertinent properties.

Furthermore, it has been shown that the surface characteristics, such as wetting ability, roughness, surface charge, and presence and density of functional groups, are affected by surface attributes, and in turn all these factors affect biocompatibility and adhesion on surfaces by liquids, including ink.

In order for ink to adhere to a substrate, it must have adhesion properties that make it capable of wetting the material. If this is to occur, the surface tension of the ink must be lower than the surface energy of the substrate. There are a number of criteria required in order to print effectively. The ink must not "bleed" into the substrate, which causes blurred images. It must evenly coat the surface and give the correct color. Upon drying, it must remain affixed to the surface and not peel or chip.[9]

The end products of biomaterials research are devices and materials that are mass produced for medical applications. A surface modification process that is too complex will be difficult and expensive to commercialize.[10]

The aim of the present study is to investigate the effect of surface modification, using plasma treatment technique, on the printability of PVC film with commercially available medical grade ink GPX 9. The objective is to assess how plasma treatment affects the removal of ink from the surface of PVC.

METHODS AND MATERIALS

Materials

PVC in the form of EVA-PU-COEX medical-grade PVC pellets (grade RB1/T3M) was acquired commercially from ModenPlast S.P.A (Italy) and used as received. Anhydrous ethylene glycol, diiodomethane, Triton X-100, and absolute ethanol were obtained from Sigma Aldrich and were used as received without further purification.

Preparation of PVC Films

The medical-grade PVC pellets were produced using a noncommercial hot press at a temperature of 165°C, pressed and cut into $4 \times 5 \times 0.1\,\text{cm}$ sheets. For the purpose of plasma treatment, the PVC sheets were washed using ethanol/water solution for 15 min, and then the samples were taken out of the solution, cleaned in deionized water, and finally immersed into a Triton X-100 aqueous solution for another 15 min at room temperature in an ultrasonic bath. The samples were finally thoroughly rinsed with deionized water to remove excess solution from the surfaces. The PVC films were then dried in an air-circulating oven with a temperature of 35°C for 24 h and stored in a desiccator.

Plasma Treatment of PVC Substrates

The 4 × 5 × 0.1 cm PVC films were prepared and subjected to plasma treatment using a barrier coplanar discharge reactor under atmospheric conditions of pressure and temperature, using air as the reaction gas. The coplanar discharger consists of electrodes that are located inside a glass chamber and allow controlling the reaction conditions. The silver electrodes are separated by a ceramic insulator plate. The treatment was done using a power of 200 W and current of 1.1 A, and the samples were exposed to plasma for 15 s for each side of the film.

Surface Wetting Ability Assessment

Wetting ability of the plasma-treated PVC surface was evaluated by measuring the contact angle immediately after the treatment. For this purpose deionized water, ethylene glycol, and diiodomethane were used as the liquids. The sessile drop method was used for this purpose, and 5 μL of each liquid was placed dropwise on the PVC film, which was set up on a Surface Energy Evaluation (See) System (Advex Instruments, Czech Republic) at room temperature. For each sample 10 drops were used for each liquid measurement to minimize statistical error. Therefore, each reported contact angle value is the average of the 10 independent measurements. Contact angle values and surface energy were determined using the acid-base model. The static contact angle was recorded 30 s after the liquid drop deposition on the surface. An identical technique was utilized to determine the contact angles and surface energy of the untreated samples. The standard error of the obtained angles was ±3°.

Surface Chemistry Examination

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected at a spectral resolution of 2 cm^{-1} using an Avatar 320 (Nicolet, USA) FT-IR spectrometer equipped with a ZnSe crystal with a 45° incident angle. Each spectrum represents 64 co-added scans. Acquired spectra were analyzed using the OMNIC™ Software Suite.

Surface Topography Examination

Scanning electron microscopy (SEM) imaging was carried out on VEGA II LMU (Tescan, Czech Republic) operating in the high vacuum/secondary electron imaging mode at an accelerating voltage of 20.0 kV. The samples were sputter coated with a thin layer of palladium/gold alloy. The samples were tilted at 30° for better observation. The images were taken at magnifications of 30,000×.

X-Ray Photoelectron Spectroscopy

The XPS analysis was performed using a TFA instrument (XPS Physical Electronics, USA) equipped with a conventional hemispherical analyzer positioned at an angle of 45°. The X-ray source employed was monochromatized Al $K_{\alpha 1,2}$ (radiation at 1486.6 eV). Spectrum acquisition was performed under ultrahigh vacuum conditions. Survey-scan spectra were made at a pass energy of 187.85 eV and 0.4 eV energy step. An electron gun was used for surface neutralization. The concentration of elements was determined by using Multipak v7.3.1 software from Physical Electronics (USA).

Printing

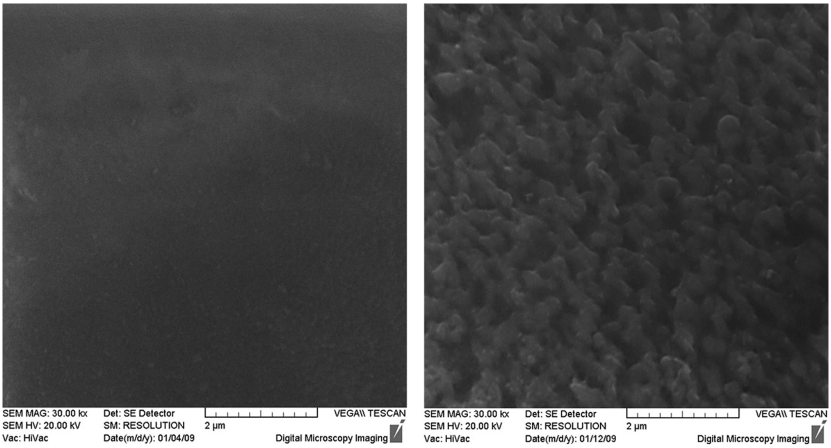
GPX9 ink series from Lemmaco Ltd. (Hungary) was used for printing the PVC films. The films were printed using a Gebr Baier KG printing machine (Germany) at 130°C. Both untreated and plasma treated samples were printed.

Tape Test/UV-Visible Spectroscopy

Scotch Magic™ tape (3M, USA) was used for this purpose to lift ink off the printed samples according to a prescribed planned number of peels. The tape was applied to the surface with consistent force and lifted off at an angle of 90° each time. After each set of "ink lift-offs" the UV-visible spectra were recorded on a Helios Gamma spectrophotometer (Thermo Scientific, USA). This was done for both the treated and untreated samples.

RESULTS AND DISCUSSIONS

The literature reveals that air plasma exposure can render most polymers surfaces hydrophilic.[11–15] As shown in Figure 1 the scanning electron microscope revealed rough surface topography images for plasma-modified and relatively smooth morphology for untreated samples, suggesting modification of the PVC surface. Similar phenomena were



(a) (b)

Figure 1. SEM images of virgin (a) and plasma-treated (b) samples.

observed and reported elsewhere recently for polyester[12] and for polyethylene.[16]

The water contact angle values decreased from 85.9° for the untreated sample to 64.9° for plasma-treated samples (Tables I(a) and I(b)), which suggests an improvement in wettability of the PVC

Table I(a). Contact angle values for untreated and plasma treated samples

	Contact angle measurements (degrees)		
Sample	Water	Diiodomethane	Ethylene glycol
Virgin PVC	85.9	43.5	60.5
Plasma treated	64.9	36.2	49.4

Table I(b). Surface energy values for untreated and plasma-treated samples

	Surface energy (mJ/m^2)				
Sample	γ^{tot}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Virgin PVC	38.8	37.8	1.0	0.0	5.1
Plasma treated	48.2	41.5	6.7	0.5	24.9

γ^{tot} is the total surface energy, γ^{LW} is the Lifshitz–van der Waals component, γ^{AB} is the polar component, and γ^{+}, γ^{-} correspond to donor and acceptor parts of the γ^{AB} respectively.

Table II. Elemental composition of the treated and untreated surfaces by XPS measurement

Sample	Carbon %	Oxygen %	Nitrogen %	Chlorine %	O/C ratio
Pure PVC	84.8	12.5	0	2.7	0.2
Plasma treated	77.8	19.9	0	2.3	0.3

surface. At the same time the surface energy increased from 38.8 mJ/m^2 for untreated samples to 48.2 mJ/m^2 for the plasma-treated samples.

Wettability changes in polymers following air plasma treatment are most commonly a result of surface oxidation, electrostatic charging, and surface morphology changes.[17] Usually, the active plasma species attack the polymer surface, resulting in the incorporation of hydrophilic functional groups such as carbonyl, carboxyl, hydroxyl, and in some cases amines on the surface of the polymer.[18,19] The increased presence of hydrophilic functional groups following air plasma modification is shown in Table II.

As seen in Table II the surface and elemental composition ratios for both native and air plasma-treated PVC show that the oxygen content increased from 12.5% to 19.9%, a 59% increase, while the carbon

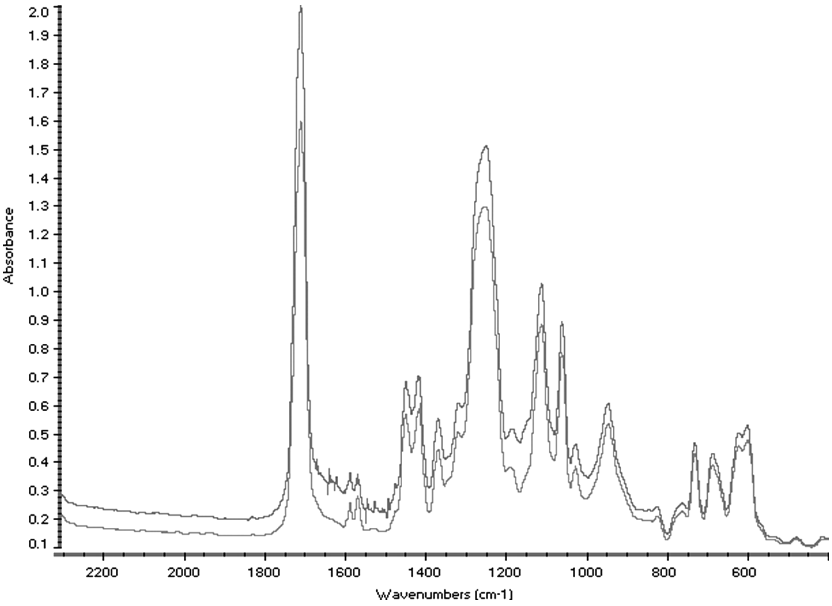
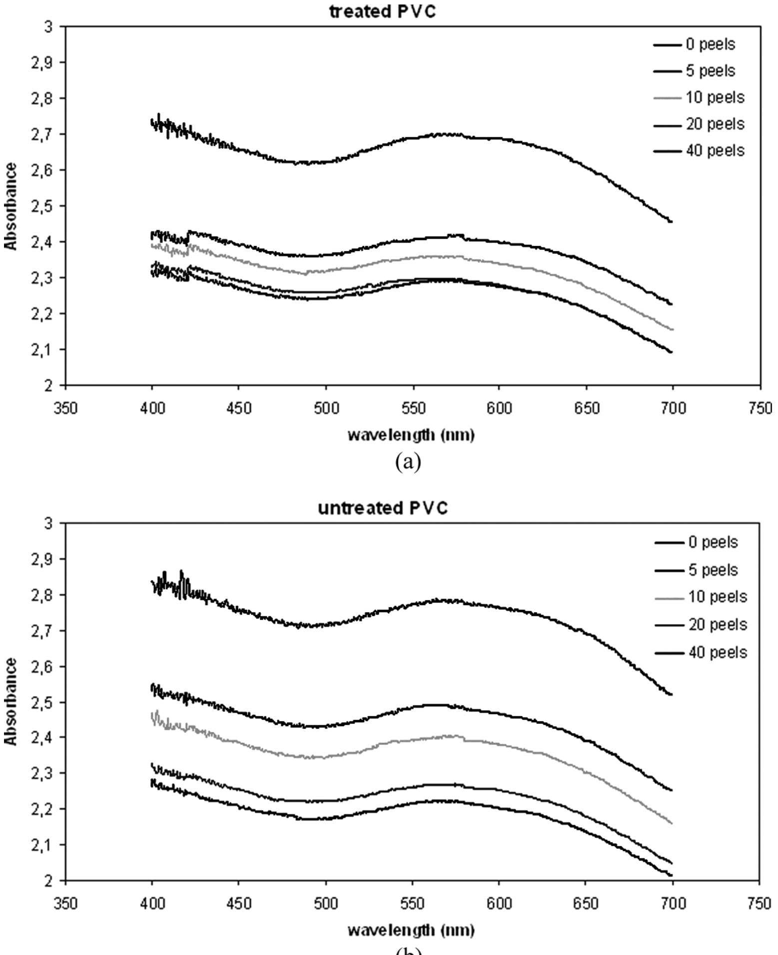


Figure 2. FT-IR spectra for plasma-treated and untreated PVC samples.

content decreased by 8.3%. This gives a total oxygen-to-carbon ratio of 0.15 for virgin and 0.26 for treated samples, representing a substantial increase of 73.3%. These data provide a clear indication for conditions of increase in hydrophilicity and wetting ability of the plasma-treated surface. The chlorine content decreased by 14.81%, probably due to PVC dehydrochloration. The FT-IR data in Figure 2 illustrate the same absorption bands for both untreated and plasma-treated samples, suggesting that the composition of the treated sample was not affected, but the treated data showed higher intensity bands, suggesting a higher



(a)

(b)

Figure 3. UV-visible data showing difference in absorbance for different sets of peels for treated (a) and untreated (b) samples.

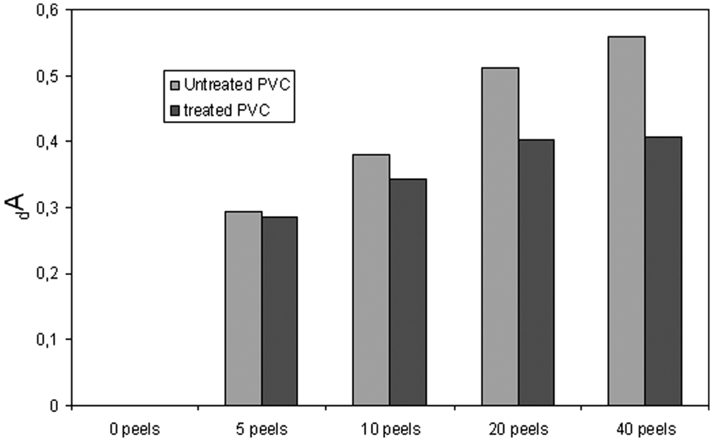


Figure 4. Difference in absorbance of printed untreated and plasma-treated samples.

concentration of the species absorbing in those regions, which include oxygen groups. This is consistent with the conclusions from the XPS data.

The peel test/UV-visible data in Figures 3(a) and (b) show that the change in absorbance for the printed untreated samples was higher for each set of peels than that for the printed plasma-treated samples. This points to the fact that the ink adhered more strongly to the plasma-treated surface than it did to the untreated surface, consequently suggesting that plasma treatment improved printability on the PVC surface. This is an indication that plasma treatment increased the hydrophilicity and reorganized the topography of the PVC, consequently increasing the wetting ability of the surface.

In Figure 4 the absorbance change ${}_{d}A$ for different sets of peels A_{np} is represented. The absorbance change is described as ${}_{d}A = A_0 - A_{np}$. Absorbance for the treated sample remained constant after 20 sets of peels of the tape to remove ink from the surface. However, absorbance for the untreated sample kept changing, even beyond 40 peels. This provides evidence that the ink adhered stronger to the surface of the treated sample.

CONCLUSIONS

Surface modification of medical-grade PVC using air plasma has been characterized using various techniques such as SEM, XPS, contact angle measurements, and FT-IR. The effects of the plasma treatment on the resulting surface, including chemical composition, wettability, and roughness, were assessed.

The effects of changes in oxygen content and hydrophilicity due to oxygen plasma treatment produced a significant alteration in oxygen groups on the treated surface, resulting in higher hydrophilicity. The change in surface wettability resulted from incorporation of these oxygenated functional groups, as indicated by XPS analysis. These results provided evidence of the fact that plasma modification induces considerable improvement in surface and adhesive properties of the samples.

Thus, it is possible to conclude that plasma modification in air is demonstrated to be a viable method to modify the surface of medical-grade PVC to improve its printability. This is significant from the point of view of development of medical devices such as catheters, blood bags, and others because stronger adherence of the ink to the surface of the device will help to prevent the ink from chipping off and eventually polluting the biological environment.

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