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Original Article

Surface Modification of Silicone Rubber Membrane by Microwave Discharge to Improve Biocompatibility

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Abstract

Wetability of biocompatible polymers can be improved by plasma surface modification. The purpose of this study was to surface modify an experimental poly (dimethylsiloxane) rubber (PDMS) material in order to improve its wetability and biocompatibility. Surface properties of the PDMS were characterized using contact angles measurement for wetability analysis. Samples of experimental silicone rubber were surface modified by first argon, hydrogen, oxygen plasma treatment. In all cases, contact angles were measured. We have observed that oxygen, argon, and hydrogen glow discharges are quite effective in reducing the water contact angle of PDMS. However, indifferently to the efficiency of the treatment, practically all of the modified surfaces recovered great part of their original hydrophobicity. Surface modified materials had comparable contact angles to surfactant modified silicone rubber, all being significantly lower than the unmodified material. Oxygen microwave discharge treatment proved an effective way of improving the wetability and biocompatibility of an experimental silicone rubber without altering bulk properties.

Keywords: Biocompatibility; Biomaterial; Plasma surface treatment; Silicon rubber Wetability.
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1. Introduction

Non-thermal and low pressure plasmas have been used in a series of surface treatment applications. The majority of plasma assisted technologies are based on low pressure processes [1]. The treatment of polymeric materials with plasma is a frequently used technique to accomplish surface modifications that affect chemical composition as well as surface topography. Moreover, microwave discharges are routinely employed in the processing of materials to deposit films as well as coatings [2-4]. In recent years, the modification of elastomer surfaces with plasma has also become an important tool in micro fluidics where elastomers such as poly (dimethylsiloxane) (PDMS) are used as substrates for micro-reactors [5]. PDMS is a hydrophobic polymer for which exposure to oxygen plasma leads to oxidation and chain

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scission as well as cross-linking and the formation of a silica-like surface [6]. Additionally, oxygen plasma is utilized to adhere the polymer permanently to other silicon-based materials. The latter method is commonly employed to create sealed channels from open microstructure surfaces obtained by soft photolithography [7]. Recent studies have also proposed reaction mechanisms for the functionalization of PDM surfaces using a variety of plasmas created from gases such as argon, oxygen and CO_2 [8-10].

To investigate the complex reaction between the plasma and the polymer surface, it is important to understand the plasma parameters and their effect on the surface modification. In most of the reports, the plasma excitation source power (RF or Microwave) is compared with extent of surface modification, but in practice, it is not only the excitation power but also the pressure, degree of ionization and other plasma parameters that affect the polymer surface. Hence it is important to consider the effect of all the other plasma properties (microscopic plasma parameters, like ion energy, ion flux, degree of ionization etc.) to analyze the surface modification of polymers.

In our current experimental observation, we used a microwave plasma source to modify the surface of silicone rubber samples. The microwave plasma has significant advantage over other techniques like Radio Frequency Glow Discharge (RFGD) frequently used in polymer surface modifications [10].

Microwave sources can be operated at low pressures (10-3 to 10-1 mbar), which reduces

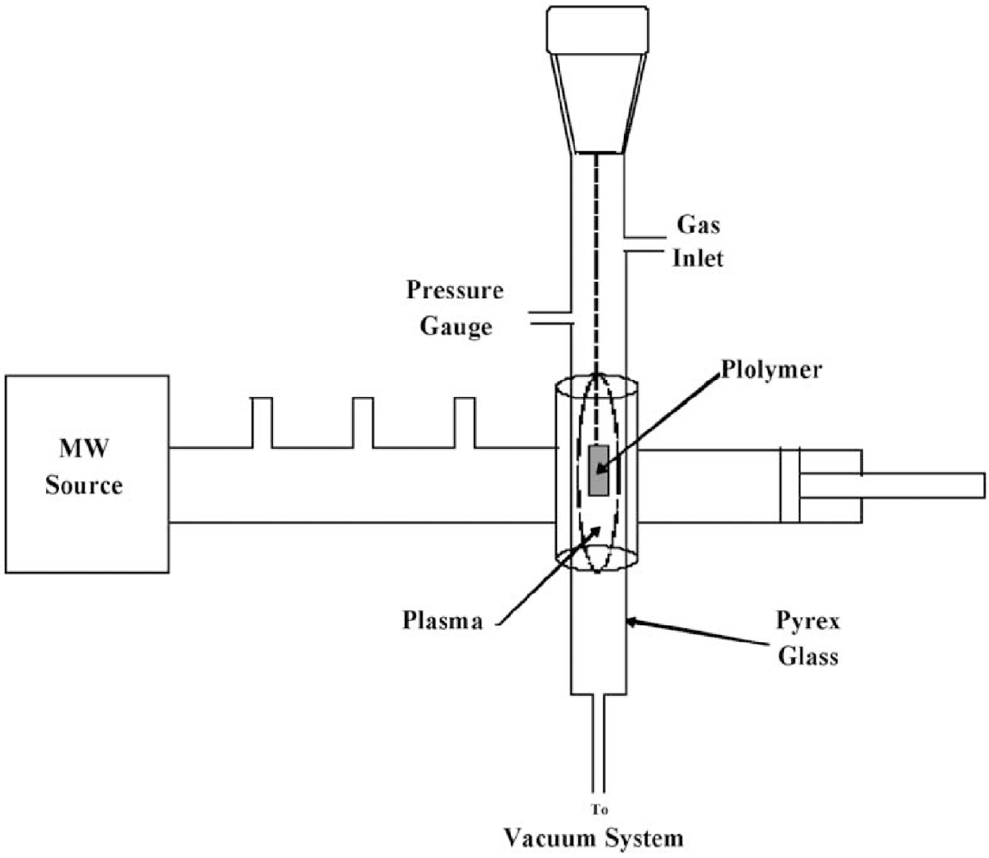

Figure 1. The experimental plasma system for the plasma treatment of PDMS.

Table 1. The data of the contact angle measurement immediately and after 24h.

Type of gas	Hydrogen	Oxygen	Argon	Xenon
Immediately	20	31	34	43
After 24 hours	40	35	64	79

the risk of gas phase contamination during processing. Moreover the plasma properties can be controlled conveniently by adjusting the microwave power. Hence surface modification of this polymer becomes important. In this paper we demonstrate the effect of microwave plasma on the surface property of PDMS with argon (inert), xenon (inert), hydrogen (reactive) and oxygen (reactive).

2. Experimentals

The plasma surface treatment was reached in microwave-induced plasma with surface wave at power level of 100 W. Experimental setup is shown in Figure 1. Microwave generator was coupled to the load via ferrite circulator. Then microwaves propagated through impedance tuning to surface wave launcher (Figure 1). As it can be seen, it is truly surfaguide. In order to get the high electric intensity we used two short metal tubes (20 cm in height and 5 cm in inter diameter) that were cooled by in/out water circulator. Experimental setup consists mainly of a surfaguide microwave (2.45 GHz, 0-300 W) generator (Sairem, GMP 03 KED), the glass vacuum chamber, rotary vane and diffusion pump, pressure Pirani gauge and needle valve.

The microwave source is particularly suited for plasma applications (etching, sputtering, ion source, discharge, diamond deposition, surface treatment and etc.) and for any industrial, medical or scientific application requiring microwave energy. It has forward and reflected power detector that define the pure power on the loud (plasma discharge). In this experiment, we use the difference of forward and reflected power as a pure power is loaded on the plasma. To decrease the reflected power we use impedance matching (three stub tuners, indicated in Figure 1).

Discharge proceeds in the homemade vacuum chamber of plasma reactor (a long Pyrex glass column 65 cm in height and 3.5

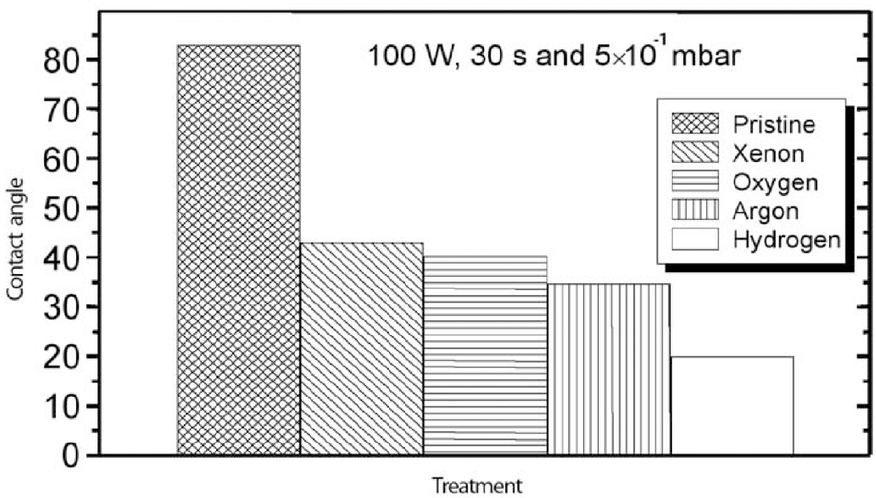

Figure 2. Contact angle of silicone as-received and immediately after exposed for 30 s to hydrogen, oxygen, argon and xenon plasma at 100 and 5×10^{-1} mbar of applied power and chamber pressure, respectively.

cm in internal diameter). The sample is dangled within the column at the plasma zone (within the short metal tubes) by plastic string and exposed to the plasma for surface treatment. During the treatment, the apparatus was continuously pumped by an 8 $m^3.h^{-1}$ oil rotary vane and diffusion pump. Before the plasma treatment, the basic pressure was pumped down to less than mtorr and then the carrier gas was introduced into the reactor chamber. The admission of the gases is controlled by needle valve while the chamber pressure is monitored by a Pirani gauge. It has been recommended prior to the treatments, commercially poly(dimethylsiloxane), (PDMS), coupons have to be cleaned in ultrasonic isopropyl alcohol baths for 10 min., sonicated in distilled water and then dried in a muffle at 80 °C for 60 min.

After dangling the sample in the column (where plasma is formed), the reactor was pumped down to less than 10^{-3} mtorr to reduce the presence of atmospheric contamination. Subsequently, the pressure was adjusted (5×10^{-1}mbar) and the plasma ignited (by high voltage igniter gun) for the predetermine pressure, power and time.

The basic parameter of wettability is the contact angle θ of liquid wetting the solid surface. The wettability of a liquid is defined as the contact angle between a droplet of the liquid (such as water) in thermal equilibrium on a horizontal surface. Depending on the type of surface and liquid the droplet may take a variety of shapes. The wetting angle is given by the angle between the interface of the droplet and the horizontal surface. The liquid is seemed wetting when $90<\theta<180$ degrees and non-wetting when $0<\theta<90$, $\theta=0$ and $\theta=180$ degree corresponds to perfect wetting and the drop spreads forming a film on the surface [10, 11]. Actually, the wetting angle θ is a thermodynamic variable that depends on the interfacial tensions of the surfaces. Let $\gamma_{l,g}$ denote the interfacial tension due to the liquid-gas surface, $\gamma_{s,l}$ refer to the interfacial tension due to the solid-liquid surface and $\gamma_{s,g}$ indicate the interfacial tension of the solid-gas surface. In thermodynamic equilibrium the wetting angle θ is given by Young's law:

$$\gamma_{s,g} = \gamma_{s,l} + \gamma_{l,g} \mathrm{Cos}(\theta) \qquad (1)$$

For two-phase flow in porous media the wetting angle influences the strength of the capillary pressure. Let θ denote the wetting angle between the interface and the pore wall, then the capillary pressure p_c in a pore of size becomes:

$$p_c \cong \frac{2\gamma}{a} Cos(\theta) \qquad (2)$$

Contact angles were estimated with a homemade optical system. A drop of liquid (10 µl) was placed on a specially prepared plate of substratum and the image was immediately sent via the digital camera (Canon, power shot pro 1, 8 mega pixcls, 7× optical zoom) to the computer for analysis and contact angle estimation.

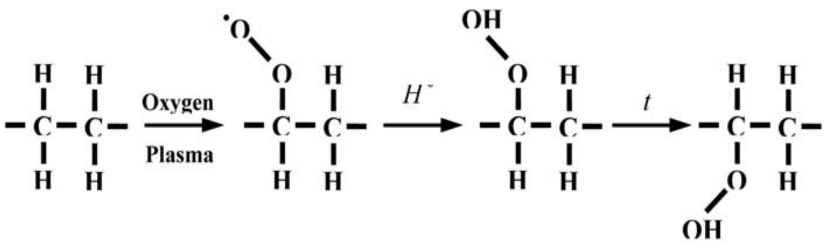

Figure 3. Schematic representation of the possible mechanism responsible for the hydrophobic recovery in microwave plasma treated polymers.

3. Results and discussion

Figure 2 depicts the water contact angles of PDMS samples as received and 10 min. after exposure for 30 s to hydrogen, oxygen, argon and xenon plasmas at 100 W. As one can observe, all four treatments caused θ to decrease. Furthermore, another very interesting detail shown in Figure 2 is that hydrogen plasma is extremely efficient in increasing the hydrophilicity of the silicone rubber. Other authors, Rangel *et al*. [12] in different circumstances (RF plasma with oxygen, argon, hydrogen), also observed different effect. They conclude that oxygen plasma is extremely efficient in increasing the hydrophilicity of the silicone rubber.

Table 1 contains the data of the contact angle measurement immediately and after 24 h. It shows that effect is transitory and there are at least two explanations for it [13-16]. Yasuda *et al*. [17] for instance, attribute it to the rotation of polar groups around the polymeric backbone into the polymer bulk. Other authors [18] affirm that contamination or nonspecific surface degradation effects cause such recovering. In this case such as Rangel *et al*. [12] we believe that the first mechanism, namely the rotation of surface polar groups, is the main responsible for the observed tendency to recuperate the original hydrophobicity.

Figure 3 depicts the situation where the rotation of polar groups would take place. Inelastic collisions, mainly involving species on the polymer surface and energetic electrons in the plasma, can result in chemical bonds breakage creating free radicals in the polymer. Reactions between atomic oxygen and free radicals may add peroxides (O_2^- radicals) to the surface, as shown in the Figure 3 [12].

4. Conclusions

The exposure of silicone surface to different microwave plasmas (hydrogen, oxygen, argon and xenon) resulted in the increase of its biocompatibility, but hydrogen plasma has the best result. However, in any circumstances the surface tended to recover its original hydrophobicity.

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