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Treatment of PVC using an alternative low energy ion bombardment procedure

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ABSTRACT

In many applications, polymers have progressively substituted traditional materials such as ceramics, glasses, and metals. Nevertheless, the use of polymeric materials is still limited by their surface properties. Frequently, selective modifications are necessary to suit the surface to a given application. Amongst the most common treatments, plasma immersion ion implantation (PIII) has attracted the attention of many researchers owing to its versatility and practicality. This method, however, requires a power supply to provide high voltage (tens of kV) negative pulses, with a controlled duty cycle, width and frequency. Owing to this, the implementation of PIII on the industrial scale can become economically inviable. In this work, an alternative plasma treatment that enables low energy ion bombardment without the need of a high voltage pulse generator is presented. To evaluate the efficiency of the treatment of polymers, polyvinylchloride, PVC, specimens were exposed to 5 Pa argon plasmas for 3600 s, at excitation powers, P, of between 10 and 125 W. Through contact angle and atomic force microscopy data, the influence of P on the wettability, surface free energy and roughness of the samples was studied. Surface chemical composition was measured by X-ray photoelectron spectroscopy, XPS. To evaluate the effect of aging under atmospheric conditions, contact angle and XPS measurements were performed one and 1334 days after the treatment. The plasma potential and ion density around the driven electrode were determined from Langmuir probe measurements while the self-bias potential was derived with the aid of an oscilloscope. From these data it was possible to estimate the mean energy of ions bombarding the PVC surface. Chlorine, carbon and oxygen contamination were detected on the surface of the as-received PVC. Upon exposure to the plasma, the proportion of chlorine was observed to decrease while that of oxygen increased. Consequently, the wettability and surface energy increased after the treatment but such modifications were not stable after aging: the contact angle increased for all the samples, modifying the initially hydrophilic surface into a highly hydrophobic one. Consistently, the surface composition also changed after aging: there was carbon enrichment due to further losses of oxygen and chlorine. Another relevant factor for the elevation of θ was the change in morphology induced by the treatment. At greater powers, the uniform matrix of the PVC was transformed into a columnar structure containing randomly distributed sharp pillars. Interpretation of such results is proposed in terms of the total energy deposited in the solid by ionic collisions.

1. Introduction

The relatively low cost of polymers with desirable properties such as durability, flexibility and chemical inertness is responsible for their widespread application. Currently, polymers can be found in many everyday applications, such as plastic bags, food packages, window frames and goggle lenses. Their application in sophisticated devices, which include taste and odor sensors, memory devices, solar cells, light-emitting diodes, and bone prostheses [1–6], has also increased. In these situations, to implement the application, the adjustment of the surface properties is necessary.

The applicability of polymers as biomaterials, for instance, is determined by their interactions with corporeal fluids. Polymeric materials, such as polyurethane and PVC, have been employed to produce catheters, blood storage bags and insulators for pacemaker wires [7,8]. In the chemical industry, treated polymers are used as perm-selective membranes to separate aqueous solutions, organic compounds with similar boiling points, and polar/non-polar compounds [9,10]. In all of these cases, the adjustment of the surface properties is necessary.

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Another example to illustrate the importance of superficial modifications on polymers can be found in microelectronics, where the growing demand for miniaturization requires the removal of layers in the confection of devices. In cell phones, digital cameras and portable printers, the flat cable connectors must have reduced dimensions and be flexible. Such requirements can be fulfilled through the deposition of conductive metallic patterns onto polymers [11]. Since the adhesion of a film onto an inert surface is weak and adhesive layers are inconvenient in these cases, polymer surface activation is of paramount importance. Indeed, the development of conductive patterns directly on the polymer surface by changing its electrical properties would be the ideal procedure.

Amongst the available surface treatments, the exposure to glow discharge plasmas [12] constitutes a cheap, simple and versatile technique. Plasma treatment allows wide control of the induced modification via adjustments in the process parameters, such as, applied power, sample temperature, gas flow and pressure [13]. In this way, it is possible to modify selectively the superficial layers without affecting the bulk properties (mechanical resistance and flexibility, for instance).

The modifications induced by the plasma result from incorporation or removal of species, producing active sites and structural alterations [12]. More intense modifications are attained when the substrate immersed in the plasma is biased with negative pulses of high voltage, enabling positive ions to be implanted in the sample. The energy transferred to the solid by ion deceleration is enough to cause excitation, ionization, bond fragmentation, emission of species and atomic dislocations, inducing compositional alterations and structural reorganizations. Such a process, known as Plasma Immersion Ion Implantation (PIII), was proposed in 1987 by Conrad [14] and Tendys et al. [15].

Several reports have shown the efficacy of PIII for the controlled modification of polymer properties [16–18]. It has been verified, in recent works, that the reactivity of PVC, Teflon™, polyurethane and Nylon™ are strongly influenced by bombardment with high energy ions [19,20]. Highly hydrophilic or superhydrophobic surfaces may be produced, using the same pristine material, by simply changing the treatment conditions.

In some cases, the negative pulses used in PIII must have magnitudes of up to a few hundreds of kV. Furthermore, it is important to control the pulse frequency and the ratio between the on-time and the total pulse width (duty cycle) to assure the effectiveness of the process. Owing to such demands, the pulsed power supply represents the greatest cost involved in implementing PIII on an industrial scale. The development of a plasma treatment technique avoiding the use of such equipment would make the treatment considerably more economic.

In this work, results obtained by the treatment of polymers via ion bombardment without using a high voltage power supply are presented. In the present case, the substrate biasing has been performed using the same radiofrequency signal employed to excite the discharge. The application of a high frequency voltage to the sample holder induces a negative DC bias on it, which attracts positive ions of the discharge. In this case, however, the ion acceleration is much smaller than that attained using a pulsed high voltage and consequently the modifications are milder. The main objective of the present work was to investigate the extent of the modifications induced in commercial PVC surfaces by low energy ion bombardment by this alternative configuration of the plasma processing apparatus.

2. Experimental details

Commercially pure PVC sheets of 0.4 mm thickness were cut in 10 mm × 30 mm pieces. Prior to the treatment, the samples were sonicated in a solution of distilled water and detergent for 15 min, rinsed in flowing tap water, sonicated again in isopropanol and then dried in a muffle furnace at 60 °C for 15 min.

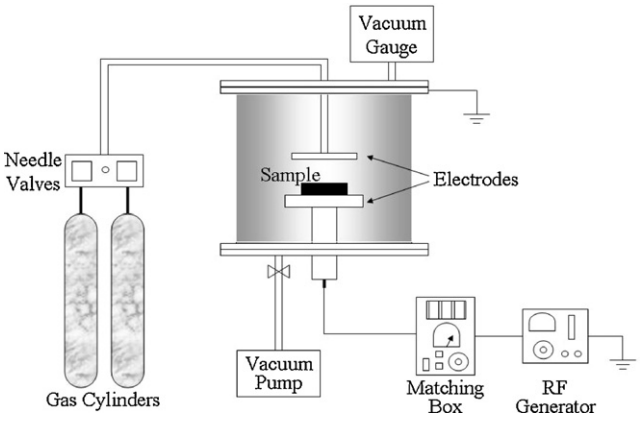

Fig. 1. Experimental apparatus used for the plasma treatment of the PVC.

The cleaned samples were placed in the plasma reactor depicted in Fig. 1. Basically the system is comprised of a 5 L cylindrical glass tube evacuated by an 18 m^3/h-rotary vane pump. Gas flow is adjusted by needle valves while the pressure is monitored by a Pirani gauge. The extremities of the chamber are sealed with aluminum disks which contain inlet ports to gas connections, pressure gauge and vacuum pump. Within the chamber are two stainless-steel parallel-plate electrodes. The upper one has a showerhead through which the gases flow to the reactor.

After pumping the system down to 1 Pa, the argon flow was adjusted until the pressure in the chamber reached 5 Pa. The gas was provided by White Martins (99.999% purity). The plasmas were then generated by the application of radiofrequency power (RF, 13.56 MHz), through a matching network, to the lower electrode, which also served as the sample holder. In such a configuration, a self-bias is developed at the electrode, attracting positive ions. Exposure time to the bombardment plasma was 3600 s. The RF power was varied from 10 to 125 W. Plasma pressure and exposure time were chosen to match the conditions employed in a previous study [20] in which PVC was exposed to high energy argon ion bombardment.

The effect of the plasma treatment on the chemical composition of the PVC surface was evaluated by XPS. Data were collected for the virgin and plasma treated PVC a day after the treatment and following aging in the laboratory atmosphere for 1334 days. A Microtech – ESCA 3000 spectrometer was employed in such experiments under a base pressure of 2×10^{-8} Pa, using the Mg Kα radiation, and achieving a resolution of about 0.8 eV.

The receptiveness of the PVC surface to other materials has been assessed by contact angle measurements [21]. Using a procedure described elsewhere [22], the surface free energy was evaluated from θ values obtained from deionized water and diiodomethane. Inspections were performed one and 1334 days after the treatment. Three water droplets were placed onto different positions on each sample; the results presented are the average of 30 measurements.

Surface topography was evaluated by atomic force microscopy, AFM, in air using a XE-100 Park Systems. Images (5 μm × 5 μm) were acquired in non-contact mode with 512 × 512 pixels for each sample. For this, silicon tips of 5 nm nominal radius were assembled on cantilevers with a resonance frequency ≥200 kHz. The images