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An XPS study of pulsed plasma polymerised allyl alcohol film growth on polyurethane

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Abstract

The growth of highly functionalised poly allyl alcohol films by pulsed plasma polymerisation of $CH_2{=}CHCH_2OH$ on biomedical grade polyurethane has been followed by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Film thickness is observed to increase approximately linearly with plasma modification time, suggesting a layer-by-layer growth mode of poly allyl alcohol. Water contact angle measurements reveal the change in the surface free energy of wetting decreases linearly with plasma modification up to the monolayer point after which a constant limiting value of -24 mJ m^{-2} was attained. Films prepared at 20 W plasma power with a duty cycle of 10 μs:500 μs exhibit a high degree of hydroxyl (–OH) retention with minimal fragmentation of the monomer observed. Increasing the plasma power up to 125 W is found to improve –OH retention at the expense of ether formation generating films close to the monomer stoichiometry. Duty cycle plays an important role in controlling both film composition and thickness, with longer off times increasing –OH retention, while longer on times enhance allyl alcohol film growth.

Keywords: Pulsed plasma polymerisation; Allyl alcohol; Biomaterials; Thin films; Polyurethane; XPS; Contact angle

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1. Introduction

Many polymeric materials while possessing excellent bulk properties such as chemical inertness, tensile strength, elasticity or density for a particular application may not exhibit ideal adhesive or wetting interactions at the surface. Surface modification is often employed to tune the surface functionality and improve interactions in the interfacial region [1,2] thereby optimising the performance of the polymer. Plasma surface modification is a convenient technique which can achieve profound changes in the surface chemical functionality of a material by enabling control over key factors such as wetting or adhesive properties without changing the bulk properties of the solid [3]. A plasma is a gaseous mixture of electrons, radicals, ions and excited molecular states which are created by inelastic collisions between high energy electrons and ground state atoms or molecules [4]. In recent years modification of surfaces by plasma treatment has been the subject of extensive research in both industry and academia with coatings developed for application in the fabrics [5], biomaterials [6,7], electronics [8] and optics [9] sectors.

In contrast to many other types of wet chemical treatments, plasmas have a unique ability to initiate free radical and ionic reactions without the need to apply heat or catalysts. There is also greater freedom in the choice of the reacting gas and a wide range of functional monomers have been investigated including alcohols [10,11], amines [12–14], cyano groups [15], carboxylic acids [16], anhydrides [17], epoxides [18], fluorocarbons [19,20], ferrocenes [21] and aromatic compounds [22]. As a result the potential of plasma modification and polymerisation for enabling surface properties to be tuned to a particular application has attracted great interest from the biomaterials community where both surface and bulk structural properties play an important role in material performance.

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Plasma polymerisation can be achieved using either a continuous wave (CW) process or by pulse mode. There is a wealth of literature concerned with the application of CW plasma polymerisation processes [3]. The presence of high energy electrons and ions in the plasma generate a high density of activated gaseous monomer species which polymerise to generate films possessing a high degree of cross-linking. Although CW plasma polymerisation is effective in altering surface properties there is little control over surface functional group density due to decomposition of the monomer under plasma excitation which results in poor retention of functional groups. To address this issue, in recent years there has been interest in polymerisation occurring from pulsed plasma methodologies. Pulsed plasma systems offer processes advantages by permitting formation of high quality films under much lower power inputs than are usable under CW conditions [23]. By utilising a pulsed system, polymerisation takes place during both the 'on' and the 'off' periods, with conventional polymerisation reactions such as radical additions or cationic chain transfer taking place in the off cycle leading to higher retention of the monomer functionality.

Here we investigate the application of pulsed plasma polymerisation for coating biomedical grade polyurethane (PU) with polymeric allyl alcohol films. PU was selected due to its desirable bulk properties for biomedical applications such as elasticity, tensile strength, durability, tear resistance and ease of fabrication. The versatility of PU's originates from their composition of alternating rigid 'hard' diisocyanate and flexible 'soft' aliphatic polyether or polyester segments [24] which can be varied depending on the desired application. Currently PU is employed in a range of applications including wound dressings, catheters, pacemakers, artificial heart and arterial grafts [25]. The ability to control their wettability through the generation of surface films with controlled surface –OH density would be desirable to extending their range of biomedical applications [26]. Allyl alcohol ($CH_2{=}CHCH_2OH$) is a desirable monomer to introduce hydroxyl functionality to a surface, however it particularly susceptible to C–O cleavage and as a result is unstable under high power CW plasma conditions [27]. It is also of interest to note that allyl alcohol polymer films cannot be readily synthesized by wet chemical radical polymerisation due to degradative chain transfer processes which prevent high molecular weight polymers forming [28].

Previous investigations of plasma polymerisation of allyl alcohol have employed continuous wave conditions where relatively high powers ~20 W [29] or 60 W [30] have been utilised during film preparation. A detailed study of allyl alcohol polymerisation over aluminium substrates revealed powers as low as 1 W were necessary under CW conditions to retain film functionality [31]. A subsequent pulsed plasma investigation over silicon [32] also revealed good –OH retention could be achieved using 300 W plasma power and duty cycles of 1 ms on and 30 ms off to generate films of thickness 100–300 nm. Here we report on the growth, surface morphology and composition of pulsed plasma polymerised allyl alcohol films synthesised under low power (10–125 W) conditions on biomedical grade PU. Using low power and slower deposition rates we aim to retain –OH functionality and generate ultra thin films with tuneable wettability.

2. Experimental

2.1. Materials and plasma polymerisation

Allyl alcohol (AA) (Aldrich > 99%) was subjected to several freeze–thaw cycles prior to use. Thin films (1.5 mm) of PU (Estane, 58245 NAT 031, Noveon) were prepared by compression moulding of beads between sheets of release film (Tygaflor) using a Fontyne Press (Mackey Bowley) at 220 °C and 50 kN m^{-2} pressure. Prior to compression, beads were dried overnight in a vacuum oven at 80 °C to remove excess water. Films were cut into 1 cm × 3 cm strips after pressing, and then sonicated in distilled water for 10 min. They were finally washed in ethanol before use.

A schematic of the plasma reactor is shown in Scheme 1. It consists of a large tubular glass reactor 5 cm in diameter and 25 cm length into which samples were centred and the reaction chamber evacuated to base pressure of $\sim 3.0 \times 10^{-3}$ Torr by a rotary pump (Trivac B, Leybold). All vacuum seals were grease-free to minimise contamination. Allyl alcohol vapour was dosed into the chamber via a needle valve at a constant pressure of 1.1×10^{-1} Torr. Pressures were measured with a thermocouple gauge, calibrated to have a linear response over the operation range of the reactor. The reaction chamber was purged with monomer vapour for 5 min prior to and after experiments to ensure the flow was stable, and subsequently to allow time for passivation of the surface.

The pulsed plasma was produced via an RF generator (RFG150 Coaxial Power Systems) operating at 13.56 MHz, inductively coupled to the reactor through an externally wound copper coil via an L–C matching network (MN150 Coaxial Power Systems). The matching network was adjusted to minimise reflected power. These were in turn connected to an oscilloscope (Farnell) and 10 MHz pulse generator (Thurlby Thandar Instruments). The pulse generator was used to set differing duty-cycles ($t_{on}/(t_{on} + t_{off})$) which were monitored via the oscilloscope.

The effect of peak power was investigated over the range 10–125 W whilst employing a duty cycle of 10 μs:500 μs and treatment time of 400 s. The effect of duty cycle on film deposition rate and composition was studied by variation of the on or off time duration at 20 W peak power. The total treatment time was varied in each instance to maintain a constant number of cycles in each experiment. Treated samples were stored under vacuum in a dessicator prior XPS and contact angle analysis which were performed within 3 h of their preparation.

2.2. X-ray photoelectron spectroscopy (XPS)

XP spectra were obtained using a Kratos AXIS HSi photoelectron spectrometer with a charge neutraliser and Mg Kα excitation source (1253.6 eV). Energy referencing was