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Surface modification and ageing of PMMA polymer by oxygen plasma treatment

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A B S T R A C T

We present a study on ageing of polymethyl methacrylate (PMMA) polymer treated with oxygen plasma. Oxygen plasma was created with an RF generator operating at a frequency of 27.12 MHz and a power of 200 W. The oxygen pressure was 75 Pa. The samples were treated for different time from 5 s to 60 s. The chemical modifications of the surface after plasma treatment were monitored by XPS (X-ray photoelectron spectroscopy), while the wettability and ageing effects were studied by WCA (water contact angle measurements). The samples were aged in dry air or in water. In the case of dry air, the least pronounced ageing was observed for the sample treated for 60 s. For samples aged in water, however, the lowest ageing rate was observed for the sample treated for 5 s. The samples were ageing slightly faster in water than in air. We also investigated the temperature effect on ageing of plasma treated samples. A set of samples was stored in a refrigerator at 5 °C and the other set was placed into an oven at 50 °C. The ageing rate of the samples stored at 5 °C was significantly lower than for the samples stored at 50 °C, so cooling the samples help keeping the required surface properties.

1. Introduction

Polymers are generally characterized by a low surface energy and hence poor adhesive properties. In order to assure good adhesion between polymer and a coating, the surface of polymer must be activated first. This can be achieved by plasma treatment. By this technique it is possible to modify the surface properties of polymers without affecting the bulk properties. The main drawback of plasma treated surface is ageing. Functional groups formed on the plasma treated surface are not stable with time, as the surface tends to return to its untreated state. Thus the surface is losing its hydrophilic character. The ageing behaviour of plasma treated polymers depends on different parameters, such as ageing medium, temperature, crystallinity, humidity, etc. There are two processes which are usually responsible for surface ageing: the first one is the reorientation of the polar groups into the bulk polymer and the second is the mobility of small polymer chain segments into the matrix, both leading to a decrease in surface energy. It was reported that polymers surrounded by a hydrophilic environment, such as water, maintain their hydrophilicity since the aqueous environment has affinity for the polar groups and forces them to stay on the surface [1]. In contrast, a non-polar environment will force the polar groups into the bulk of the material and will result in a great loss of hydrophilicity. It was also reported that hydrophobic recovery is faster in humid air than in dry air [1].

The chain mobility mainly occurs in the amorphous region while the mobility in the crystalline region is fairly limited because of orderly packed structure. Therefore more crystalline polymers are ageing more slowly. Since plasma treatment can increase the surface crystallinity due to selective etching of the softer amorphous phase, the polymers treated for longer times are usually ageing slower [1–4]. This is not always true as too long treatment times may again lead to faster ageing due to overtreatment leading to formation of small fragments loosely bound on the surface. Such surface has a greater tendency to ageing because of migration of small fragments into the bulk.

In this paper we present a study on surface ageing of polymer polymethyl methacrylate (PMMA), which is often used in biomedical applications. The rate of surface ageing was studied for PMMA polymers treated for different time when stored in dry air or in water. The effect of temperature on surface ageing was studied as well.

2. Experimental

Plasma treatment was performed in a cylindrical discharge chamber made of Pyrex with a length of 0.5 m and an inner diameter of 36 mm. The system was pumped with a two-stage oil rotary pump with a pumping speed of 16 m^3/h. The base pressure was a few Pascals. Plasma was created with an inductively coupled

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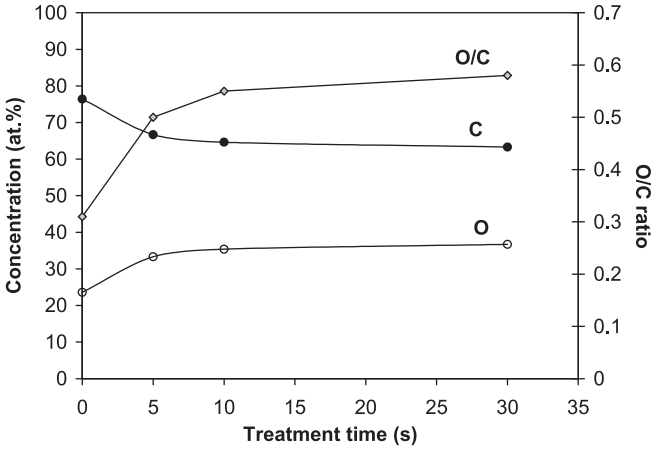

Fig. 1. Surface composition of PMMA (in at.%) for untreated sample and samples treated for different periods.

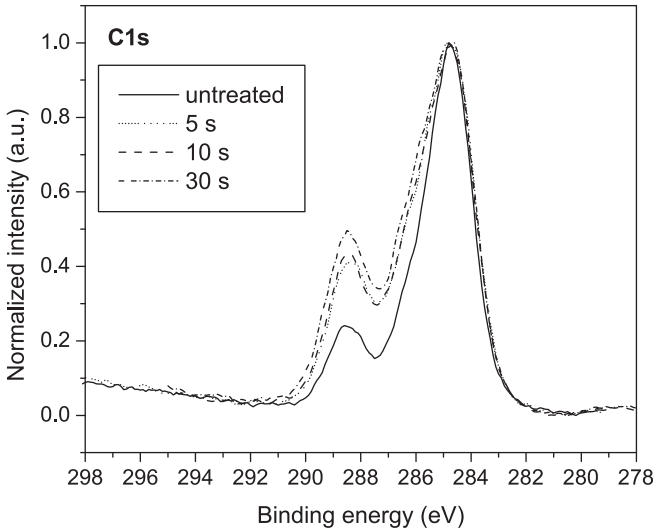

Fig. 2. Comparison of high-resolution XPS spectra of carbon C1s for untreated sample and samples treated for different periods.

RF generator, operating at a frequency of 27.12 MHz and a nominal power of about 200W. Commercially available oxygen was leaked into the discharge chamber. The pressure was fixed at 75 Pa. The plasma parameters were measured with a double Langmuir probe and a catalytic probe. The plasma density was of the order of 10^{15} m^{-3}, the electron temperature about 3 eV, and the density of neutral oxygen atoms of the order of 10^{21} m^{-3}. Samples were treated for different time from 5 to 60 s.

After plasma treatment the chemical modifications were analysed with X-ray photoelectron spectroscopy - XPS (TFA XPS Physical Electronics) to determine the change in chemical composition of the surface. The samples were excited by X-rays over a 400 μm spot area with a monochromatic Al $K\alpha_{1,2}$ radiation at 1486.6 eV. Photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. Survey scan spectra were made at pass energy of 187.85 eV. Since the samples are insulators, we used an additional electron gun to allow for surface neutralization during the measurements. Carbon C1s high-resolution spectra were taken at

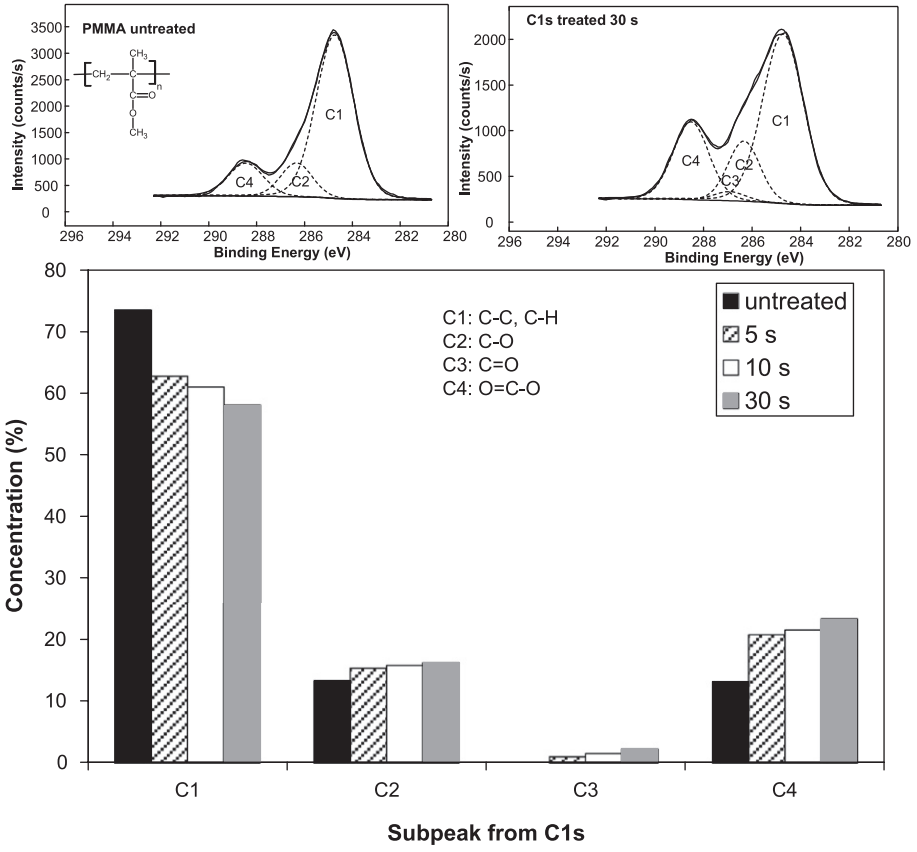

Fig. 3. Comparison of concentration of different chemical states of carbon atoms for untreated sample and samples treated for different periods.